CHAPTER ONE

1 Introduction

1.1 Background

A composite is defined as a substance consisting of two or more materials, one being a dispersed material and the other, a binding material (or matrix), which holds together both materials and are combined to form a useful engineering material, possessing certain properties not present in the constituents. On a microscopic scale, it is inherently inhomogeneous but can often be assumed to be homogeneous on a macroscopic scale for certain engineering applications. The constituents of a composite retain their identities: they do not dissolve or otherwise merge completely into each other, although they act in synergy [1, 2]. Composite technology is not new. From time immemorial, our ancestors made bricks by mixing clay and straw. This was the earlier form of composite technology. The straw was the fibre reinforcement and the clay was the matrix. Today, with the continuous development of new reinforcing materials and resins, the state-of-the art composite involved the selection of the right reinforcement with the right matrix [2].

The term wood thermoplastic composites (WTC) refer to any composites that contain wood (of any form) and thermosets or thermoplastics. The use of wood filler in plastics has been in existence for some time now. As far back as 1916, Rolls-Royce used a gear lever knob made of wood filled plastic, less than a decade after the patenting of the first synthetic resins. WTC resurfaced as a modern concept in Italy in the 1970s and became popular in North America in the early 1990s. By the start of the 21st century, it was spreading to India, Singapore, Malaysia, Japan and China, leading to a renewed interest in the use of natural fibres, also known as agro-based resources, for composites. These resources include wood, agricultural plants and residues, grasses, water plants and a wide variety of waste agro-mass including recycled wood, paper and paper products. There has been intensive fundamental research in WTC in universities all over the world, where better materials are being developed from renewable resources. These materials have higher wood contents, better interface properties, improved processing technologies and effective additives [3-5].

Although the use of wood-derived fillers for thermoplastics has gained acceptance in recent years, the plastics industry is still being dominated by inorganic fillers. In the year 2000, the amount of fillers and reinforcements used in plastics was estimated to be 2.3×10^6 tonne (2.3×10^9 kg). Fibreglass, calcium carbonate and other mineral fillers accounted for 93% of this market, while natural fibres account for 7%. This is likely to grow with the introduction of improved technology for compounding and an enhanced compatibility between fillers and matrix, resulting from the use of coupling agents which permits the use of higher filler contents [6, 7].

Presently, environmental concerns have driven the demand for bio-degradable materials such as plant-based natural fibre reinforced polymer composites. These composites are fast replacing conventional materials in many applications, especially in automobiles, where tribology (friction, lubrication and wear) is important. Also, plant fibre resources are renewable, widely distributed, locally available, mouldable, anisotropic, hydroscopic, recyclable, versatile, non-abrasive, porous, visco-elastic, easily available in many forms, biodegradable, combustible, compostable and reactive. It possesses a high aspect ratio, high strength-to-weight ratio and have good insulation properties (sound, electrical and thermal). The fibre structure is hollow, laminated, with molecular layers and an integrated matrix. Some of these properties such as biodegradability and combustibility, might be considered as shortcomings, but these features provide a means of predictable and programmable disposal not easily achieved with other resources. Plant fibres can be combined with other resources such as plastics, glass, metals and synthetics. The objective is to combine two or more materials in such a way that a synergism between the components results in a new material that is better than the individual components [8].

The earth is endowed with renewable plant resources, one of which is wood. Wood is a natural cellulose composite material of botanical origin that is useful for many applications because of its many excellent structural and chemical properties. It is a composite of cellulose fibres in a matrix of lignin, a natural glue, has a good strength-to-weight ratio, aesthetic appearance [9-12] and very versatile due to its unique characteristics and comparative abundance. However, it also suffers a number of disadvantages. First, it is hygroscopic, absorbing moisture from the surrounding environment. This leads to poor resistance against fungal and insect attack, swelling and shrinkage resulting from water absorption and desorption [11]. Also, wood is very polar due to the presence of hydroxyl groups in the cellulose, leading to poor adhesion or compatibility when used with a non-polar thermoplastic resin in WTC [13]. The high level of moisture absorption of wood fibres and the poor adhesion with hydrophobic polymeric matrices can lead to de-bonding with age, thereby lowering mechanical the properties [14]. In addition, wood is thermally unstable, degrading at temperatures above 200°C. Therefore, lower processing temperatures are generally essential because of the possibility of lignocellulosic degradation and/or the possibility of volatile emissions that could affect composite properties. Therefore, processing temperatures are thus limited to about 200°C, although it is possible to use higher temperatures for short periods. This limits the type of thermoplastics that can be used with wood fibres to commodity thermoplastics such as polyethylene (PE), polypropylenes (PP), polyvinyl chloride (PVC) and polystyrene (PS) which can melt or be processed below 200°C. It is important to note that these low-priced plastics constitute about 70% of the total thermoplastics consumed by the plastics industry [7]. Therefore, it presents a cheap, readily available matrix for WTC production. Despite the above mentioned limitations of wood fibres, its properties can be modified through physical and chemical technologies in order to improve the performance of the final composite.

WTC are produced by adding wood particles as fillers in a polymer matrix and pressing or moulding at high temperature and pressure. Colorants, coupling agents, stabilizers, blowing agents and lubricants can be added to help in tailoring the end product for the desired applications [15, 16]. It is one of the dynamic sectors of today's plastic industry with an annual average growth of 18% in North America and 14% in Europe [17]. Commonly, compression moulding is used in processing WTC. This process has the limitation of producing a simple shape that may not necessarily be compact. However, injection moulding results in a compact and complex shape of the finished article. It has an added advantage of being applied in a wider scope especially in industrial/domestic applications [18].

In North America, WTC is gaining acceptance in the construction industry in applications such as: decking, window profiles, railings, siding and roofing. Interior moulding applications are also receiving attention. The automotive industry in Europe has been leading in the use of WTC for interior panel parts and developing furniture applications. Furthermore, manufacturers in Asia are targeting the furniture industry in addition to interior and construction applications [19].

1.2 Justification

WTC can be referred to as green composites designed with the lowest possible environmental hazards. So much harm has been done to the environment by the consequences of material choice and design in research and everyday life. New directions in research must therefore be considered that will effect a positive change in environmental degradations and material usage. Therefore, the use of wood waste as fillers in WTC presents a class of material with environmentally benign attributes that can reduce the use of inorganic fillers in composites production. The term 'filler' in this context is used to describe wood flour, an inert and solid material in the form of discrete particles which are physically dispersed in the polymer matrix, without significantly affecting the molecular structure of the polymer.

Generally, the use of fillers in composites is intended to achieve but not limited to the followings [20]:

1. To increase stiffness, strength and dimensional stability
2. To increase toughness or impact strength
3. To increase heat deflection temperature
4. To increase mechanical damping
5. To reduce permeability to gases and liquids
6. To modify electrical properties
7. To reduce the cost of the product

Therefore, filler selection in WTC is not just an art but a science and various factors such as listed below would have to be considered in the choice [20];

1. Cost and availability
2. Wettability or compatibility with the polymer
3. Effect on polymer flow characteristics

4. Physical properties

5. Thermal stability

6. Chemical resistivity

7. Abrasiveness or wear

8. Toxicity

9. Recyclability

Certainly, the idea of adding fillers in WTC production is to reduce cost. Therefore, the filler must be abundant within the region where it is to be used. This is to avoid the additional cost of importing it.

Malaysia is very fortunate because of her floristic richness, especially with regard to the timber species. The timber industry is undoubtedly one of the major contributors to the Malaysian economy [21]. One of these timbers is the Red balau (*Shorea dipterocarpaceae*). The different species are widely distributed throughout Peninsular Malaysia and is one of the most abundant of the heavy hard woods. It is used in the construction and building industies for bridges, beams, power line posts, railway sleepers, heavy duty flooring, to mention a few [22]. Despite the abundance of this and other timbers, continual felling for use in applications mentioned above, constitutes a great threat to forestation. Deforestation is a critical problem, not only because it depletes a natural resource that cannot be replaced overnight, but also because of its far-reaching side effects. Environmental problems like desertification, soil erosion, flooding mudslides, siltation and sedimentation, habitat destruction and species extinction, salt and chemical degradation are a result of deforestation. Such loss of forests affects the climate, in that carbon dioxide absorption is decreased, partially leading to the greenhouse effect. Furthermore, it is accompanied by economic, health and social hardships brought about by people trying to live and cope with a drastically changed environment [23]. In addition, with today’s method of harvesting, only about 70% of the biomass contained in the trees is used [24]. Wastes from wood harvest and processing are usually disposed and left to rot, or at best used as fuels, still constituting environmental hazards. Hence the use of wood wastes in the form of wood saw dust in WTC production will alleviate these environmental problems constituted by indiscriminate disposal of wood wastes.

Low density polyethylene (LDPE) is a thermoplastic material, produced exclusively by high pressure free radical polymerization. The numerous short-chains branches in LDPE reduce its degree of crystallinity, resulting in a flexible product with a low melting point and density. However, long-chain branches confer desirable processing characteristics, high melt strengths, coupled with relatively low viscosities. Such characteristics eminently suit the film-blowing process products, which are its original outlet, accounting for more than half of all its use. Major applications include low-load commercial and retail packaging applications and trash bags. Other uses include diaper backing, shrink-wrap, vapour barriers, agricultural ground covers and green house covers. LDPE can be coated onto cardboard to create a water proof and heat-sealable composite widely used in fruit juice and milk cartons. Minor uses are in the wire and cable insulation and flexible pipe. Items made from injection or blow moulding of this resin are flexible and reasonably tough, making them suitable for application such as squeeze bottles and food storage containers. It is cheap (about RM9 per kilogramme), is used in relatively, large quantities and has relatively modest physical properties [25]. Furthermore, LDPE has poor rigidity and low softening point which to some extent limits its scope of applications. Combining wood in the form of wood flour with plastics, especially LDPE, leads to a new product which combines the strength of wood with the ease of processing and aesthetic characteristics of plastics, offering a unique and durable product that extends the applications of LDPE beyond its natural capability because of the improved properties conferred by the wood. Products from this combination are suitable in domestic uses, such as: flower pots, cutlery holders and serving trays. Other uses could include mobile phone casing, optical glass holders and electronic remote control casing.

Presently, issues relating to sustainable development and environmental preservation are receiving increasing attention from the world community. Also, new environmental and societal concerns have led to increased search for new products and processes that are compatible with the environment. Therefore, sustainability, industrial ecology, eco-efficiency and green chemistry are guiding the development of the next generation of materials, products and processes. Consequently, products based on wood from renewable forest and biomass feedstock can form a basis for the production of sustainable eco-efficient (eco-friendly) products, which can compete and capture markets currently dominated by petroleum-based sources. Accordingly, incorporating wood resources in composites materials will further reduce the dependence on petroleum reserves and a new agricultural, environmental, and manufacturing and hence consumer benefits will emerge [26] which will represent an engine of sustained economic development and employment opportunities while preserving the environment.

There have been some arguments on the sustainability and renewability of wood and the need to maintain the forests. Forest resources play a major role in the conversion of carbon dioxide to oxygen which is essential for human life. With the continuing debate over clean air, the need to retain a large portion of the forest resources for oxygen generation is one of the major arguments (along with other environmental and multiple use considerations) for not cutting trees. Secondly, there will be increased competition for land use as the world population increases. In 1830, the world population was 1 billion. Over the next hundred years, it doubled to 2 billion. At the present rate of growth, the population increases by 1 billion people every eleven years. Bio-based composites provide an opportunity to fill a growing need for materials. However, there will be greater need for food and feed. In future, the need for food will mean that forests are converted to agricultural lands in order to produce food and feed and the residues from these crops used for composites. In addition to the debate on land use, given that the land will be used for agricultural purposes, there will be strong competition for the resource to go into paper, textiles and bio-energy and not be used for composites [8]. However, the problem of sustainability has to do with the ability of humans to properly manage the bio-based resources the earth is endowed with. Presently, Malaysia is a major exporter of tropical timber products with an export value of RM21.5 billion in 2005, making the forestry sector one of the major income earners for the country. The country still has a relatively large area of production forests that are being managed for the continuous supply of timber resources and they are likely to consist, solely, of logged forests in the near future. More so, the total forested area in Malaysia was 19.48 million ha in 2005 or almost 60% of the total land area. Out of this 14.39 million ha or about 74% has been designated as Permanent Reserved Forest (PRF); to be sustainably managed for the benefit of present and future generations [27]. In addition, Malaysia is home to over 2,650 species of timber. Its location in the tropics means that her trees have 365 days of growing in a year. This allows the trees ample time to grow and develop without seasonal interruptions [28]. In addition, more than half the wood from a felled tree is unusable for processing into finished products because it consists of thin branches. The idea of using the wastes to make high quality wood substitutes is attractive because it reduces the rate at which forests need to be felled. This will reduce shortage of timber and the need to import it [4]. Also, with the availability of residue from sawmill, a new application is needed since this can be converted into reinforcing fillers in wood/plastic composites. Furthermore, sustainability of wood, the ability to re-grow it together with low energy consumption and biodegradability make them a better choice environmentally. Therefore, the use of wood as fillers in WTC should result in biodegradable and environmentally friendly composites.

Generally, cellulose is the most abundant natural polymer in the world. It has been reported that the earth is blessed with an almost inexhaustible reservoir of plants which is reproduced year after year through photosynthesis. Annual production of starch and cellulose through photosynthesis amounts to approximately seventy billion tones. This is an enormously high yield when compared with the finite world reserves of the major non-recurrent materials such as petroleum products.However, it is important to note that only about 3% of these annually renewed natural raw materials are been used productively. This clearly shows the immense, but scarcely utilized resources that nature offers to us year after year. The forest and to a lesser extent the agro-based plants, are the main sources of cellulose. Furthermore, every tree produces, on an average, approximately 13 to 14 grams of cellulose per day. Making more effective and versatile use of the natural raw material of wood and its valuable constituents is one of the most challenging tasks for the present and the future. If the average plant (on a dry weight basis) contains 40% cellulose, the annual bio-based resource would be approximately 2000 million dry tons. This compares to 2.25×10^9 tons which is the estimated world reserves of petroleum and natural gas. While the bio-based resource is renewable, the petroleum resources are deposited and formed over billions of years and as such, are limited in stock [8, 24].

The need for a concerted focus on WTC research cannot be over emphasized. This is because there is a greater awareness of the need for materials in an expanding world population and increasing affluence. At the same time, we have an awareness that our landfills are filling up, our resources are being used up, our planet is being polluted, that non-renewable resources will not last forever and that we need more environmentally friendly materials [8]. Therefore, this research addresses the need to exploit the vast resources of wood that are wasted and to seek for a better way to reinforce plastics with it, such that the product is not only useful, but also environmentally safe for household and industrial uses. Furthermore, the long-term sustainability of our nation's forests can be improved by creating valuable composite products from bio-based materials.

Notwithstanding the numerous advantages natural fillers offer over mineral fillers, the hydrophilic character, intrinsically connected with the presence of O-H groups in the chemical structure of its main macromolecular components such as cellulose and hemicellulose, has been a long standing challenge. As a result of this hydrophilic nature, their compatibility with relatively hydrophobic polymer matrices is low, leading to poor fibre-matrix interfacial adhesion. To achieve better compatibility, surface treatments are usually applied prior to compounding. Commonly used surface treatment methods and materials (agents) include: silane coupling, alkalination, isocyanate and maleic anhydride. Alhough these methods and agents have been successful in improving the interfacial bonding, the high cost of the chemicals and disposal of the effluents pose other challenges [29]. Therefore, it is obvious that new methods are required for fibre surface modification.

Due to its environmental benefits, heat treatment of wood has been applied to modify the surface of natural fillers. In addition to changing the chemistry of the wood surface, thereby making it less hydrophilic, heat treatment could also result in loss in mechanical strength of wood [11, 30]. Consequently, using heat-treated wood as filler in WTC should, in principle, worsen the properties. On the other hand, the changes imposed by heat treatment reduce the polarity of wood and make it a more compatible material with the non-polar thermoplastic matrix. Therefore, taking these characteristics into account, heat-treated wood can improve WTC properties more than untreated ones. It also presents an environmentally safe route of wood modification as no chemicals are used and no effluents generated. Hence, the focus of this research is to utilise thermally modified wood flour in WTC production.

1.3 Research objectives

This research is aimed at enhancing the properties of WTC by subjecting the red balau wood flour to high temperature treatment and incorporating coupling agents.

Other specific objectives are to:

- investigate the effects of thermal treatment on the chemical constituents of wood flour, using FTIR and established methods of wood chemistry.
- assess the effects of heat treatment on the thermal degradation behaviour of wood.
- evaluate the effects of heat pre-treated and untreated wood flour and coupling agents on the mechanical and dynamic mechanical properties of WTC over a range of compositions and coupling agent concentrations.
- study the effects of heat pre-treatment on the thermal degradation and crystalline behaviour of the resultant WTC.
- study the effects of exposing WTC made from untreated and pre-heat-treated wood to different environmental conditions on the thermal, dynamic mechanical, mechanical and morphological properties.
- examine the water absorption kinetics and properties of untreated and pre-heat-treated wood composites.

1.4 Scope of work

This thesis discusses the relationship between components and properties of untreated and pre-heat-treated red balau/LDPE composites, determined through a series of systematic studies. Firstly, composites were compounded and injection moulded under specified conditions. The effects of heat pre-treatment, filler loading and coupling agent concentration on the thermal, mechanical and dynamic mechanical properties of the composites were discussed. Then, composites were exposed to different environmental conditions, of: water, soil burial, outdoor and indoor. The effects of these environments on the thermal, mechanical and dynamic mechanical properties of the composites exposed were discussed, relative to the unexposed (control) composites.

While red balau filled LDPE is the material of interest for this thesis, it is not in the scope of this research to study in detail the chemistry and biology of the wood flour. However, aspects pertinent to the composites performance, including surface morphology and basic chemical constituents of red balau wood flour were examined. It is also beyond the scope of this thesis to discuss the effects of additives or components in the composites other than the polymer, filler and the compatibiliser used. Furthermore, the environmental exposure discussed in this thesis is meant to relate the effects of different environmental conditions to composites properties and not an assessment of biodegradability.

1.5 Thesis outline

The effects of thermal treatment of wood flour on the properties of red balau saw dust filled LDPE composites is the essence of this dissertation. It is divided into the following chapters;

Chapter one presents an overall introduction to composites; its technology and uses. Justifications, research objectives and scope of work are also presented.

Chapter two provides a review of literature of the basic chemical constituents of wood and different treatment methods employed by other researchers to checkmate the disadvantageous attributes of wood in WTC, highlighting the effects on the properties of the composites.

In chapter three, the materials and methods are highlighted including detailed testing methods employed in this research.

Chapter four focuses on the presentation of results and its discussion of the influence of heat treatment of red balau wood flour on the properties of dry as-moulded and conditioned specimens. Properties of composites made from the untreated wood flour were also presented.

Finally, chapter five presents the general conclusions and recommendations for further work.

CHAPTER TWO

2 Literature Review

2.1 Preamble

Wood can be defined as a three dimensional biopolymer composite material, consisting of an interconnected network of cellulose, lignin, hemicellulose, with minor amounts of extractives and inorganics, contained in a cellular structure, made mainly, from carbon, hydrogen and oxygen [12, 31, 32]. Woods are divided into hardwoods and softwoods. Hardwood trees (angiosperms), generally have broad leaves, and they are deciduous in the temperate regions of the world and contain a special cell called a vessel element. Softwood trees (conifers or gymnosperm) are cone-bearing, generally have scale-like or needle-like leaves, are not deciduous and do not contain vessel elements. The terms hardwood and softwood have no direct application to the hardness or softness of the wood [33].

2.2 Wood components

2.2.1 Cellulose

The basic structural component of all plant fibres is cellulose. It is the most important organic compound produced by plants and the most abundant on earth. The molecules consist of glucose units, linked together in long chains, which are in turn linked together in bundles called microfibrils [34]. It is the major chemical component of plant fibre wall and contributes 40-45% of the wood’s dry weight. It is a glucan polymer (a homopolysaccharide), composed of linear chains of D-glucopyranose linked together by ß-1,4-glycosidic bonds. The actual building block for cellulose is the cellobiose, since the repeating unit in cellulose is a two sugars unit.

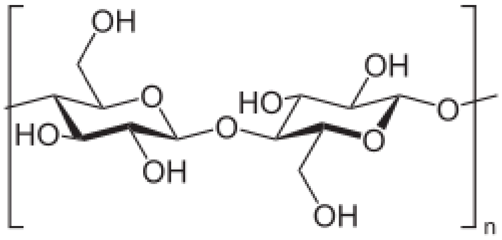


Figure 2.1: Structure of cellulose [31]

The number of glucose units in a molecule of cellulose, known as the degree of polymerisation, *DP*, varies from 1,000 in native wood to 10,000 in bleached kraft pulps. Each D-anhydroglucopyranose unit possesses hydroxyl groups at C2, C3 and C6 positions, capable of undergoing the typical reactions known for primary and secondary alcohols. Due to its molecular structure, cellulose possesses characteristic properties such as: hydrophilicity, chirality, degradability and broad chemical variability initiated by the high donor reactivity of hydroxyl groups. In addition, cellulose molecules are completely linear, with a strong tendency to form intra- and inter-molecular hydrogen bonds by the hydroxyl groups on these linear cellulose chains, which stiffen the straight chain and promote aggregation into a crystalline structure that give cellulose a multitude of partially crystalline fibre structures and morphologies [31, 35, 36].

Most cellulose derived from wood is highly crystalline, with high packing density and may contain as much as 65% crystalline regions. The remaining portion with lower packing density is referred to as the amorphous cellulose. The molecular chains pack in layers and are held together by weak van der Waals forces. The layers consist of parallel chains of anhydroglucopyranose units and the chains are bound together by intermolecular hydrogen bonds. This structure is referred to as native cellulose or cellulose I [31]. Thus, bundles of cellulose molecules aggregate together in the form of micro-fibrils, consisting of highly ordered (crystalline) regions alternating with less ordered (amorphous) regions. The microfibrils build up to form the cellulose fibres. Because of its fibrous structure and strong hydrogen bonds, cellulose has high tensile strength [36]. Cellulose is insoluble in most solvents including strong alkali. It is difficult to isolate it from wood in pure form; because it is intimately associated with the lignin and hemicelluloses [35].

2.2.2 Hemicellulose

Hemicelluloses are also found in all plant fibres. They comprise a group of polysaccharides bonded together in relatively short, branching chains, consisting of five and six carbon-ring sugars and are intimately associated with microfibrils, embedding the cellulose in a matrix. They are strongly bonded to cellulose fibrils presumably by hydrogen bonds. Hemicellulosic polymers are branched, fully amorphous and have significantly lower molecular weights than cellulose. As a result of its open structure that contain many hydroxyl and acetyl groups, hemicellulose is partly soluble in water, easily hydrolysed in acids and they are hygroscopic [37]. "Hemicellulosics" is a collective term for a great many structures of heteropolysaccharides of plant origin, forming plant cell walls along with cellulose. They include xylans, arabinoxylans, glucuronoxylans, glucomannans and galactomannans xyloglucans [34].

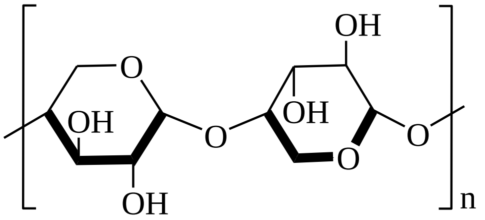


Figure 2.2: Structure of hemicellulose [31]

2.2.3 Lignin

Lignin can be defined as the residue left after the plant material is hydrolysed with strong acids. Lignin is the compound which gives rigidity to the plant, without which plants, especially trees cannot attain great heights. It is considered to be largely responsible for strength and durability of wood. In fact, trees stand upright because lignin supports their integrity. Lignin is a three-dimensional polymer with an amorphous structure, highly aromatic polymers of phenylpropane units with a high molecular weight. It has the least affinity for water among the three main components of the plant cell wall. Hydroxyl, methoxyl and carbonyl groups have been identified in lignin. Lignin has been found to contain five hydroxyl and five methoxyl groups per building block. It is believed that the structural units of lignin molecule are derivatives of 3, 4-methoxy phenylpropane. It is considered to be a thermoplastic polymer, with a glass transition temperature of around 90°C and melting temperature of around 170°C. It is not hydrolysed by acids, but soluble in hot alkali, readily oxidised and easily condensable in phenol [34, 38].

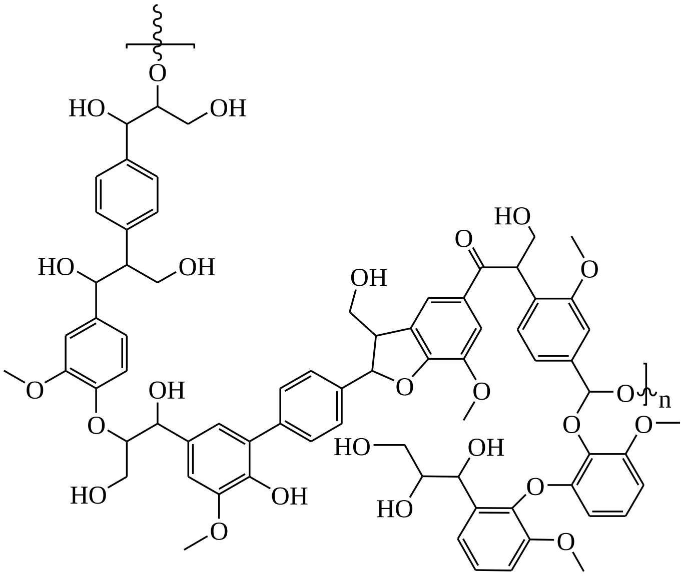


Figure 2.3: Structure of lignin [31]

2.2.4 Extractives and inorganics

Besides these three principal components, plant materials contain non-structural components, namely: extractives (typically 4–10%), inorganic ash (between 0.2% and 0.5% in wood and up to 19% in rice hulls and some other plant materials) and water. Examples of extractives are terpenes, pinenes, tannins, carbonyl compounds, etc. They are responsible for odour in wood, can diffuse to the wood surface during drying and can hinder adhesion. In addition, some of them possess antimicrobial properties [34].

The structure, microfibriller angle, cell dimensions, defects and the chemical composition are the most important variables that determine the overall properties of plant fibres. These properties include;

- Good tensile strength, heat, sound and electrical insulating properties.
- Combustibility

  This is an advantage from the waste point of view because products can be disposed off at the end of their service life through burning and energy is generated at the same time.
- Biodegradability

  Due to the tendency of plant fibres to absorb water, they degrade under certain conditions through the action of bacteria/or fungi.
- Dimensional stability.

  As a result of the hygroscopic nature, plant fibres are naturally not dimensionally stable under changing moisture conditions. Nevertheless, this may be controlled by appropriate modification methods.
- Reactivity

  The O-H groups present in the cell wall components do not only provide sites for water absorption, but are also useful for chemical modifications to enhance durability, dimensional stability and improved bonding when used in WTC [34].

However, wood is very hygroscopic because of the presence of hydroxyl (O-H) groups within the cell wall. This poses water absorption and compatibility problems when processed with thermoplastics [9, 12], which lead to swelling and shrinkage resulting from moisture absorption and desorption, thus leading to poor mechanical properties of the resultant product. As a result, the use of WTC in industrial and domestic applications is limited. Therefore, some modifications become necessary to control the adverse effects of this limitation.

2.3 Wood modification methods

Despite the seeming disadvantages of wood because of the nature of its cell wall components, the use of wood in WTC production is absolutely necessary. Therefore, there is need to alter the cell wall chemistry in order to achieve the properties of interest. Wood modification has been defined as any treatment of wood that enhances its properties but does not involve the production of substances that contain toxic residues [39]. The essence of wood modification is to achieve a desired property enhancement during the service life of the modified wood. It is expected that the modified wood should be non toxic under service conditions and should not release any toxic substances during service or at the end of life following disposal or recycling [40].

Many studies have been carried out to improve the disadvantageous properties of wood. It is worthwhile to review some of the modification methods.

2.3.1 Chemical treatment

Chemical modification of wood is defined as the reaction of a chemical reagent with the wood polymeric constituents, resulting in the formation of a covalent bond between the reagent and the wood substrate [40]. Chemical treatment of wood fibre is employed to improve the properties of the composites and to promote better adhesion between the natural reinforcement and the matrix. Chemicals may activate hydroxyl groups or introduce new moieties that can effectively interlock with the matrix [41].

2.3.1.1 Alkaline treatment

Mercerization, the alkaline treatment of natural fibres, is one of the common methods of producing high quality fibres for WTC production. Alkaline treatment results in the disruption of the hydrogen bonding in the network structure of the wood polymers, thereby increasing the surface roughness. It reduces fibre diameter, increases aspect ratio, increases the amount of crystalline cellulose and removes natural and artificial impurities, thereby producing a rough surface topography, and consequently, better fibre-matrix interface adhesion and increased mechanical properties [42]. It leads to an increase in the number of reactive sites by increasing the amount of cellulose exposed on the fibre surface and allows for better wetting of the fibre by increasing the surface roughness, resulting in better mechanical interlocking. In addition, it has an effect on the degree of polymerization, and molecular orientation of cellulose crystallites due to the removal of the cementing substances like lignin and hemicellulose [43]. The main reaction is between O-H groups of cellulose and the hydrogen of the alkali. The hydroxyl group is ionised to the alkoxide according to the equation below [41, 42]:.

$$\text{Fibre-OH} + \text{NaOH} \rightarrow \text{Fibre-O}^{-}\text{Na}^{+} + H_2O \qquad (2.1)$$

The type of alkali (KOH, LiOH and NaOH) and its concentration affect the degree of modification. Studies have shown that NaOH treatment results in higher modification than other alkalis [44].

Farsi [45] investigated the influence of chemical modification of wood flour using NaOH on the mechanical performance of wood/polypropylene composites. The author reported that alkali treatment improves the tensile and flexural strengths of the composites. This was attributed to the improved compatibility between wood flour and PP matrix and noted that alkali treatment reduces micro voids and fibre-PP debonding in the interface region. However, izod impact strength was found to decrease due to the fact that the debonding behaviour at the interface between the fibre and the PP matrix absorbs more impact energy in the modified composites than the untreated ones. Liu *et al*. [46] studied the effects of alkaline treatment on the structure, morphology and thermal properties of native grass fibres as reinforcements for polymer matrix composites. Chopped grass fibre was soaked in 5% and 10% solution of NaOH for between 1 and 16 h. Results from this study revealed that the amounts of lignin and hemicellulose reduced with alkali treatment and time. It was also observed that the degradation peak temperature of the grass fibre increased with the treatment and treatment duration, indicating an increase in thermal stability. This was attributed to the removal of hemicellulose with alkaline treatment. In another report, Jacob *et al*. [47] examined the effects of NaOH concentrations of 0.5, 1, 2, 4 and 5% on sisal fibre used to reinforce natural rubber. It was observed that maximum tensile strength was obtained with 4% NaOH treatment at room temperature. Also, Mishra *et al.* [48] observed that 5% NaOH treated sisal fibre resulted in better tensile strength than that treated with 10% NaOH in sisal reinforced polyester composites. The authors concluded that higher concentration of NaOH causes excessive delignification of natural fibres resulting in weaker or damaged fibre.

2.3.1.2 Acetylation

Acetylation, a reaction that introduces an acetyl functional group (CH_3COO^-) into an organic compound, is another chemical method of wood modification. This involves the esterification of the accessible hydroxyl groups and causes plasticization of cellulosic fibres. Pre-treatment of fibres with acetic anhydrides substitutes the polymer hydroxyl groups of the cell wall with acetyl groups, thereby converting the hydrophilic hydroxyl group in the cell wall of the wood and intercellular regions to hydrophobic groups, according to the chemical reaction below:

$$\text{Wood-OH} + CH_3CO\text{-}O\text{-}OC\text{-}CH_3 \xrightarrow[\text{conc } H_2SO_4]{CH_3COOH} \text{Wood-O-CO-}CH_3 + CH_3\text{-CO-OH} \qquad (2.2)$$

The hydroxyl groups that react are those of the minor components, i.e. lignin and hemicelluloses. The hydroxyl groups in the crystalline regions of the fibre are closely packed with strong inter-chain bonding, and are not accessible to chemical reagent. [44]. Acetylation has been reported to result in a rough fibre surface of flax fibre, with a number of voids that provide better mechanical interlocking with polystyrene matrix. It was also observed to have resulted in better thermal stability and improved fibre-matrix interactions in composites [49, 50].

Acetylation can reduce the hygroscopic nature of natural fibres and increase the dimensional stability of composites. It was reportedly used in the surface treatment of natural fibre reinforced polymer composites in order to improve the mechanical properties of the composites [51]. Mishra *et al.* [48] treated sisal fibre with 5 and 10% NaOH for 1 h at 30°C and acetylated by soaking in glacial acetic at the same condition before being soaked finally in 50 ml acetic anhydride containing a drop of H_2SO_4 for 5 min. Hybrid composites resulting from the use of this fibre and glass fibre in a polyester resin were reported to exhibit better mechanical properties than the untreated composites.

2.3.1.3 Silane treatment

Silane is a chemical compound with chemical formula SiH_4. Silanes are used in glass fibre composites as coupling agents for better adhesion between glass fibre and matrices and to stabilize the composite material [52]. These chemicals are hydrophilic compounds with different groups appended to silicon so that one end interacts with the polymer matrix while the other end interacts with the hydrophilic filler forming a bridge between them [44]. Silane coupling agents reduce the number of cellulose O-H groups in the fibre-matrix interface. In the presence of moisture, hydrolysable alkoxy group leads to the formation of silanols. The silanols then react with the hydroxyl groups of the fibre, forming stable covalent bonds with the cell wall that are chemisorbed onto the fibre surface. Therefore, the hydrocarbon chains, provided by the application of silane, restrain the swelling of the fibre by creating a cross-linked network due to the covalent bonding between the matrix and the fibre. This influences the wettability of the fibres, thus improving the chemical affinity to the matrix.

The reaction schemes are given below [52]:

$$CH_2CHSi(OC_2H_5)_3 + 3H_2O \rightarrow CH_2CHSi(OH)_3 + 3C_2H_5OH \qquad (2.3)$$

$$CH_2CHSi(OH)_3 + \text{Fibre-OH} \rightarrow CH_2CHSi(OH)_2O\text{-Fibre} + H_2O \qquad (2.4)$$

The uptake of silane by natural fibres is dependent on a number of factors, such as: hydrolysis time, the organofunctionality of silane, temperature and pH. Silane treatment has been applied to glass fibre filled vinyl ester composites for surface modification [53]. In this report, Kim *et al*. observed that silane coupling modified the bulk properties of the resin to a certain extent. Silane coupling agents were also found to be effective in modifying the natural fibre-polymer matrix interface by increasing interfacial strength. It has been reported that the interaction between the silane coupling agent modified fibre and matrix was much stronger than that from alkali treatment, leading to composites with higher tensile strength from silane treated than the alkali-treated fibres [54]. Agrawal *et al.* [52] studied the effects of silane treatment on the activation energy and crystallization kinetics of oil palm fibre reinforced phenol formaldehyde composites and reported an improvement in the thermal stability of the composites, but observed no significant difference in the activation energies. The authors observed that although the thermal stability of the composites was improved, to certain extents, there were no appreciable changes in the nucleation mechanism of the composites, following silane treatment. Grubbström *et al.* [55] studied the silane cross-linking of extruded recycled LDPE/wood composites using a combination of silane (vinyl trimethoxy silane) and peroxide (dicumyl peroxide) mixed in a w/w ratio of 12:1 (high peroxide content) and 25:1 (low peroxide content) on a 50% wt of wood flour in the recycled LDPE matrix. Results from this research revealed that composites with low peroxide concentration in the silane solution (25:1) was the most favourable composition for extrusion as no unintentional cross-linking took place and also resulted in greater improvements in the composites properties. In addition, FTIR spectroscopy indicated Si-O-C bridges between the wood and the polymer which confirms the improved strength of the composites.

2.2.1.4 Benzoylation

Benzoylation is an important transformation in organic synthesis. Benzoyl chloride which is often used in fibre treatment includes benzoyl ($C_6H_5C{=}O$) which is responsible for the decreased hydrophilic nature of the treated fibre and improved interaction with the hydrophobic matrix. The reaction between the cellulose O-H group of the fibre and benzoyl chloride is shown below [49]. The fibre was first treated with NaOH to activate the cellulose O-H groups in the reaction below:

$\text{Fibre-OH} + \text{NaOH} \rightarrow \text{Fibre-O}^{-}\text{Na}^{+} + H_2O$ (2.5)

(2.6)

Manikandan Nair [49] used NaOH and benzoyl chloride (C_6H_5COCl) solution to treat the surface of sisal fibres for polystyrene-sisal fibre composites. The fibre was initially pre-treated with an alkaline solution in order to activate the hydroxyl groups of the cellulose and lignin, then suspended in 10% NaOH and benzoyl chloride solution for 15 min. The isolated fibres were then soaked in ethanol for 1 h in order to remove the benzoyl chloride and finally washed and dried in an oven at 80°C for 24 h. It was observed that the thermal stability of the treated fibre composites was higher than the untreated ones.

2.3.1.5 Peroxide treatment

Peroxide treatment of cellulose fibre has attracted the attention of various researchers due to the ease of processing and improvement in mechanical properties. Organic peroxides are a specific functional group ROOR, containing O-O. They decompose easily to form $2RO^{\cdot}$ free radicals, which then react with the hydrogen atoms of the matrix and cellulose fibres. For example, the peroxide initiated free radical reaction between polyethylene matrix and cellulose fibres is shown below [56, 57]:

$\text{RO-RO} \rightarrow 2\text{RO}^{\cdot}$ (2.7)

$\text{RO}^{\cdot} + \text{PE-H} \rightarrow \text{ROH} + \text{PE}^{\cdot}$ (2.8)

$\text{RO}^{\cdot} + \text{Cellulose-H} \rightarrow \text{ROH} + \text{Cellulose}^{\cdot}$ (2.9)

$$\mathrm{PE}^{\cdot} + \mathrm{Cellulose}^{\cdot} \rightarrow \mathrm{PE\text{-}Cellulose} \qquad (2.10)$$

Benzoyl peroxide, BP, $(C_6H_5CO)_2$ and dicumyl peroxide, DCP, $(C_6H_5C(CH_3)_2O)_2$ are organic peroxides used in natural fibre surface treatment. Usually, in peroxide treatment, fibres are coated with BP or DCP in a solution of acetone for about 30 min after alkali pre-treatment [56, 57]. Sreekala *et al*, [56] observed that high temperature favoured the decomposition of the peroxide and that peroxide-treated oil palm fibre-reinforced composites exhibit high tensile strength. In another report, the tensile strength of composites from peroxide treated fibres was found to increase and a decrease in hydrophilicity of the fibres was also observed [57]. Sapieha *et al*. [58] reported that addition of a certain amount of BP or DCP to cellulosic fibre-LDPE systems during processing significantly improved the mechanical properties of the composites. The improvement was attributed to the peroxide-induced graft polymerisation of polyethylene onto cellulose surfaces.

2.3.1.6 Maleated coupling

Maleated coupling agents have been widely used to strengthen fibres and fillers reinforced composites [59-61]. Maleic anhydride is not only used to modify fibre surfaces, but also the matrix. For example, MAPP is commonly used on PP, in order to achieve better interfacial bonding and improvement in mechanical properties of the resulting composites [62-64]. The PP chain permits the cohesiveness of maleic anhydride and produces maleic anhydride grafted polypropylene, MAPP. Treating fibres with hot MAPP provides covalent bonds across the interface. The copolymer is activated by heating (at about 170°C) before fibre treatment. The cellulose fibre is then esterified. After this treatment, the surface energy of the cellulose fibre significantly increases to a level close to that of the matrix. This results in better wettability and higher interfacial adhesion of the fibre [65]. Mishra *et al.* [66] reported an appreciable reduction in water absorption of banana, hemp and sisal reinforced Novolac composites.

Mechanical properties were also observed to have improved. Tensile and flexural modulus, hardness and impact strength of the plant fibre reinforced composites were reported to have increased after maleic anhydride treatment. Mohanty *et al.* [67] employed MAPP as coupling agent in the surface treatment of jute fibres and reported that best results were achieved at 30% fibre loading with 0.5% MAPP concentration at 5 min impregnation time. A 72.3% increase in flexural strength was observed with the treated fibre composites. In addition,

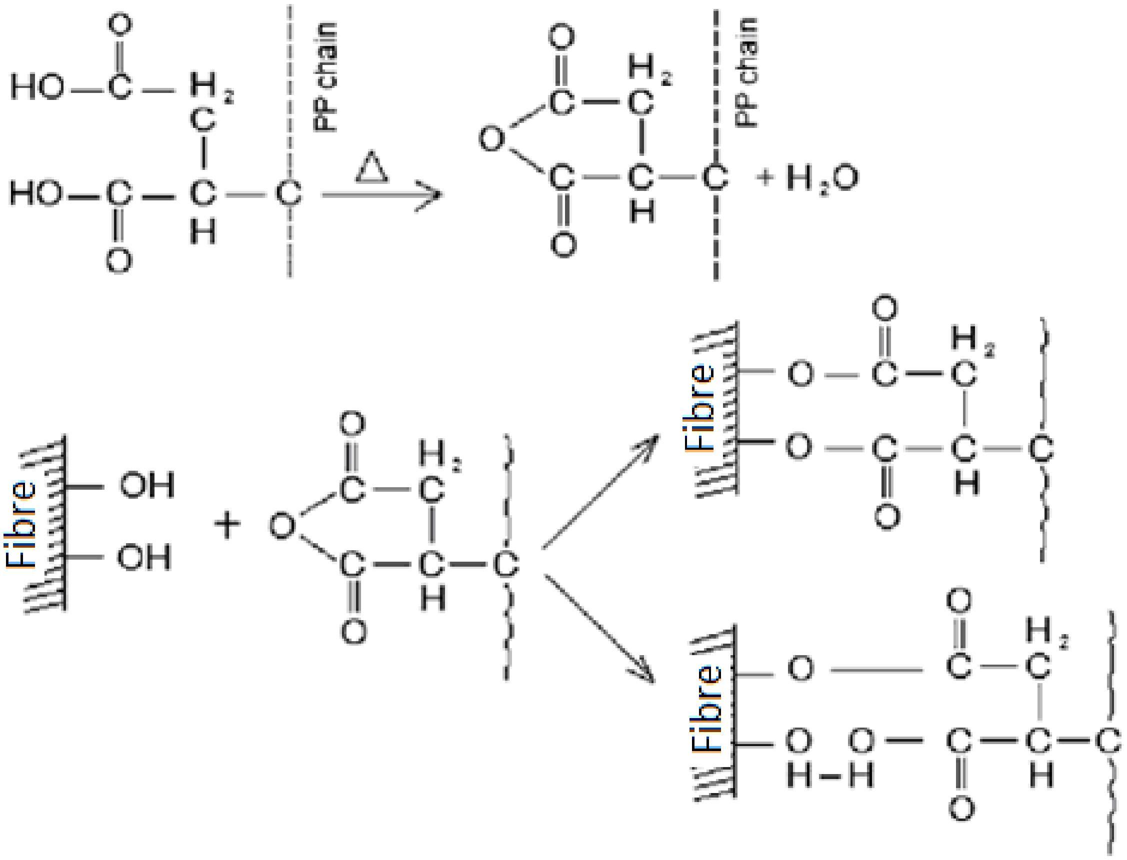


Figure 2.4: The reaction of cellulose fibres with hot MAPP [65]

2.3.2 Physical modification

In physical modification, the use of chemicals is not involved although the process is intended to effect some chemical changes in the wood structure. Therefore, effluents are not generated and no hazardous residue remains. Interestingly, the properties of the wood are altered to ameliorate one or more of its disadvantages.

2.3.2.1 Plasma treatment

Plasma technology is an effective method of modifying the chemical as well as the topography of the surface of materials in order to improve adhesion without altering their bulk properties [68]. Plasma discharge can be generated by either corona or cold plasma treatment. Both methods are considered as plasma treatment when ionized gas has an equivalent number of positively and negatively charged atoms that react with the surface of the material. The difference between the two categories of plasmas is the frequency of the electric discharge. High-frequency cold plasma can be produced by microwave energy, whereas, lower frequency alternating current discharge at atmospheric pressure produces corona plasma [42].

Martins *et al.* [69] conducted a cold plasma functionalization of sisal fibres and finely divided high density polyethylene (HDPE) powder using dichlorosilane to improve interfacial adhesion between the two dissimilar substrates. An improvement in mechanical properties due to plasma treatment was achieved. Scanning electron microscopic images indicated that some compatibilisation of the two plasma modified phases had taken place when compared to non-plasma treated composites. Sever *et al.* [29] investigated the effects of oxygen plasma treatments of jute fibres in improving the mechanical properties of jute/HDPE composites. Low and radio frequency plasma systems were used at different plasma powers of 30, 60 and 90 W for 15 min. The reports revealed that interlamina shear stress (ILSS), tensile and flexural properties increased with increasing plasma power up till 60 W, but decreased when the plasma power was increased to 90 W. This was attributed to the fact that high plasma powers may etch the bulk of the fibre and weaken it, thereby reducing the mechanical properties of the resultant composites.

2.3.2.2 Thermal treatment

The thermal modification of wood is defined as the application of heat to wood in order to bring about a desired improvement in the performance of the material [40]. Thermal treatment is one of the ways of improving wood quality. It has been reported to be an effective method to improve wood dimensional stability and/or its durability. High temperature treatment of wood results in several changes occurring in the wood chemistry. Hemicelluloses are degraded, producing simple sugars which may undergo reversible reactions to form highly branched polysaccharides. There is also the degradation of hemicelluloses and part of the cellulose to form furan type compounds. Thermal softening of the cell wall matrix, mainly lignin, also sets-in. This enables cross-linking to occur between carbohydrate polymers and/or between lignin and carbohydrate polymers resulting in an increase in the crystallinity of the amorphous cellulose, with consequent improvement in dimensional stability and decreased hygroscopicity of wood [10, 30, 70]. It has been reported that as wood is progressively heated to higher temperatures, production of condensable fractions occurs, with loss of water and volatile extractives at temperatures below about 140°C. Above this temperature, dehydration reactions also begin to occur, as the so-called ‘water of constitution’ is lost, leading to a decrease in O-H content and these assume greater importance as the temperature is raised further [40].

Heat-treated wood has been applied to WTC in order to improve specific properties. Okamoto *et al*. [71] used steam exploded beech, Japanese cedar and red meranti wood flour for the manufacture of WTC using PMMA, PVC and PS as matrices. This report showed an increase in the modulus-of-rupture and elasticity when compared to the untreated wood composites. It was also observed that the water resistance of the resultant composites was improved upon addition of heat-treated wood flour, due to the hydrophobicity of the heat-treated wood. Kaboorani [72] investigated the thermal properties of composites made from heat-treated wood and PP and concluded that the thermal stability of the wood and the resultant composites were greatly enhanced. Decomposition of hemicelluloses and structural changes in cellulose and lignin were reported to be responsible for the improved thermal stability. Robin and Breton [73] studied the effects of wood fibre heat-treated at 230°C on wood/recycled HDPE composites. Significant improvements in tensile and flexural modulii were observed when heat-treated fibre was used, relative to untreated fibres, but no appreciable increase was observed for the elongation-at-break. It was concluded that better adhesion of the fibre to the matrix was responsible for this behaviour. This result was corroborated by Kaboorani *et al.* [74] who studied the reinforcement of HDPE with wood, treated at 175°C, 190°C and 205°C and the effects of these treatments on the mechanical properties of the resultant composites. From this report, it was inferred that the use of heat-treated wood in WTC is a good way of building-up the performance of the composites. This was attributed to the increased compatibility between the polar wood and the non-polar polymer, which led to improved tensile strength and modulus of elasticity. It was even argued that heat-treated wood enhances the performance of coupling agents in WTC.

Wood, like any natural fibre is naturally hydrophilic. Derived from lignocellulosic sources, they contain strongly polarized O-H groups. This makes wood inherently incompatible with thermoplastics, due to poor mixing, resulting in poor interfacial adhesion between polar hydrophilic wood flour and non-polar hydrophobic matrix [44]. The study of ways of improving the interfacial adhesion between bio-fillers and polymer matrix is very important for the application of composites in industrial materials. This is because of the wide distribution, renewability and recyclability of lignocellulosics, which can greatly expand the applications for these low-cost materials in high performance composites.

2.4 Wood thermoplastic composites

2.4.1 Natural and man-made fibre/fillers/hybrid composites

Composites consist of a heterogeneous combination of components differing in composition, morphology and usually physical properties. This allows for the achievement of specific physical, chemical and mechanical properties. Traditionally, talc, calcium carbonate, mica, glass or carbon fibres are used in composites production. Man-made fibre-reinforced polymer composite materials are quite attractive because of their ease of fabrication, economy and superior mechanical properties. This category of materials offers a number of distinct advantages, such as high specific modulus, specific strength, superior corrosion resistance, improved fatigue properties, and low manufacturing cost, over the more conventional engineering materials. Hassan *et al*. [75] studied the properties of glass fibre reinforced PP composites and reported improvement in tensile and flexural properties. The improvement was attributed to the fact that glass fibre is an effective reinforcing material for PP, especially with compatibiliser, as it has the ability to transfer the applied load to the strong and stiff fibre through the fibre- matrix interface. However, disposal at the end of service life can pose a problem to the environment. In addition, glass fibre causes skin irritation and respiratory problems when mistakenly inhaled [16].

There have been reports on hybridisation of wood/natural fibre composites with man-made fillers/fibres. Gwon *et al.* [76] hybridised PP/wood composites with talc, kaolin and zinc borate and reported that kaolin and talc-filled hybrid composites showed better mechanical performance because of their stacked plate type of shape, while zinc borate, a massed cubed shaped filler exhibited lower mechanical and higher water absorption properties. In a related development, Yeh and Gupta [77] hybridised wood-PP composites with nanoclay. The authors found that pre-compounding wood flour with polymer, followed by incorporation of clay in a second step, resulted in an increase in stiffness, retention of strength and a reduction in the rate of water absorption. It was concluded that adding nanoclay is an alternative method for increasing the properties of wood composites instead of adding extra wood flour up of concentration in excess of 55 wt%, as this results in processing difficulties. Similarly, Panthapulakkal and Sain [78] added short glass fibre to PP–hemp fibre composites and evaluated the effects of hybridization on the water absorption/kinetics of moisture uptake and mechanical properties of the resultant composites. Reports revealed that incorporation of glass fibre significantly reduced the water absorption tendency and improved the retention of tensile strength. A Fickian mode of moisture absorption and a dependence of the diffusion coefficient on glass fibre content were also reported for the composites.

There have been several reports on the ability of natural fillers to improve the properties of WTC [13, 18, 26]. However, certain draw backs, such as the tendency to form aggregates during processing, low thermal stability and low resistance to moisture, greatly reduce the potentials of wood fibres as fillers in polymers. Another major limitation is the poor compatibility exhibited between polar (hydrophilic) wood fibres and non-polar (hydrophobic) polymer matrix, which leads to the non-uniform dispersion of the fibres within the polymer matrix, resulting in poor mechanical properties. Nevertheless, composites made from renewable resources are generally considered as environmentally safe materials [16]. Table 2.1

shows the physical and mechanical characteristics of different fibres (Natural and man made).

Table 2.1: Mechanical properties of some natural and man-made fibres [16]

Fibre	Density (g/cm^3)	Elongation (%)	Tensile strength (MPa)	Young's modulus (GPa)
Cotton	1.5-1.6	7.0-8.0	287-800	5.5-12.6
Jute	1.3	1.5-1.8	393-773	26.5
Flax	1.5	2.7-3.2	345-1035	27.6
Hemp	1.5	1.6	690	70.0
Ramie	1.5	1.2-3.8	400-938	61.4-128.0
Sisal	1.5	2.0-2.5	511-635	9.4-22.0
Coir	1.2	30.0	175	4.0-6-0
Soft wood	1.5	-	1000	40.0
E-glass	2.5	2.5	2000-3000	70.0
S-glass	2.5	2.8	4570	86.0
Aramide	1.4	3.3-3.7	3000-3150	63.0-67.0
Carbon	1.4	1.4-1.8	4000	230.0-240.0

2.4.2 Processing of wood thermoplastic composites

WTC processing can be defined as the engineering activity concerned with operations carried out on polymeric materials/filler systems in order to increase their utility. Primarily, it deals with the conversion of raw polymeric/filler materials into finished products, involving not only shaping but also compounding, leading to morphology stabilization and thus, value-added products [79].

2.4.2.1 Extrusion/Compounding

Compounding/extrusion is the feeding and dispersing of fillers and additives in the molten polymer. In an extrusion process, pre-mixed or separate polymer and wood components are fed into the extruder through a hopper along with additives and are melted and further mixed upon heating by heaters and screw rotation (shearing) and are ultimately shaped while passing through a profile die [80]. Mixing is an operation that is intended to reduce the non-uniformity of the material and can be accomplished by inducing physical motion of the components [79]. This can be carried out either in a two roll mill, high speed mixer or in a twin screw extruder [81]. Blending the wood fibre with a polymer is the key step of WTC production because the compounding process helps to uniformly distribute the wood fibre and coupling agents in the thermoplastic matrix, decrease the pore ratio, and stabilize the filler/matrix interaction [82]. However, there has been no criterion for determining the optimum compounding conditions. Usually, the compounding conditions vary with the mixing machine type, compounding steps, weight ratio of the wood fibre and polymeric matrix, moisture content of the wood fibre and species of the thermoplastics and wood fibre. Sometimes, it may be difficult to isolate these factors. It has been reported that short compounding time, appropriate mixing temperature and moderate rotation speed improved the compounding quality, mechanical and the dynamic mechanical properties of the resultant composites [83, 84].

Rozman *et al*. [85] compared the effects of two different blending systems (an internal mixer and a single screw extruder) on the mechanical properties of oil palm-empty-fruit-bunch/polypropylene composites. Mixing was conducted for the internal mixer at 180°C at a rotation speed of 25 rpm. The single-screw extruder was operated at a rotation speed of 20 rpm at temperatures along the heating zones of 160, 170, and 180°C. They reported that compounding with the internal mixer produced composites with higher tensile strength, tensile modulus, and impact strength relative to the extrusion technique. This is because the internal mixer is thought to have produced better filler dispersion and improved the wetting of the filler surface.

The counter-rotating and the co-rotating twin-screw extruder (TSE) are also widely used as processing equipments employed in the manufacture of WTC, especially the intermeshing, co-rotating type. Fully intermeshing twin screws provide a narrow residence time distribution, therefore, provides uniform thermal history to the wood fibres, which prevents wood degradation. Co-rotating screws are effective in alternating the direction of applied stresses through the use of different mixing elements, thereby producing different mixing effects. Two types of mixing are widely used. They are the dispersive mixing and the distributive mixing [86] Dispersive mixing is the breaking-up of clumps or agglomerates of particles into the ultimate particulate size, while distributive mixing is the distribution of particles without decreasing their size. However, the effects of these two types of mixing on the preparation of WTC pellets are not clear [87].

Shakouri *et al*. [80] studied the effects of die pressure on the mechanical properties of WTC in extrusion process. A counter rotating twin screw extruder was used and the die pressure varied by changing the die outlet diameter in designed modular dies. Results revealed that increase in die pressure (smaller die cross section), led to an increase in compactness of the material and improved the tensile and flexural strengths. It was concluded that the strength-pressure relationship could govern the selection process of the equipment (size), especially when WTCs are intended for load-bearing applications. Similarly, Yeh and Gupta [88] examined the effects of processing conditions on the mechanical and water absorption properties of WTC. Counter and co-rotating twin screw extruders were used in the compounding process at different screw speeds of 85 and 150 rpm. This report showed that at a given wood content, the mechanical properties were similar, but using high screw rotation speeds, whether in the co-rotation or counter-rotation modes and long residence times, lowered the rates of moisture absorption even in the absence of a coupling agent. Caulfield *et al*. [89] maintained that extrusion being the most common processing method for WTC, is capable of processing highly viscous WTC and can also shape long, continuous profiles that are common in applications such as building materials.

2.4.2.2 Moulding

Moulding of plastics can be referred to as the confinement of a mass of molten plastic in a cavity of defined dimensions, called mould, while it hardens to the desired shape or finished article.

Compression moulding/injection moulding

Generally, compression moulding is the most commonly used method for moulding thermosetting plastics. In this method, dried plastic, in the form of powder or pellet, is heated to near the curing temperature, then loaded directly into the mould cavity. The temperature of the mould cavity is held at 150˚C–200˚C, depending on the material. The mould is then partially closed and the plastic, which is liquefied by the heat and the exerted pressure, flows into the recess of the mould. At this stage, the mould is fully closed and the flow and cure of the plastic is complete. Finally, the mould is opened and the completely cured moulded part is ejected [90]. Compression moulding has also been applied to thermoplastics in WTC production [91, 92]. Tungjitpornkull and Sombatsompop [93] investigated the effects of processing techniques on the mechanical properties of E-glass fibre reinforced wood/PVC composites by employing extrusion and compression moulding techniques. It was reported that the mechanical properties of composites from compression moulding were higher than that from extrusion. It was adduced that the shearing stress by the composites flow and deformation in compression moulding were relatively lower when compared to the extrusion process, suggesting that less shear induced degradation of the glass fibres were expected in the compression moulding process. In addition, the specific density of composites from compression moulding was considerably higher than that from the extrusion process; meaning that there is better compaction of the composites in compression moulding. However, compression moulding is adequate only when non-complicated shapes are required.

In injection moulding, the polymer is softened and conveyed with a screw in a manner similar to extrusion and the polymer is pushed, through a runner system, into a cavity or multiple cavities of a mould. The mould is cooled and eventually the mould separates and the solid parts are ejected [94]. Injection moulding has replaced compression moulding for some polymers, due to the advantages in materials handling and automation. The selection of correct parameters is crucial for the quality of injection moulded WTC products. Correct temperature is of utmost importance, since at temperatures above 200˚C, wood fibres start to degrade. It has been reported that when composite with high percentage of wood is injected (more than 50%), the injection speed has to be increased, otherwise the melt does not fill the cavity completely [95]. Injection moulding has been applied extensively in WTC research [96, 97]. Although injection moulding of WTC pellets produces more complicated parts, the limitation is that the wood content is assumed to be lower than that of extrusion. Jam and Behravesh [98] studied the challenges of producing injection moulded WTC using spruce wood (particle size less than 50 µm and HDPE) with 60-70% wood content. The results of this study revealed that increasing the mould temperature could enhance mould filling for wood contents up to 60%, while composites of 70% wood content present an incompletely filled mould resulting in defects in the final product. Nevertheless, when complex shapes of the products are desired, the injection moulding process is the best choice [18].

CHAPTER THREE

3 Experimental

3.1 Materials

Red Balau (*Shorea dipterocarpaceae*), a heavy hardwood saw dust was obtained from Heseh Woow Sdn Bhd, Klang, Selangor and Maltimber Industries, Malaysia. It was milled to between 40-100 mesh (400-150 µm) using a locally fabricated mill. The moisture content before heat treatment was less than 7%. Commercially available LDPE (Titanlene LDI300YY) with a density of 920 kg/m^3, molecular weight of 350,000 – 380,000 g/mol and MFI 20 g/10 min with a load of 2.16 kg at 190˚C, was supplied by Titan Petchem (M) Sdn Bhd. Malaysia was used as the matrix. Maleic anhydride grafted linear low density polyethylene, MAPE (Orevac 18302N), 0.8% grafting, with a density of 921 kg/m^3 was supplied by Arkerma, France, and used as the compatibiliser. Table 3.1 shows the properties of the raw materials.

Table 3.1: Properties of LDPE and MAPE

Property	Unit	LDPE	MAPE	ASTM test method
Melt index	g/10 min	20	1	D1238
Density	g/cm^3	0.92	0.921	D1505
Vicat softening point	˚C	87	88	D1525
Tensile strength at yield	MPa	11.77	23	D638
Tensile strength at break	MPa	9.81	-	D638
Elongation at break	%	120	810	D638
1 % Secant modulus	MPa	186.39	-	D638
Low temperature brittleness	˚C	-35	-	D746

3.2 Chemical characterization

3.2.1 Chemical constituents of wood flour

Acid insoluble lignin was determined using the ASTM D1106 standard [99]. Hemicellulose and cellulose were analysed according to the method described by Rowel *et al.* [31]. Extractives of moisture free samples were assessed using ASTM D1105 standard method with slight modifications [100]. After extracting a known mass with 95% ethanol and ethanol-toluene solution for six hours respectively, the percentage mass difference was calculated. A known mass of the extracted, oven dried moisture-free wood was also taken through three rounds of hot water extractions. The combined percentage mass of the extractives was then taken. The ash content was determined according to the ASTM E1755 [101].

3.2.2 Fourier transform infrared spectroscopic analysis

FTIR-ATR spectra of samples were recorded using the FTIR spectrophotometer (Spotlight 400, Perkin Elmer, USA), combined with a universal ATR accessory at a resolution of 4 cm^{-1} for 64 scans in the range of 650-4,000 cm^{-1}. Samples were pressed against the diamond crystal of the ATR unit. A pressure applicator with a torque knob ensured that the applied pressure was uniform for all measurements. A background spectrum of the clear window was recorded prior to sample spectra acquisition. The spectrum of the background was subtracted from that of the sample before conversion into transmittance units.

3.3 Determination of the apparent density of the wood flour

The apparent density of the wood flour was determined with some modifications according to the ASTM E212 [102]. A measuring cylinder of known volume, V, was placed on a weighing balance and the weight tarred to zero. The moisture-free wood flour was carefully loaded into the cylinder until it was completely filled and overflowing. A spatula was used to level off the powder flush with the top of the measuring cylinder. Care was taken not to shake or move the measuring cylinder. It was then tapped gently on the side in order to settle the wood flour and hence avoid spilling in transfer. The filled cylinder was weighed to the nearest 0.1 g in order to determine the mass, *M*, of the wood flour. The apparent density was calculated using the following equation:

$$\rho = \frac{M}{V} \qquad 3.1$$

where: *M* is the mass of the wood flour in grams and *V* is the volume of the measuring cylinder.

3.4 Processing

3.4.1 Wood pre-treatment

Untreated wood sawdust was dried in an oven at 60˚C for 48 hours to a moisture content of less than 1% and stored in sealed plastic bags over dried silica gel in desiccators for not more than 24 h prior to compounding. Wood sawdust was spread on an aluminium tray to a maximum height of between 8-10 mm in order to provide maximum heat transfer for efficient thermal modification. Heat pre-treatment was carried out at 180˚C and 200˚C. The oven temperature was raised to the desired temperature and the wood flour placed in it. It was left at this temperature for an effective treatment time of 1 h.

3.4.2 Compounding

LDPE, MAPE, wood flour were pre-mixed in different compositions at 200 g portions and compounded in a twin screw co-rotating extruder (Brabender KETSE 20/40 Lab Compounder, Germany, with screw diameter of 20 mm and L/D ratio of 40). The barrel temperatures along the barrel zones from were set at 150-150-150-155-155-155°C the hopper to the die and screw speed of 250 rpm was used. The melt pressure was varied between 34-39 bars (3.4-3.9 MPa) depending on the wood content, while the die temperature was between 164°C-178°C. Vacuum venting was used to remove the volatile compounds. The samples were extruded through a circular die of 3 mm in diameter. The extruded strand was cooled in a water bath and pelletised. Extruded pellets were oven dried at 80°C for 24 hours and stored in sealed plastic bags for about 24 h before injection moulding. Composites were prepared at three different fibre loadings of 9%, 20% and 37% by weight (equivalent of 20%, 40% and 60% by volume) based on the total weight of the composites, while MAPE was applied at 0, 2, 4, 6, 8 and 10 wt% MAPE based on the total weight of LDPE in the composite. The formulations of the composites are presented in Table 3.2.

3.4.3 Injection moulding

Pellets were injection moulded into tensile and impact test pieces using a 55 tonne BOY® 55M injection moulding machine at a barrel temperature of between 150°C and 155°C, an injection pressure of between 100-120 bars and mould a temperature of 25°C. Single gated 8 and 4 cavity impact and tensile standard bar moulds respectively were used in the moulding. The dimensions of the dumb-bell shaped tensile test pieces were in accordance with ASTM D638 type I [103].

Table 3.2: Formulations of composites

Sample code	Weight of LDPE (%)	Weight of MAPE (%)	Weight of wood flour (%)	Wood treatment temperature (˚C)
LDPE	100	0	0	-
LDPE/$W_{UN/9/0}$	91		9	-
LDPE/$W_{UN/20/0}$	80		20	-
LDPE/$W_{UN/37/0}$	63		37	-
LDPE/$W_{180/9/0}$	91		9	180
LDPE/$W_{180/20/0}$	80		20	180
LDPE/$W_{180/37/0}$	63		37	180
LDPE/$W_{200/9/0}$	91		9	200
LDPE/$W_{200/20/0}$	80		20	200
LDPE/$W_{200/37/0}$	63		37	200
LDPE/$W_{UN/9/2}$	89	2	9	-
LDPE/$W_{UN/20/2}$	78		20	-
LDPE/$W_{UN/37/2}$	61		37	-
LDPE/$W_{180/9/2}$	89		9	180
LDPE/$W_{180/20/2}$	78		20	180
LDPE/$W_{180/37/2}$	61		37	180
LDPE/$W_{200/9/2}$	89		9	200
LDPE/$W_{200/20/2}$	78		20	200
LDPE/$W_{200/37/2}$	61		37	200
LDPE/$W_{UN/20/4}$	76	4	20	-
LDPE/$W_{UN/37/4}$	59		37	-
LDPE/$W_{UN/20/6}$	74	6	20	-
LDPE/$W_{UN/37/6}$	57		37	-
LDPE/$W_{180/20/6}$	74		20	180
LDPE/$W_{180/37/6}$	57		37	180
LDPE/$W_{200/20/6}$	76		20	200
LDPE/$W_{200/37/6}$	57		37	200
LDPE/$W_{UN/20/8}$	72	8	20	-
LDPE/$W_{UN/37/8}$	55		37	-
LDPE/$W_{UN/20/10}$	70	10	20	-
LDPE/$W_{UN/37/10}$	53		37	-
LDPE/$W_{180/20/10}$	70		20	180
LDPE/$W_{180/37/10}$	53		37	180
LDPE/$W_{200/20/10}$	70		20	200
LDPE/$W_{200/37/10}$	53		37	200

3.5 Conditioning

Injection moulded tensile test specimens were subjected to different environments expected to be encountered in the service life of the composites in order to assess the effects of such environments on the composites properties.

3.5.1 Water absorption tests

Water absorption tests were performed on samples cut from tensile test stripes using ASTM D570 [104]. Samples of 50.0 x 13.0 x 3.3 mm dimensions were dried at 90°C to a constant weight. It was then immersed in distilled water at room temperature for 190 days. At predetermined time intervals, samples were removed, wiped with a blotting paper and immediately weighed to 0.0001g accuracy then returned to the water. The measurement was taken in less than 1 minute of removal from water. Three samples were used for each measurement and the average value was recorded.

3.5.2 Thickness swelling

The thickness swelling of the water soaked specimens was taken by marking three points along the length of the samples. At pre-determined intervals, samples were removed, wiped and the dimensions on the marked spots taken by a Mitutoyo (Japan) digital calliper. Three samples were used and the average result was reported.

3.5.3 Outdoor exposure

The out door weathering test was conducted according to ASTM D1435 [105]. Specimens were attached to a rack with a rack holder and adjusted to face the equator at an angle of 45°. The rack was placed in an open area, free from being overshadowed by other objects. Specimens were exposed to different environmental conditions such as rain, sunlight, wind, etc from April 1st to December 31st 2011. At the end of the test period, samples were collected, wiped clean and left to dry in air for 24 h at room temperature before mechanical, thermal and dynamic mechanical tests were conducted in order to determine the extent of properties degradation. Samples were exposed at the University of Malaya, Main Campus, geographically located on latitude 03˚ 07′ north of the Equator and longitude 101˚ 39′ east of the Prime Meridian. The mean temperature and total rainfall at the University of Malaya, Kuala Lumpur, Malaysia was compiled for each month according to the data obtained from the Malaysian Meteorological Agency and presented in Table 3.3.

3.5.4 Indoor exposure

Samples were arranged on a rack and exposed to ambient conditions in the laboratory from April 1st to December 31st 2011. At the end of the period, samples were removed and tested for thermal, mechanical and dynamic mechanical properties.

3.5.5 Burial tests

Samples were buried in garden soil to a depth of 30 cm in an open space free from shade for a period of 9 months from April 1st 2011 to December 31st 2011. At the end of the period, samples were removed, washed, wiped clean and left to air-dry at ambient conditions for 24 h prior to testing. Thermal, mechanical and dynamic mechanical tests were carried out on the buried samples in order to access the degree of degradation as a result of soil burial.

Table 3.3: The University of Malaya weather data from April 1st to December 31st 2011 [106]

Month	Mean relative humidity (%)	Mean rainfall (mm)	Mean temperature (°C)	
			Day	Night
April	85.5	10.4	28.2	25.5
May	80.2	9.7	28.8	26.2
June	81.4	4.7	27.4	26.6
July	79.6	3.5	27.9	26.4
August	83.0	9.2	28.3	25.8
September	84.1	8.1	27.7	25.8
October	85.5	9.2	27.7	25.3
November	86.6	5.5	27.5	25.1
December	84.8	8.0	27.3	25.2

3.6 Thermal analysis

3.6.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out in order to investigate the thermal decomposition behaviour of the composite materials by using the Perkin Elmer TGA 6 (USA) between 10-12 mg samples of each of the composites was used in a ceramic crucible, over a temperature range from 30^{o}C to 700^{o}C, at a heating rate of 10^{o}C/min. The tests were conducted in a nitrogen atmosphere at a flow rate of 20 mL/min. Samples were taken from the injection moulded tensile test specimens. From each specimen, samples were taken from the nearest, middle and furthermost portion from the gate of the mould cavity and subjected to TGA analyses. The weight change with temperature was analysed using the Pyris software. Derivative peak temperature (DT_p) was defined as the temperature of the maximum derivative of the weight change with time.

3.6.2 Differential scanning calorimetry (DSC)

DSC was carried out using the Perkin Elmer Diamond DSC, USA, (Hyper DSC) on 5-7 mg samples, crimped in aluminium pans. Samples were chosen as previously explained for the TGA. Each sample was characterised between -50°C to 200°C at a scan rate of 10°C/min. The specimen was heated to 200°C and held at this temperature for 2 minutes to erase the thermal history, then cooled under nitrogen atmosphere at a flow rate of 20 mL/min and heated again. The melting temperature, $T_{m,}$ was taken as the peak of the endothermic curve, while the crystallization temperature, T_c, was the peak of the exothermic curve.

3.7 Dynamic mechanical analysis (DMA)

DMA tests were carried out on rectangular test strips cut from the middle section of the tensile test specimen with 60.0 mm x 13.0 mm x 3.3 mm average dimensions in the three point bending mode with a support span of 50 mm, using a TA Q-800 dynamic mechanical analyzer from TA Instrument U.S.A. Each specimen was ramped from -100^{o}C to 100^{o}C at a scan rate of 2^{o}C/min under nitrogen at a fixed frequency of 1 Hz and an amplitude of 15 µm. The storage modulus, loss modulus and tan delta peaks were obtained using the TA universal analysis software.

3.8 Mechanical testing

3.8.1 Tensile Testing

Tensile tests were carried out using the universal testing machine (Instron 5569, USA) equipped with a load cell of 50 kN and a mechanical extensometer according to ASTM D638

[103]. The tests were done under ambient conditions at a cross-head speed of 5 mm/min (10%/min). A zero span of 50 mm was chosen for the extensometer. Injection moulded dumb-bell shaped specimens were used for the tests (Figure 3.1). The distance between the jaws of the clamp was fixed at 95 mm. The averages of at least five reproducible results were reported. The tensile modulus was calculated at a 0.5% strain.

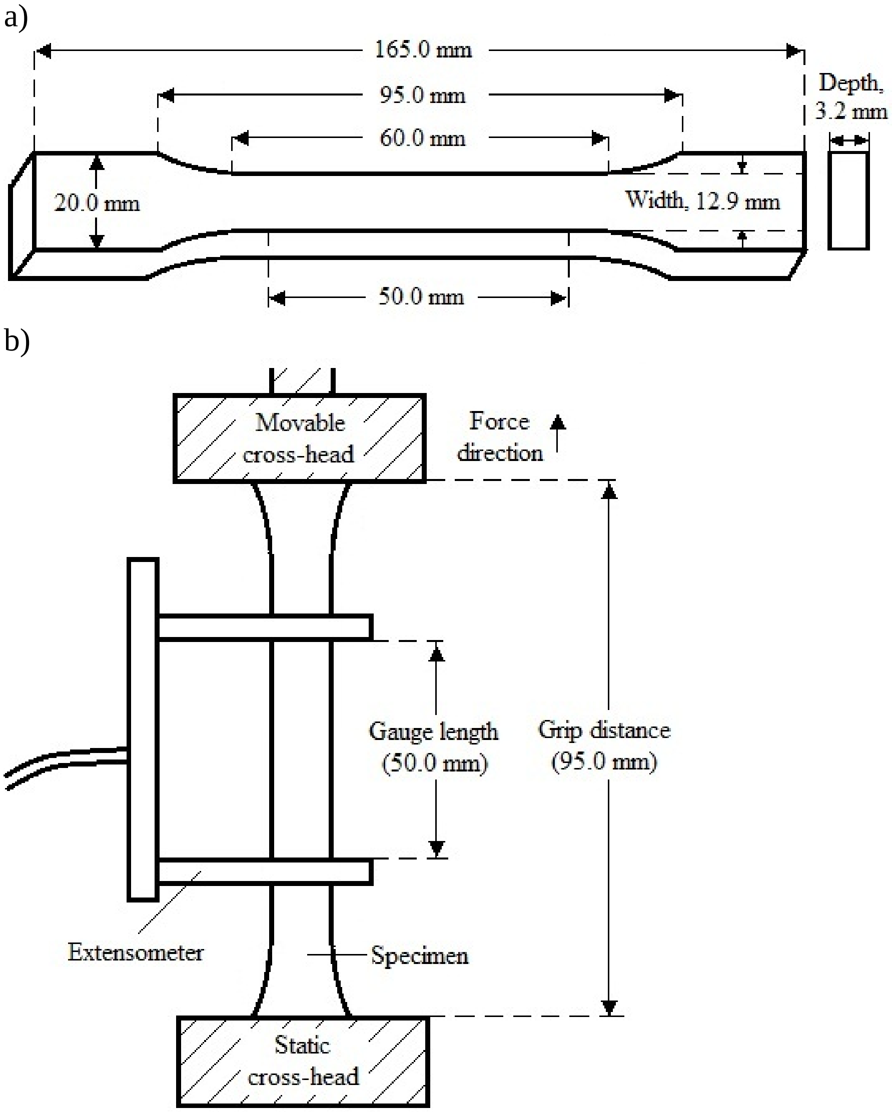


Figure 3.1 Tensile testing: a); specimen dimensions and b); set up

3.8.2 Flexural testing

The same instrument used for tensile testing was used for the flexural testing but on a three point bending mode according to ASTM D790 [107]. Tensile test specimens were used with a span of 50 mm. Maximum deflections of 30 mm and a crosshead speed of 1.28 mm/min were maintained throughout the experiment. The speed of the crosshead was calculated using the equation;

$$R = \frac{ZL^2}{6d} \qquad 3.2$$

where L and d are the specimen support span and depth respectively. The specimen thickness became the depth because the specimens were mounted in the flat position. Z is the straining rate of the outer fibre (equal to 0.01). L was fixed at 50 mm. Ten samples were tested and the values of the best six results were recorded. Figure 3.2 shows the arrangement of the specimen during the test.

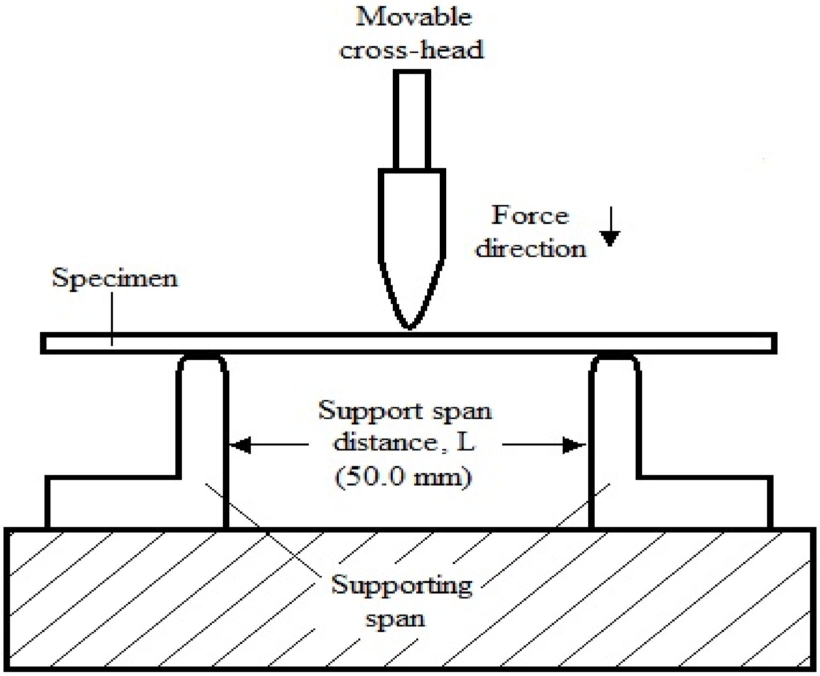


Figure 3.2: Set up of flexural testing

3.8.3 Impact testing.

The charpy impact test measures the energy absorbed by a standard notched bar specimen while breaking under an impacting load. Impact test bars of average dimensions 6 mm x 12 mm x 80 mm were notched at the centre of one edge in order to produce single edge notch (SEN) impact test specimen. The notch angle was set at 45°. Each batch was notched with four different notch-to-depth ratios (a/D) of 0.1, 0.2, 0.3 and 0.4 using a *Ray-Ran* notch cutting machine. The support span-to-depth ratio (S/D) was maintained at 4 throughout the experiment. The impact test was carried out in the Charpy mode using an Instron (Dynatup 9210, USA) falling weight impact tester with a V-shaped impactor tup. The test was run at ambient temperature, with a fixed impactor load weight (m) of 6.448 kg. The impactor height was adjusted to provide an impactor velocity (v) of 2.9238 ms^{-1} and impact energy of 13.9512 J. The impactor tup struck the specimen midway between the supports. For each batch, a minimum of 10 specimens were tested and the results presented were taken from the average of at least 8 reproducible data. ASTM standard E23 [108] was used as a standard in calculating the impact properties. The single edge notch (SEN) impact test specimen and set up are shown in Figure 3.3.

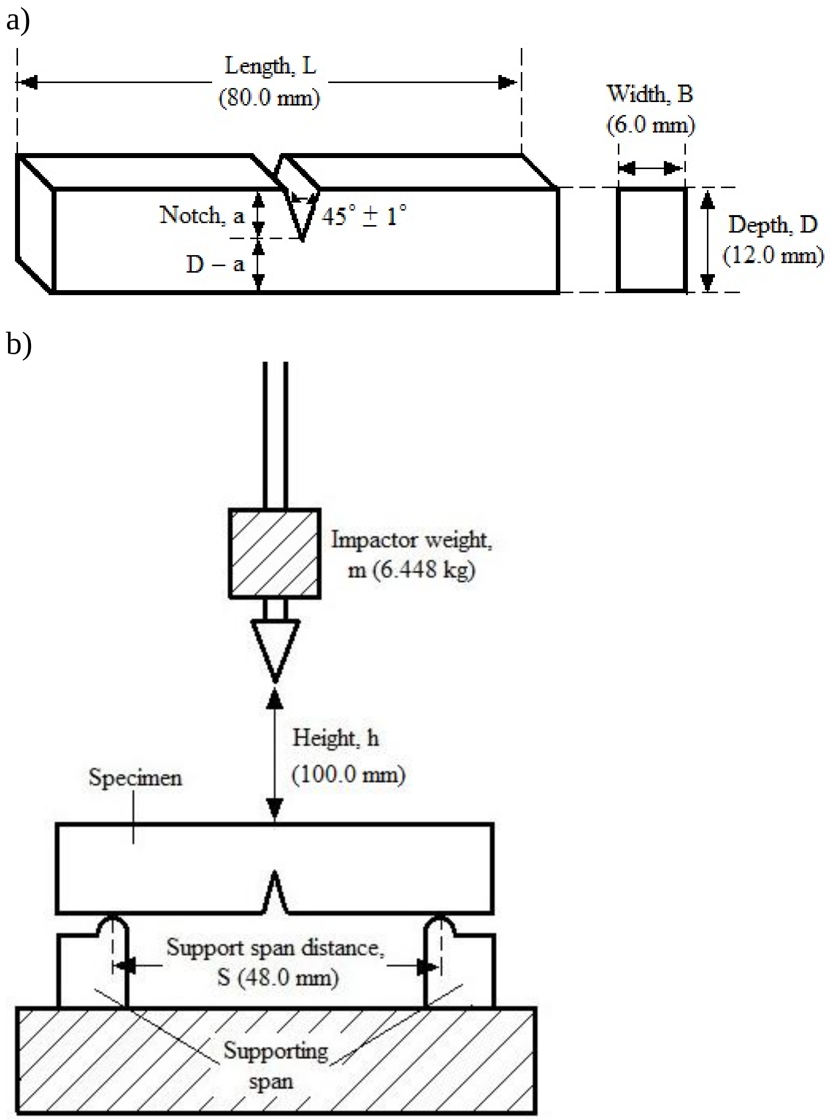


Figure 3.3: Impact testing: a) Specimen dimensions and b) set up

3.8.4 Scanning electron microscopy, SEM

The fractured surface of the tensile and impact test specimens was observed using the Leica S440 scanning electron microscope at an accelerating voltage of 10 kV after gold sputtering to a thickness of 0.014 µm to avoid unnecessary charges.

CHAPTER FOUR

4 Results and Discussion

4.1 Wood flour characterisation

4.1.1 Thermal treatment of wood flour

Thermal treatment, as a wood modification method, is intended to change the chemistry of the wood cell wall polymers and render the wood more hydrophobic. Figure 4.1 presents the TGA/DTG thermograms of untreated and treated wood flour at 160°C, 180°C and 200°C. Treatment temperature higher than 200°C was not achievable due to the limitations of the oven. Also, lower treatment temperature was not considered as wood flour treated at 160°C does not impart any thermal improvement to the wood flour, relative to the untreated material (Figure 4.1). The thermograms of untreated wood flour and that of treated material at 160°C overlapped, indicating that no appreciable changes were imparted to the wood flour treated at 160°C. Therefore, 180°C and 200°C were the treatment temperatures reported in this study. Previous researchers [74] had treated wood flour as fillers in WTC at 175°C, 190°C and 205°C.

4.1.2 Chemical composition

Basically, the major components of the wood cell wall are cellulose, hemicellulose and lignin. Minor constituents include the extractives and inorganics (ash). The % chemical composition of treated and untreated wood flour are shown in Table 4.1. The results suggest that carbohydrates are more susceptible to thermal degradation than lignin at the treatment temperature. Hemicellulose degraded faster than cellulose, as the values decrease from 29% in untreated wood to 28% and 25% when wood is subjected to heat treatment at 180°C and 200°C, respectively. The higher crystallinity of cellulose relative to hemicellulose may have conferred better resistance to thermal degradation in cellulose. Zaman *et al.* [109] have suggested that cellulose (a linear homo-polysaccharide of b-D-glucopyranose) is more thermally stable than hemicellulose. On the other hand, a steady increase in lignin content was observed as the treatment temperature increased. This clearly indicates that lignin is more thermally stable than carbohydrates and is in agreement with previous reports [110, 111].

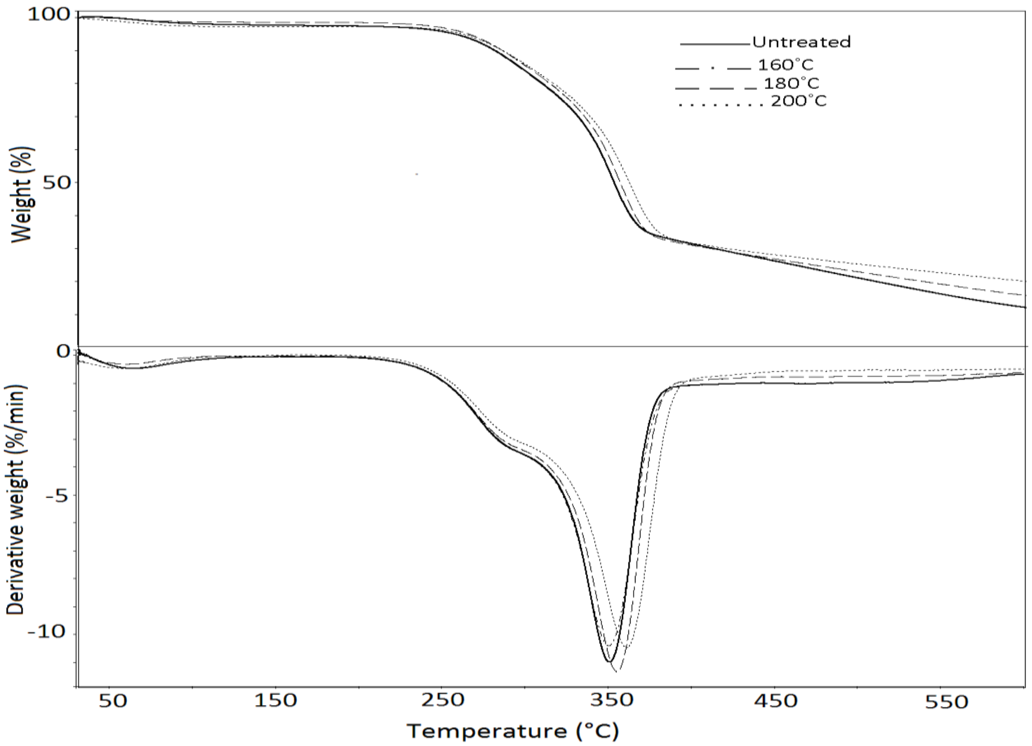


Figure 4.1: TGA/DTG thermograms of untreated and heat-treated wood flour

Table 4.1: Chemical composition of red balau saw dust

Wood treatment temperature (°C)	Lignin (%)	Hemicellulose (%)	Cellulose (%)	Extractives (%)	Ash (%)
Untreated	29	29	41	2	2
180	27	28	42	2	2
200	31	25	42	3	2

Total extractives were also determined for the untreated and heat-treated wood samples. There was no significant difference. It should be mentioned here that detailed compositions of this fraction was not studied in this investigation. The ash content of the wood samples indicated no particular trend. The total values obtained are in excess of 100%. Generally, in wood analysis, values between 98-101% are accepted, but frequently, values deficient in (or in excess) by about 10% are have been reported [112]. The reported values are within this range.

4.1.3 FTIR analysis of wood flour

FTIR is an important analytical tool used to study and identify the presence of functional groups in a molecule. The FTIR spectra of heat-treated and untreated wood flours are presented in Figure 4.2. The spectra look similar as all the samples exhibit characteristic signals of lignocellulosics. A broad peak of cellulose hydroxyl groups (O-H) appears at 3,335 cm^{-1} and another peak at 1,733 cm^{-1}, which is indicative of C=O aldehyde groups of hemicelluloses and lignin [113]. Despite the similarity in the spectra, a decrease in the intensity of the O-H absorption band at 3,335 cm^{-1} is observed in the heat-treated wood samples, with the wood sample treated at 200°C showing a profound decrease. This suggests that the O-H group content in the heat-treated wood is reduced after subjecting the wood flour to high temperature. This decrease occurs as a result of the elimination of O-H groups from the less ordered cellulose structure [114]. Such observation has been attributed to the decreased hydrophilicity of heat-treated wood by reduction of the potential bonding sites for water [115].

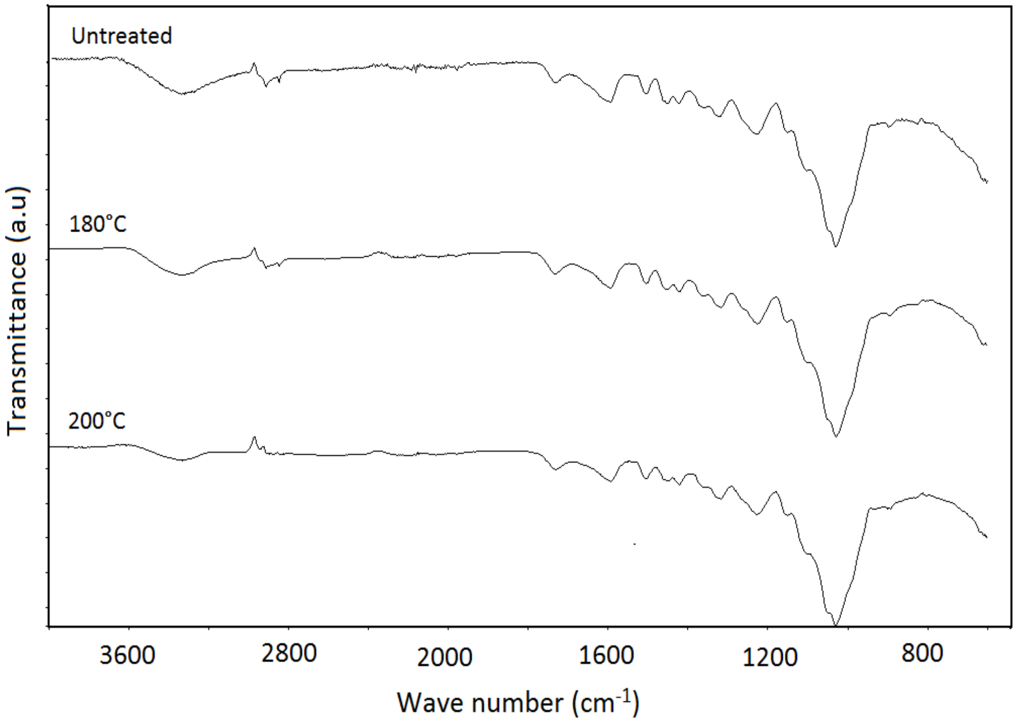


Figure 4.2: FTIR spectra of treated and untreated red balau saw dust

4.1.4 Thermal stability

Wood flour subjected to higher temperatures than drying is expected to exhibit changes in thermal properties. This is monitored using the thermogravimetric analytical technique. The principal events from the thermograms in Figure 4.1 are listed in Table 4.2. The curves exhibit two mass loss peaks. The first started at about 100°C and is attributed to the evaporation of moisture from the wood. The second peak, at between 200°C to 400°C, is due to the degradation of hemicellulose, cellulose and lignin. Lignocellulosic materials, being chemically active, decompose thermochemically in the range of 150°C to 500°C. Hemicellulose degrades between 150°C and 350°C, cellulose decomposes between 240°C and 350°C and lignin between 250°C and 500°C [116, 117]. The effect of heat treatment on the thermal stability of wood is also shown in Figure 4.1. Untreated wood has the lowest thermal stability, degrading at a lower temperature and at a faster rate than the heat-treated wood. Wood treated at 200°C reveals a higher resistance. Treating wood at 180°C indicate an intermediate thermal characteristic between the untreated and the wood treated at 200°C. However, percentage mass losses of 49%, 50% and 50% were obtained for the untreated, 180°C treated and wood treated at 200°C, respectively, with corresponding degradation peak temperatures of 351.4°C, 355.9°C and 362.4°C (Table 4.2). The increase in degradation peak temperature, T_p, of heat-treated wood over untreated ones is an evidence of improvement in thermal resistance of heat-treated wood. This trend is in agreement with previous report [118]. It has been observed that heat treatment results in the removal of hemicellulose, thereby rendering the wood more thermally stable [110] and that heat treatment of wood may improve the thermal properties by reducing its heat transfer co-efficient [119].

Table 4.2: TGA parameters of wood flour, LDPE and composites

Sample	Wood treatment temperature (°C)	T_p (°C)	Onset temperature, T_{onset} (°C)	$T_{50\%}$ (°C)	Degradation temperature range (°C)
Wood	-	351.2	255.7	352.5	213.5-397.8
Wood	180.0	356.6	275.6	355.7	207.1-391.7
Wood	200.0	362.4	297.0	361.6	226.5-400.7
LDPE	-	446.0	398.3	436.5	350.0-479.0
LDPE/$W_{UN/9/0}$	-	460.1	420.1	450.1	310.8-482.3
LDPE/$W_{180/9/0}$	180.0	455.7	361.3	434.9	250.9-478.6
LDPE/$W_{200/9/0}$	200.0	457.3	359.8	443.0	255.0-487.0
LDPE/$W_{UN/20/0}$	-	465.3	393.2	457.8	279.4-494.8
LDPE/$W_{180/20/0}$	180.0	465.5	395.6	456.5	257.2-493.6
LDPE/$W_{200/20/0}$	200.0	471.0	417.7	461.7	258.7-500.1
LDPE/$W_{UN/37/0}$	-	461.2	397.9	447.2	243.7-488.5
LDPE/$W_{180/37/0}$	180.0	460.0	366.7	440.1	232.1-488.5
LDPE/$W_{200/37/0}$	200.0	462.6	384.6	384.6	231.4-492.4
LDPE/$W_{UN/20/2}$	-	455.7	404.0	444.3	278.1-495.5
LDPE/$W_{180/20/2}$	180.0	459.3	420.5	448.5	240.9-496.2
LDPE/$W_{200/20/2}$	200.0	454.0	398.0	438.1	233.6-496.5
LDPE/$W_{UN/37/2}$	-	457.6	398.4	444.0	250.9-478.6
LDPE/$W_{180/37/2}$	180.0	460.3	405.9	443.8	218.6-497.4
LDPE/$W_{200/37/2}$	200.0	460.4	396.9	436.8	229.6-494.1
LDPE/$W_{UN/20/4}$	-	465.4	412.7	447.9	250.8-499.9
LDPE/$W_{UN/37/4}$	-	467.9	412.8	446.7	234.1-500.0
LDPE/$W_{UN/20/6}$	-	455.6	379.5	432.9	264.5-505.0
LDPE/$W_{180/20/6}$	180.0	464.6	422.4	452.7	255.2-501.7
LDPE/$W_{200/20/6}$	200.0	466.4	412.6	449.0	235.5-505.5
LDPE/$W_{UN/37/6}$	-	467.1	414.2	447.4	235.5-499.5
LDPE/$W_{180/37/6}$	180.0	467.1	420.1	453.8	233.8-502.6
LDPE/$W_{200/37/6}$	200.0	467.2	419.9	453.9	222.3-504.8
LDPE/$W_{UN/20/8}$	-	466.0	376.6	434.0	251.3-507.8
LDPE/$W_{UN/37/8}$	-	469.1	407.5	444.6	235.4-500.0
LDPE/$W_{180/20/10}$	180.0	470.2	427.4	459.0	230.0-503.8
LDPE/$W_{200/20/10}$	200.0	465.6	421.7	452.4	248.0-500.5
LDPE/$W_{UN/37/10}$	-	468.8	394.7	441.6	235.3-500.8
LDPE/$W_{180/37/10}$	180.0	468.5	408.3	448.2	239.0-497.8
LDPE/$W_{200/37/10}$	200.0	465.7	409.8	445.5	222.3-500.6

4.2 Dry as-moulded composites

4.2.1 Processing

The ability of thermoplastics to be repeatedly melted allows wood particles to be mixed with the plastic to form a composite product. In this study, wood flour in the form of particles (Figure 4.3) was used with a maximum loading of 37 wt% (the relative density of the wood flour was 354kg/m^3).

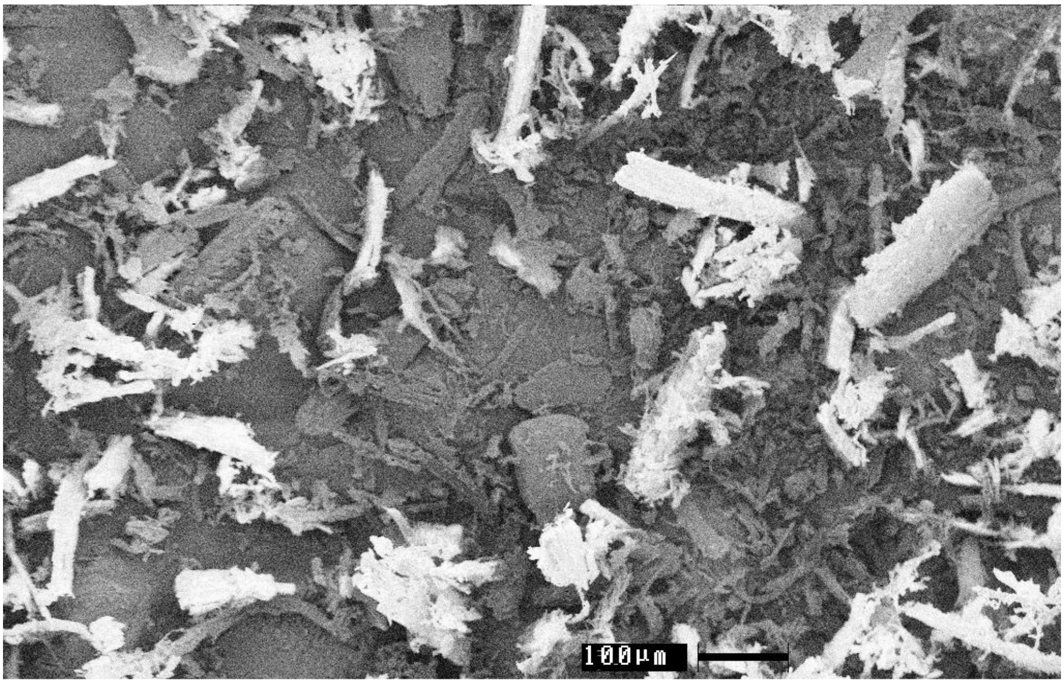


Figure 4.3: SEM micrograph of wood flour (dispersed on carbon tape)

This is because higher content of wood flour leads to processing difficulty due to high melt viscosity of the composite. Although the melt viscosity can be reduced by increasing the processing temperature, the degradation of wood at temperatures above 200°C limits the use of higher temperatures. In addition, the wood flour used in this study was heat-treated. Therefore, care was taken not to subject the wood to temperatures higher than that with which it was treated.

4.2.2 Thermal properties

Thermal analysis is defined by the International Confederation of Thermal Analysis and Calorimetry (ICTAC) as a group of techniques in which a property of a sample is monitored against time or temperature in a specified atmosphere while the temperature of the sample is programmed [120].

4.2.2.1 Themogravimetric analysis (TGA)

TGA is the branch of thermal analysis which measures the weight change of a sample as a function of temperature in the scanning mode or as a function of time in the isothermal mode in a controlled atmosphere. It is used to characterise the decomposition and thermal stability of materials under specified conditions [121].

The TGA/DTG of LDPE and composites from untreated and heat-treated wood at different filler contents are presented in Figure 4.4. From Table 4.2, it is clear that neat LDPE is more thermally stable than the wood flour. However, when LDPE is compounded with wood flour, a different thermal property profile is displayed. The thermal degradation patterns of the LDPE and the resultant composites reveal that the neat matrix is less thermally stable than the composites (Figure 4.4). The neat LDPE degrades faster with a single degradation peak at a temperature range of between 350°C and 480°C and a lower initial mass loss. It can also be seen that the degradation of wood, (although starting at a lower temperature than the neat matrix and composites), is more gradual and with a broader range. Furthermore, the degradation profiles of the composites indicate an improvement over the wood and the neat matrix, which degrade between 250°C and 500°C, over a wider range. Two degradation peaks are observed; a small peak representing the degradation of the wood flour contained in the composites occured around 350°C, while the main peak for the LDPE occured around 450°C. The main T_p values of the composites were also found to have appreciably increased over the values obtained for the neat matrix and the wood flour (Table 4.2).

Effect of wood content

From Figure 4.4, it can be seen that the thermal stability of composites containing the untreated and heat-treated wood flour increased steadily from 9 wt% till 20 wt%, then droped at 37 wt%. At 9 wt%, T_p of the untreated WTC is higher. At this composition, the amount of wood flour present is small, indicating a possibility that the thermal properties of the LDPE predominated over that of the wood flour. This masked the influence of the wood flour on the thermal stability of the composites, resulting in the observed trend. As the wood content increased to 20 wt%, a marked influence of the amount of wood flour on the thermal stability of the composites is seen. From Table 4.2, the T_p, T_{onset} and $T_{50\%}$ improved relative to the neat LDPE and the 9 wt% composites. However, as the wood content increased further, T_p is found to decrease reasonably. This is as a result of the lower thermal stability of wood when compared to LDPE [122]. Composites containing 37 wt% wood flour exhibit a reduction in thermal stability possibly because of the higher amount of filler contained which conferred lower thermal stability. In addition, T_{onset} and $T_{50\%}$, the temperature at which 50% mass of the composites degraded decreased with filler content in all the composites (Table 4.2).

Effect of heat treatment

The effect of heat treatment of wood flour on the thermal stability of WTC can be seen in Figure 4.5. For the heat-treated wood composites, $T_{50\%}$ increased up to 20 wt% and then decreased sharply at 37 wt%. Again, this could be a result of the higher amount of wood present at 37 wt%. This implies that 20 wt% can be regarded as the optimum composition at which the thermal stability of heat-treated wood composites is highest. The possible reasoning for the thermal behaviour at this filler content is that at 20 wt%, heat-treated wood, being less polar, provided a better interfacial adhesion between the fillers and the matrix. This may have resulted in a better dispersion of the fillers within the matrix which acted as barrier against the release of volatile gases during thermal degradation [123]. In addition, it has been reported that reinforcing polymers with heat-treated wood has proved to increase the thermal resistance of the neat matrix [72] possibly because the most heat-sensitive component, the hemicellulose, is reduced with heat treatment. As a result, composites from wood treated at 200°C impacted more positively on the thermal stability of the matrix than that from 180°C treated wood, which in turn showed better thermal stability than composites from untreated wood (Figure 4.5). However, composites at 20 wt% from wood treated at 200°C have the highest T_p value of 471.0°C, which is higher than that of wood and the neat LDPE, with maximum T_p values of 362.4°C and 446.0°C, respectively. This is indicative of an improvement in the thermal stability of the composites. This is due to the fact that lignin, the most thermally stable component in wood will not degrade appreciably at 200°C. Therefore, treatment at 200°C, which could significantly degrade other components of wood, will have little or no decomposition effects on lignin [111]. As a result, wood treated at 200°C has higher lignin content (Table 4.1) and leads to more thermally stable composites. Also, lignin has been found to exhibit effective antioxidant properties against free radical chain reactions which occur during thermal degradation of polyolefins [124]. It should be mentioned here that the reduced thermal stability at 37 wt% even for the heat-treated composites could be due to the fact that at higher filler loading, poor dispersion of the fillers within the matrix is inherent, with the possibility of wood-wood contact existing within the composite. Therefore, release of volatile gases during thermal degradation will be enhanced, leading to lower thermal stability.

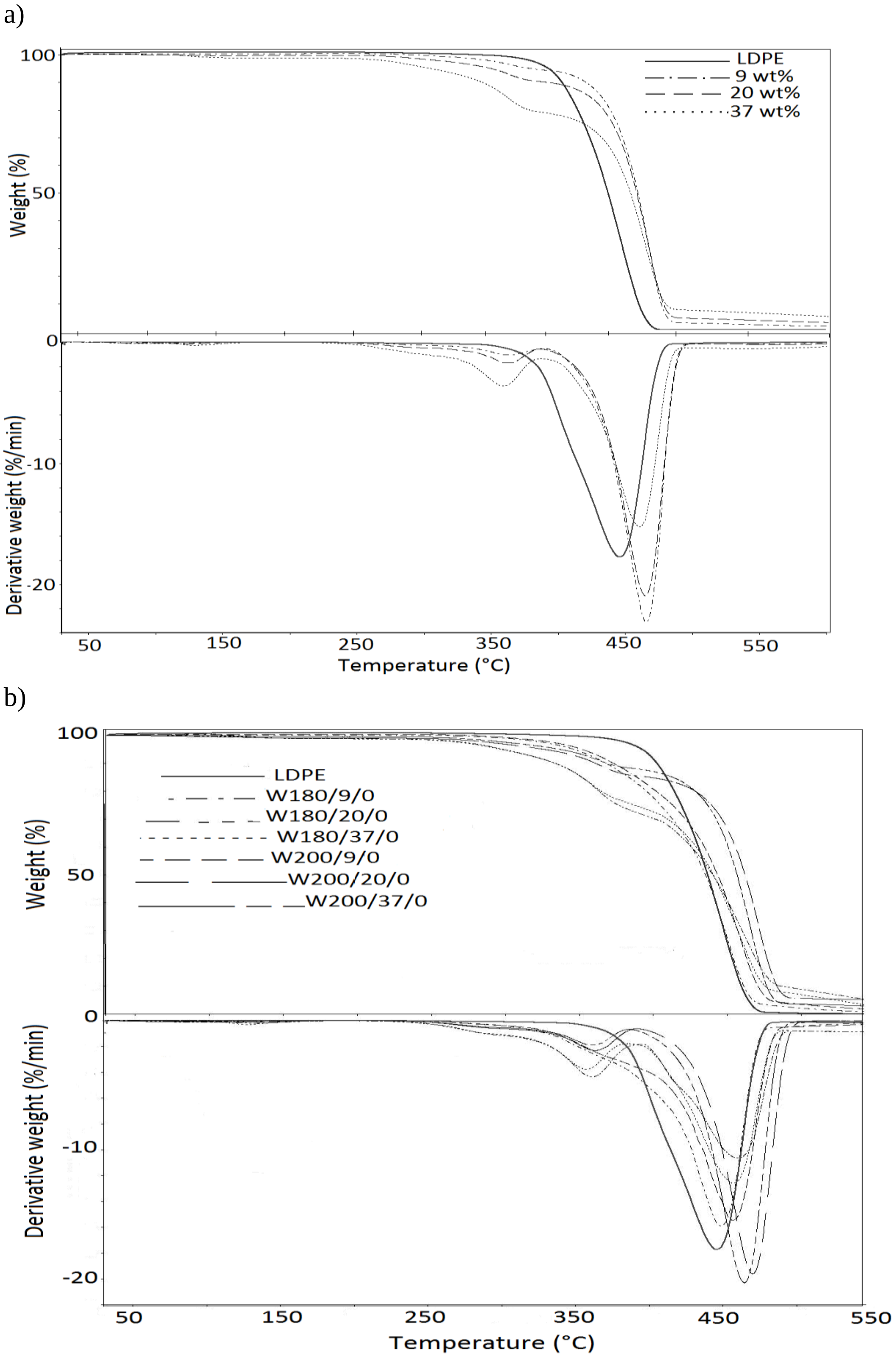


Figure 4.4: TGA-DTG thermograms of LDPE and a): untreated and b): heat-treated composites at different filler loadings

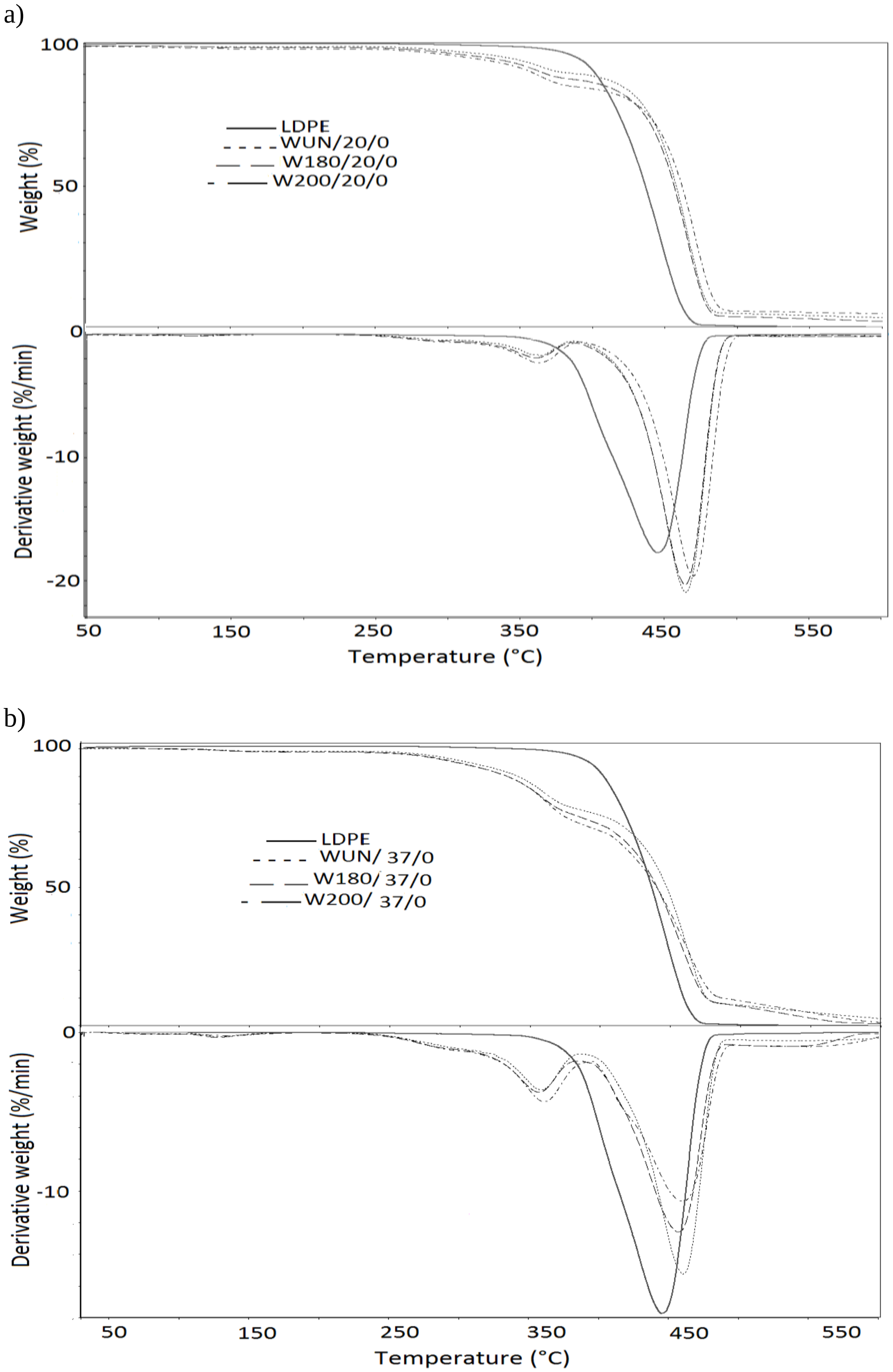


Figure 4.5: TGA-DTG thermograms of LDPE and a): 20 wt% and b): 37 wt% composites at different treatments

In general, thermal decomposition (pyrolysis) occurs when polyethylene is subjected to extremely high temperatures in the absence of oxygen. At temperatures in excess of approximately 400°C, the carbon–carbon bonds of the polyethylene backbone spontaneously break to yield two shorter chains, each of which is furnished with a terminal radical. Once the terminal radicals are produced, they may undergo ‘‘backbiting’’ reactions with backbone bonds, a few carbons further from the terminus. Backbiting results in the emission of low molecular weight alkanes and alkenes. When allowed to progress to completion, pyrolysis results in the complete conversion of polyethylene to gaseous hydrocarbons with no char produced [25]. However, conditions that can cause the thermal degradation described above are rarely encountered under normal service conditions. Therefore, judging from the T_p, the T_{onset} and the degradation temperature range obtained for the composites, it is evident that the composites will withstand temperatures expected in service life.

Effect of MAPE content

Figures 4.6 present the effect of MAPE content on the thermal degradation behaviour of untreated wood composites. Due to the poorer mechanical properties exhibited by the 9 wt% composition (to be discussed in later sections), only 20 wt% and 37 wt% compositions were studied at different MAPE contents. Although most of the curves overlapped, it can be seen from Table 4.2 that the thermal stability increased with MAPE content in the 20 wt% untreated wood composites, up to 4% MAPE. Beyond this, there seems to be no effect on the thermal stability of the composites. At this composition, the amount of wood fillers available for coupling is limited. Therefore, 4% MAPE content seems to provide the necessary interfacial adhesion necessary for good compatibility which, as observed earlier, could lead to improved thermal stability.

At MAPE content higher than 4%, a decrease in thermal stability is observed. However, at higher filler loading (37 wt%), 6% MAPE content appears to provide good wetting, leading to a more uniformly dispersed fillers within the matrix. This is responsible for the highest thermal stability achieved at this MAPE content. In addition, at this filler loading, more filler is available, meaning more compatibilisation and uniform dispersion, resulting in higher thermal stability. Similarly, MAPE content in excess of 6% did not show any appreciable improvement in thermal properties.

Considering the trend observed so far, the effect of MAPE content on the thermal stability of the heat-treated WTC were considered for 0%, 2%, 6% and 10% MAPE loadings. Attention was given to the MAPE content that gave the highest improvement in properties for the highest wood content (37 wt%). For this purpose, MAPE levels below and above this content were chosen for further studies.

The effect of MAPE content on the thermal stability of heat-treated WTC is given in Figure 4.7. For the heat-treated WTC, the addition of MAPE increased the thermal stability of the composites throughout the range of MAPE content studied. This is probably because treating wood at 180°C reduces the number of O-H groups on the surface of the wood particles, thereby reducing its polarity. This provided a platform for uniform dispersion of the fillers. Apart from this, it is also reasonable to assume that the few O-H groups left on the surface of the wood (Figure 4.2, page 55) must have reacted more efficiently with the MAPE in order to enhance better compatibility. However, the thermal stability of WTC made from 200°C treated wood decreased with MAPE content. It is possible that at this treatment, char was produced on the wood surface so that the intended compatibilisation is not achieved.

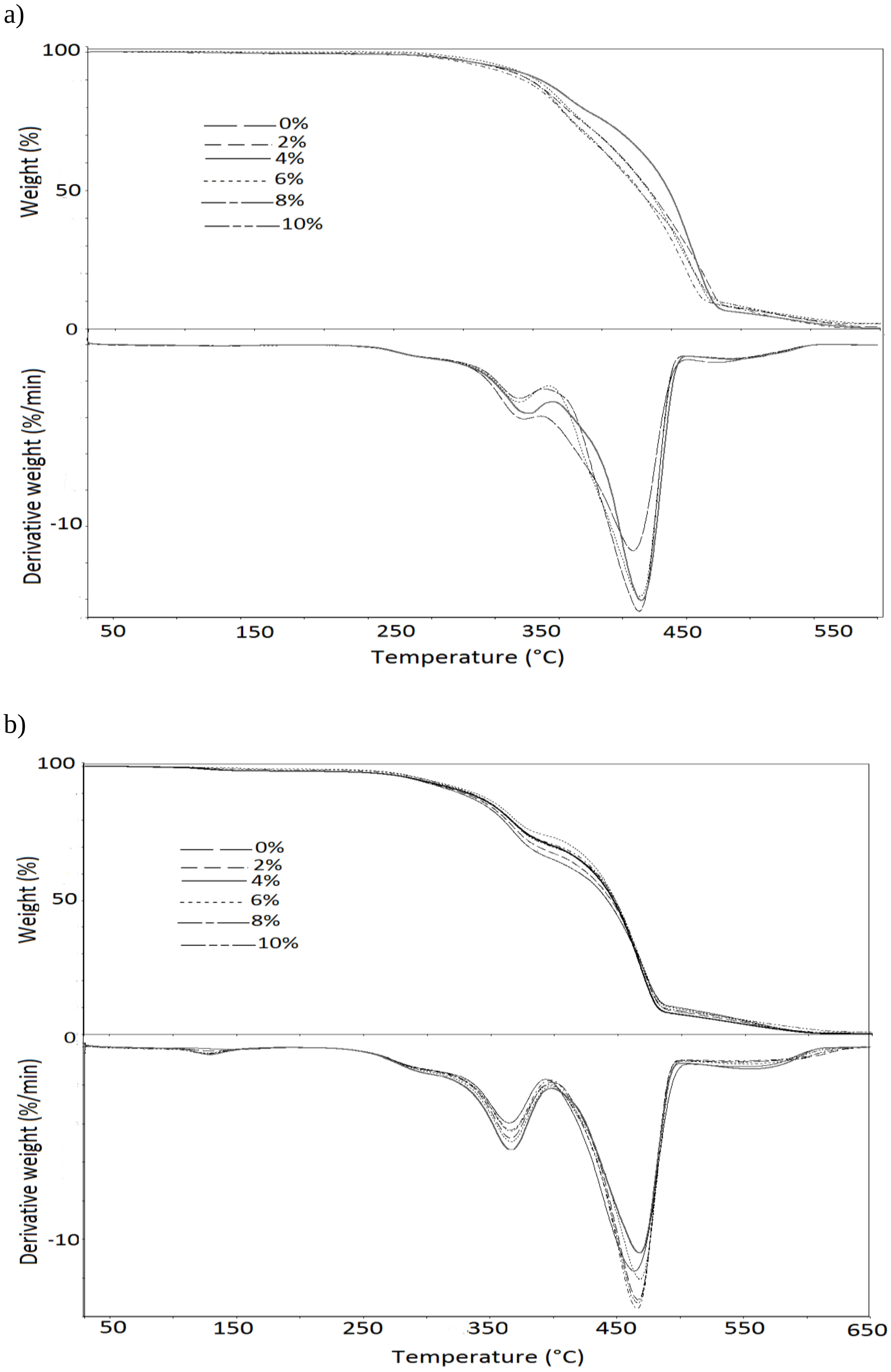


Figure 4.6: TGA/DTG thermograms of a): 20 wt% and b): 37 wt% untreated wood composites at different MAPE content

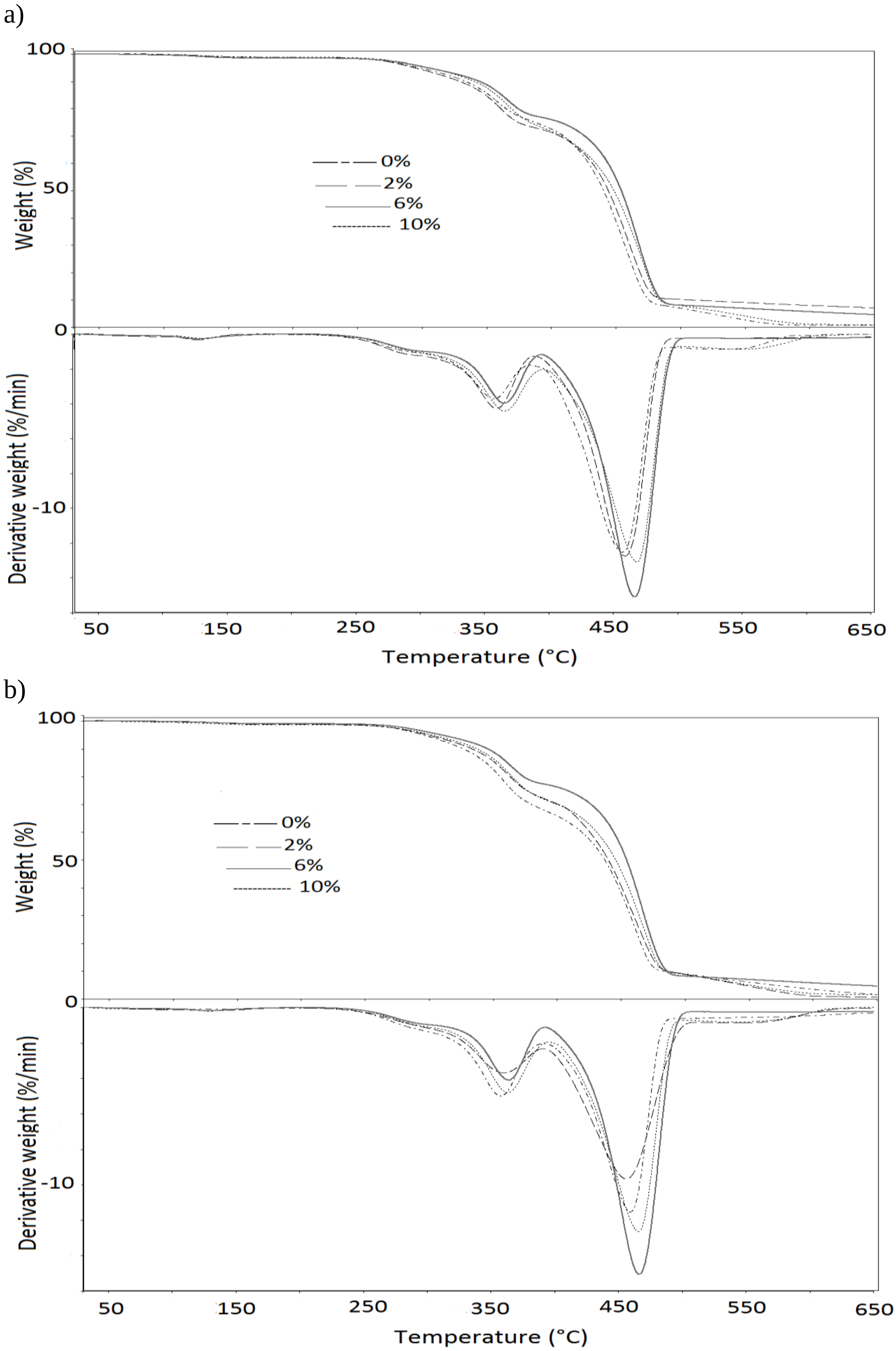


Figure 4.7: TGA/DTG curves of 37 wt% composites from wood treated a): 180°C and b): 200°C with varying MAPE contents

4.2.2.2 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is the most widely used of the thermal techniques available to the analyst. It provides a fast and easy to use method of obtaining a wealth of information about a material, whatever the intended end use. A DSC analyser measures the energy changes that occur as a sample is heated, cooled or held isothermally, together with the temperature at which these changes occur. The energy changes enable the user to find and measure the transitions that occur in the sample quantitatively and to note the temperature where they occur and so characterises a material for melting processes, measurement of glass transitions and a range of more complex events [125].

Melting behaviour

The melting point of a substance is defined as the temperature at which the solid phase exists in equilibrium with its liquid phase. When a substance undergoes a melting phase transition, the high degree of molecular arrangement existing in the solid becomes replaced by the disordered character of the liquid phase. In terms of the kinetic molecular approach, the melting point represents the temperature at which the attractive forces holding the solid together are overcome by the disruptive forces of thermal motion. The transition is accompanied by an abrupt increase in entropy and often, an increase in volume [126].

Effect of wood content

DSC curves corresponding to the cooling and the second heating scans of LDPE and composites from untreated wood at different wood loadings are presented in Figure 4.8. Data extracted from these curves are shown in Table 4.3. Incorporation of wood into

LDPE seems to have no effect on the melting temperature, T_m of the neat matrix (104.9°C). Values between 103-104°C are observed for all the composites studied. Apart from this observation, it seems that increasing wood content reduces the T_m of LDPE marginally. It has been observed that in WTC, wood particles penetrate the bulk polymer, thereby interfering with the formation of continuous polymer phase. This interruption in the polymer bulk in WTC, relative to the neat polymer, may lead to lower T_m [122]. This is in contrast with earlier findings, whereby incorporation of natural fillers into a thermoplastic matrix was reported to result in an increase in T_m of the composites [56, 127].

Effect of heat treatment

Figure 4.8 also presents the DSC curves showing the effect of heat treatment on the melting and crystallisation behaviours of the composites. Data from the DSC thermograms are summarised in Table 4.3. Heat treatment of wood seems to have no influence on the T_m of LDPE. All the composites studied exhibit similar T_m values as the neat LDPE.

Effect of MAPE content

The effect of MAPE content on the melting and crystallisation behaviour of composites from 37 wt% at different MAPE loadings, is presented in Figure 4.9. As has been observed for wood content and treatment temperature, the T_m of the composites seems to be independent of the amount of MAPE present. Values recorded are very similar, irrespective of the amount of MAPE incorporated.

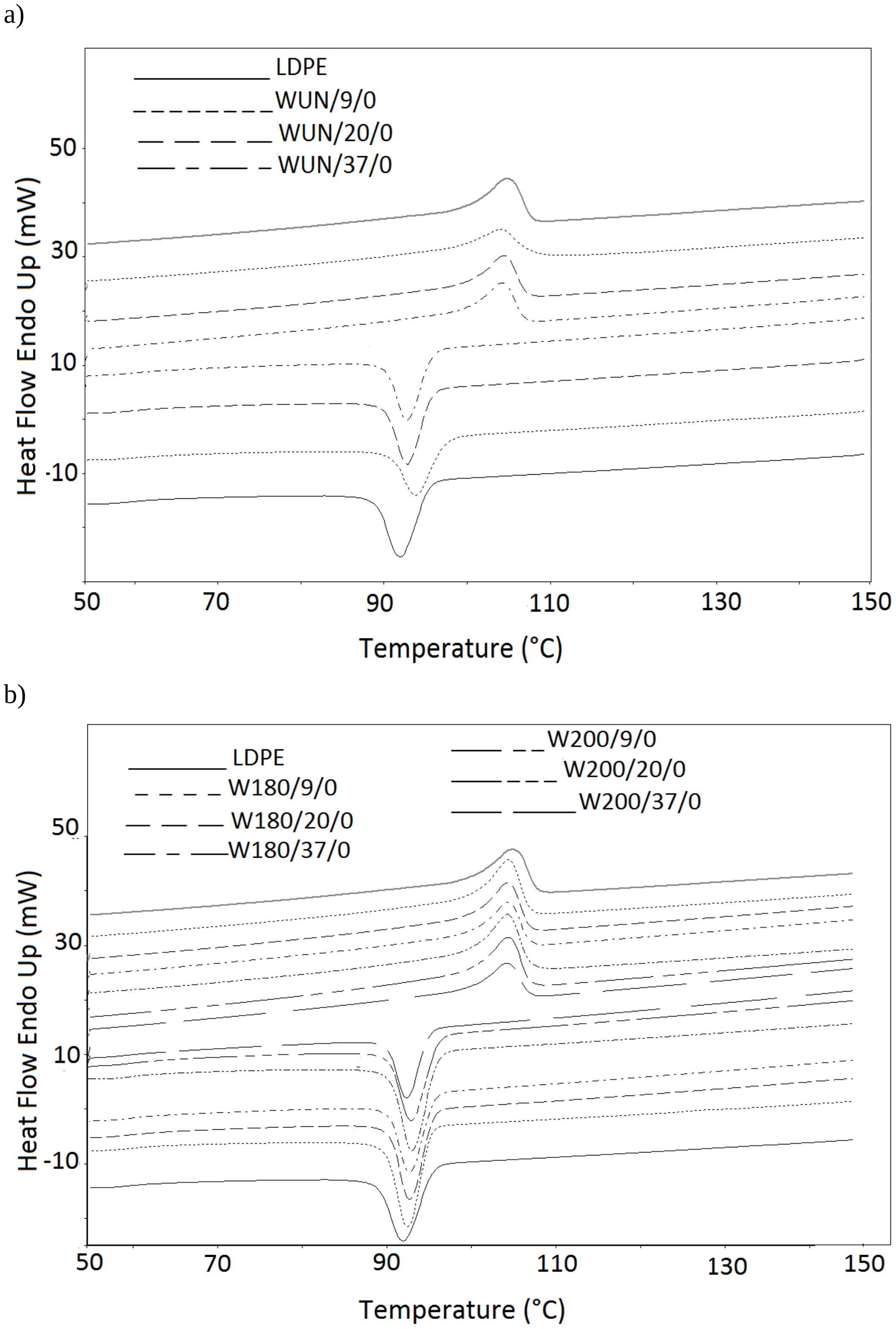


Figure 4.8: DSC thermograms of LDPE and composites containing varying amount of a): untreated and b) heat-treated wood flour

Table 4.3: DSC data of dry as-moulded samples

Sample	Wood treatment temperature (°C)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	$-\Delta H_c$ (J/g)	X_c (%)
LDPE	-	104.9	91.9	44.2	58.6	15.1
LDPE/$W_{UN/9/0}$	-	103.9	93.9	45.3	47.2	17.0
LDPE/$W_{180/9/0}$	180.0	104.4	92.5	40.1	62.4	15.0
LDPE/$W_{200/9/0}$	200.0	104.2	93.0	38.0	49.7	14.2
LDPE/$W_{UN/20/0}$	-	104.4	92.7	40.1	47.2	17.1
LDPE/$W_{180/20/0}$	180.0	104.4	92.8	38.0	45.5	16.2
LDPE/$W_{200/20/0}$	200.0	104.4	92.9	26.4	44.0	11.3
LDPE/$W_{UN/37/0}$	-	104.2	92.8	56.7	38.1	30.7
LDPE/$W_{180/37/0}$	180.0	104.4	92.8	30.5	48.8	16.5
LDPE/$W_{200/37/0}$	200.0	104.2	92.4	12.1	50.4	6.6
LDPE/$W_{UN/20/2}$	-	103.9	94.0	52.1	37.8	22.2
LDPE/$W_{180/20/2}$	180.0	104.0	93.7	30.1	42.3	12.8
LDPE/$W_{200/20/2}$	200.0	104.0	94.0	31.3	49.4	13.4
LDPE/$W_{UN/37/2}$	-	103.9	94.0	30.2	39.3	16.3
LDPE/$W_{180/37/2}$	180.0	104.0	93.9	29.3	32.3	15.9
LDPE/$W_{200/37/2}$	200.0	103.9	93.8	25.2	35.4	13.7
LDPE/$W_{UN/20/4}$	-	103.4	94.8	38.5	43.8	16.4
LDPE/$W_{UN/37/4}$	-	104.0	94.2	26.4	32.3	14.3
LDPE/$W_{UN/20/6}$	-	103.5	94.7	28.6	37.6	12.2
LDPE/$W_{180/20/6}$	180.0	103.7	94.8	24.8	39.0	10.6
LDPE/$W_{200/20/6}$	200.0	104.0	94.9	22.6	43.7	9.6
LDPE/$W_{UN/37/6}$	-	103.2	95.0	19.7	34.6	10.7
LDPE/$W_{180/37/6}$	180.0	104.4	94.0	22.5	40.4	12.2
LDPE/$W_{200/37/6}$	200.0	104.1	94.2	23.4	35.4	12.7
LDPE/$W_{UN/20/8}$	-	103.1	94.5	21.2	40.5	9.0
LDPE/$W_{UN/37/8}$	-	103.7	94.5	20.0	30.7	10.8
LDPE/$W_{UN/20/10}$	-	102.9	94.5	20.0	40.0	8.5
LDPE/$W_{180/20/10}$	180.0	103.3	94.0	21.9	43.4	9.3
LDPE/$W_{200/20/10}$	200.0	103.8	94.0	25.9	34.5	11.0
LDPE/$W_{UN/37/10}$	-	103.0	94.5	19.8	32.1	10.7
LDPE/$W_{180/37/10}$	180.0	104.1	94.3	17.7	35.2	9.6
LDPE/$W_{200/37/10}$	200.0	103.4	94.2	17.9	36.1	9.7

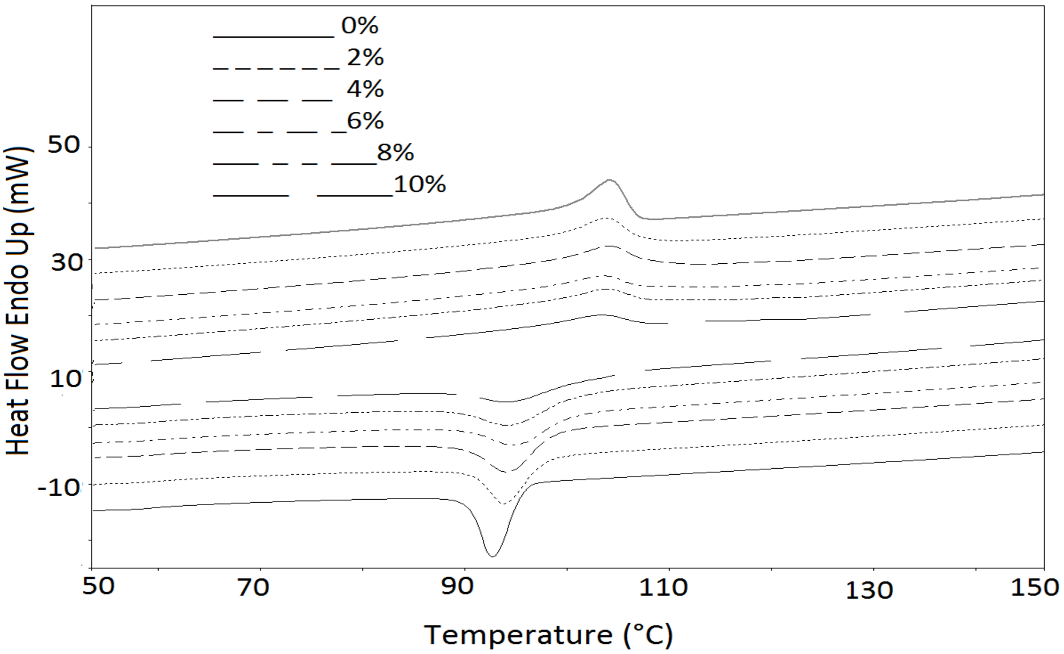


Figure 4.9: DSC thermograms of 37 wt% untreated wood composites with varying MAPE content

Crystallisation behaviour

Crystallisation is the process for the formation of a phase with long-range three-dimensional order from a disordered phase or from one that displays only local order. It provokes a discontinuous change in the enthalpy, volume, etc. Therefore, it is a first-order thermodynamic transition. Crystallisation occurs at a particular temperature below which the state of equilibrium is the crystalline state [128].

DSC analysis provides quantitative evaluation of the crystallisation behaviour of LDPE and composites. The relative percentage crystallinity of the composites was calculated according to the following equation [56],

$$X_c = \frac{\Delta H_m}{\Delta H_m^* W_m} \times 100 \qquad (4.1)$$

where X_c is the degree of crystallinity, ΔH_m is the heat of fusion, W_m is the weight fraction of LDPE in the composite and ΔH_m^* is the heat of fusion for the ideally fully crystalline LDPE, taken as 293 J/g [129].

Effect of wood content

In general, incorporation of wood flour exhibits a marginal effect on the crystallisation temperature, T_c, of LDPE (Figure 4.8). The neat matrix gives the lowest T_c value of 91.9°C, while composites from untreated wood at 9 wt% loading has the highest T_c value of 93.9°C (Table 4.3).

Loading untreated wood onto LDPE increases the X_c over the neat LDPE. This increases with wood content. The surface of untreated wood may be acting as a nucleating agent, which promotes crystalline growth and formation of trans-crystalline regions around the wood fibres [56, 130]. The higher the wood content, the higher is the formation of the trans-crystalline layer, thus leading to higher X_c.

Effect of heat treatment

Heat-treated wood seems to have no significant effect on the crystallization temperature, T_c (Figure 4.8b). Both 180°C and 200°C treated wood composites show similar trend of T_c. On the other hand, a decreasing pattern in X_c is observed for composites made from wood treated at 200°C at the various levels of loading. Wood treated at 180°C has $\mathrm{X_c}$ value of 15.0% for 9 wt%, 16.2% for 20 wt% and 16.5% for 37 wt% filler loadings respectively. These values are higher than the 200°C treated wood composites, which exhibit a downward trend in $\mathrm{X_c}$ values from 14.2% for 9 wt% through 11.3% for 20 wt% to 6.6% for the 37 wt% composites respectively. Heat treatment seems to deactivate the nucleating sites on wood, resulting in lower X_c. This deactivation is more pronounced with wood treated at 200°C since it is expected to be modified the most, through heat treatment [122]. Although heat-treated wood may contain some nucleating sites, these sites are not sufficient to influence the X_c [131]. This is evident in the X_c values for composites from wood treated at 180°C which showed a slight increase in X_c at 20 wt% and 37 wt%, relative to the neat matrix. It has been reported [127] that at higher filler loading, the particles act as diluents to the matrix and restrict crystal growth, thereby slowing down crystallization. Therefore, for the heat-treated wood composites, the higher the wood loading, the more is the resistance to the formation of crystal structures, leading to lower X_c.

Effect of MAPE content

The effect of different levels of MAPE loading is presented in the thermograms in Figure 4.9. Generally, incorporation of MAPE reduced the X_c of the composites at all the filler loadings and treatment temperatures studied (Table 4.3). However, for the untreated wood composites, X_c reduces more drastically in the 37 wt% composites than the 20 wt% counterparts. At 37 wt%, X_c decreased from 30.7% in composites without compatibiliser to 16.3% and 14.3 % when 2% and 4% MAPE is incorporated respectively. As the MAPE content increased further from 6% to 10%, a levelling-off effect is observed with no further changes in X_c. In addition, at 20 wt%, a decreased is observed as the MAPE content increased form 2% to 6%. Thereafter, only a marginal decrease is seen. It has been reported [132] that increased interaction between fillers and matrix reduces the nucleating ability of the filler, thereby reducing the X_c. On addition of MAPE, better interaction is expected between the wood and the LDPE as a result of the replacement of the O-H groups on the wood surface by the acetyl groups of MAPE. Furthermore, the substitution of the O-H groups in wood with the acetyl groups of MAPE must have introduced some stearic hindrance in the composites system that hinders the easy re-alignment of the polymer chains as crystallisation takes place from the melt [133]. This might have led to the observed behaviour in untreated wood composites. Similarly, the reduction of X_c in composites made from wood heat-treated at 180°C follows the same pattern as the untreated wood composites. However, the rate of decrease is not as high as the untreated wood composites. This is expected because having undergone heat treatment, the number of O-H groups available for coupling with MAPE is reduced, which may have also reduced the phenomenon of stearic hindrance resulting from the action of the coupling agent. In addition, this category of composites already exhibit low X_c relative to the untreated wood composites without compatibiliser. Nevertheless, no particular trend is observed for composites made from 200°C treated wood on addition of different MAPE levels.

4.2.3 Dynamic mechanical analysis

The term ‘‘dynamic mechanical analysis’’ (DMA) is used loosely to describe a broad range of techniques that measures a sample’s physical response to an applied oscillatory strain. Such experiments are used to determine the elastic and damping components of a sample’s response to mechanical perturbation as a function of frequency, time or temperature [25]. It involves imposing a small cyclic strain on a sample and measuring the resulting stress response, or equivalently, imposing a cyclic stress on a sample and measuring the resultant strain response [134]. The resulting information may be used directly to evaluate a material’s suitability for a specific application or in the investigation of the various mechanical transitions of materials [25].

4.2.3.1 Theoretical considerations

Consider applying a sinusoidal strain to an ideal elastic solid as shown in Figure 4.10;

$$\varepsilon(t) = \varepsilon_0 \cdot \sin(\omega t) \tag{4.2}$$

where ε is the strain and ω is the angular frequency.

At any point in time, the stress will be proportional to the strain according to Hooke’s law;

$$\sigma(t) = E \cdot \varepsilon(t) = E \cdot \varepsilon_0 \cdot \sin(\omega t) = \sigma_0 \cdot \sin(\omega t) \tag{4.3}$$

where σ is the applied stress.

Thus, for an ideal solid, the stress will be a sinusoidal function in-phase with the strain and the ratio of the amplitude of stress and strain will be the storage (real) modulus of the material.

$$E' = \frac{\delta_0}{\varepsilon_0}\cos(\delta) \qquad (4.4)$$

where δ is the phase angle

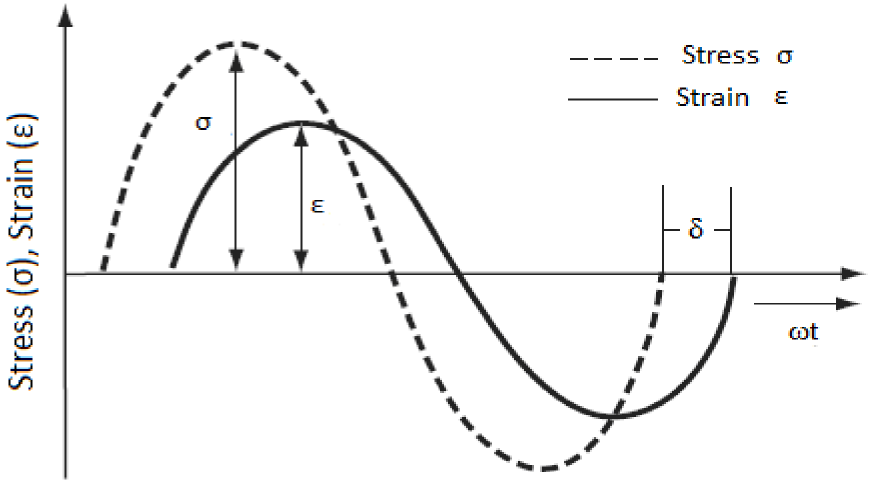


Figure 4.10: Stress and strain in dynamic mechanical analysis [134]

Now, consider what happens if a sinusoidal force is applied to an ideal liquid;

$$\gamma = \gamma_0 \cdot \sin(\omega t) \qquad (4.5)$$

At any point in time, the stress will be proportional to the strain rate in accordance with Newton's law of motion;

$$\tau(t) = \eta \cdot \dot{\gamma}(t) = \frac{\eta \cdot d\gamma(t)}{dt} = \eta \cdot \gamma_0 \cdot \omega \cdot \cos(\omega t) = \eta \cdot \gamma_0 \cdot \omega \cdot \sin\left(\omega t + \frac{\pi}{2}\right) \qquad (4.6)$$

Thus, for an ideal liquid, the stress will be a sinusoidal function of 90° out-of-phase with the strain. This 90° phase difference between sinusoidal stress and strain in liquids is the key to the use of DMA as a tool for characterising visco-elastic materials. Since a visco-elastic material has properties intermediate between those of an ideal solid and an ideal liquid, it exhibits a phase lag somewhere between 0° (ideal solid) and 90° (ideal liquid). Thus, DMA applies a given strain and measures the resulting stress as well as the relative amplitude of stress and strain (the modulus) and the phase lag, which is a measure of the relative degree of viscous character to elastic character [133].

4.2.3.2 Storage modulus, E′

The storage modulus, E', is closely related to the load bearing capacity of a material and is linked to the flexural modulus (E). It is a measure of the energy stored in the material during a cycle and describes the elastic character or the solid-like nature of the material, given by Equation 4.4. In order to obtain the material's stiffness as a function of temperature, DMA experiment was performed on the neat LDPE and composites from untreated and heat-treated wood flour.

Effect of wood content

Figure 4.11 presents the variation of E' with temperature for untreated wood flour at different filler loadings. From this figure, a decreasing trend in E' is observed as the temperature increased. However, E' of the composites is higher than that of the neat LDPE throughout the temperature range employed in this experiment. This disagrees with the findings of Yang *et al.* [135], who observed that at lower temperatures, E' of the composites is very close to that of the matrix because the filler do not contribute meaningfully to the stiffness of the matrix. However, their finding is in agreement with this study, i.e. the E′ curves tend to converge at higher temperature. E′ values for LDPE and composites were found to decrease steadily with increase in temperature. This is as a result of the matrix softening at higher temperature due to segmental mobility [136]. However, an abrupt decrease is noticed between -15°C to 10°C which is believed to correspond to the glass transition region of the matrix. Thereafter, an appreciable decrease could not be observed (from 50°C) as the matrix approaches its softening temperature. The reinforcing effect of the wood filler in the composites allows stress transfer from the matrix to the filler [137], thereby maintaining reasonably high *E′* values at high temperature. This may be responsible for this trend. *E′* values increased with wood content (Table 4.4).

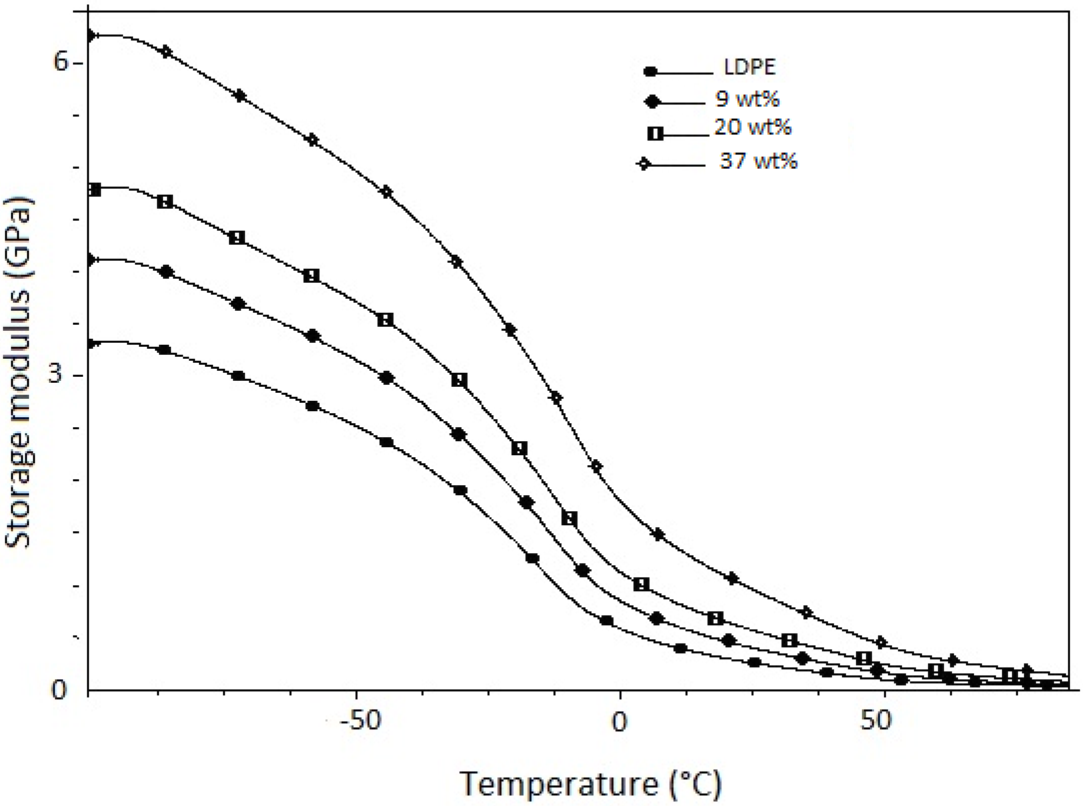


Figure 4.11: Storage modulus of LDPE and composites as a function of wood content

Fillers have a significant role in increasing the *E′* of polymeric matrices. As can be seen from Figure 4.11, *E′* values at 25°C, $E'_{25°C}$, increased with filler loading. The reinforcing ability of the fillers may be accountable for this observation. It has been reported [136] that at lower filler loading, restriction of the matrix by the filler is also reduced due to insufficient fillers, leading to highly localized strains occurring in the matrix at low stresses. This results in the breaking of the bond between the matrix and the filler, leaving the matrix diluted by the non-reinforcing de-bonded fillers. However, at higher filler loading, the stress is more evenly distributed throughout the composite, thereby increasing E'. In addition, as the temperature increases, the presence of fillers restricts the flow of the matrix polymer. This restriction is proportional to filler loading [135], thereby enabling the material to maintain a relatively high modulus.

Effect of heat treatment

The effect of heat treatment on the composites E' is presented in Figure 4.12a. Heat treatment seems to have a marginal effect on the E'. E' seems to improve slightly with incorporation of wood flour treated at 200°C (Table 4.4). At 25°C, E' values of 0.97, 0.96 and 1.07 GPa are observed for 37 wt% untreated, 180°C and 200°C treated wood composites respectively. Composites made from wood treated at 180°C have E' values lower than untreated wood composites. This may imply that heat treatment at 200°C influences the interfacial stiffness resulting from better filler-matrix interactions.

Effect of MAPE content

Figure 4.12b presents the effect of MAPE content on the storage modulus of composites at 37 wt% wood loading. Addition of MAPE showed no significant increment in the E' of the composites studied. The uncoupled wood composites exhibited higher E' values at -100°C, $E'_{-100^\circ C}$ (6.3 GPa) than the coupled composites. This is in line with earlier findings, whereby incorporation of MAPP into PP-wood flour composites was found to lower E' as a result of the formation of a thin and irregular polymer layer which could assist the formation of plastic deformation zone around the fibre [138]. However, as the temperature increased to 25°C, E' values dropped to 0.97 GPa for the uncoupled composites, similar to E' values of the coupled composites.

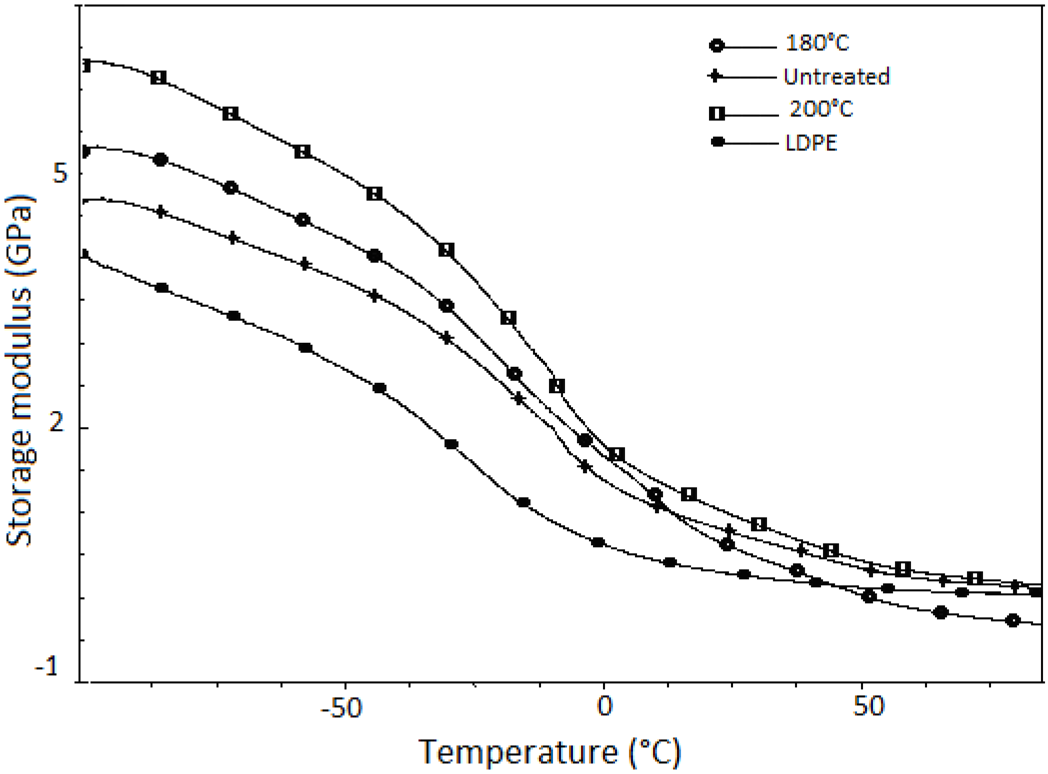
Table 4.4: DMA data of dry as-moulded samples

Sample	Wood treatment temperature (°C)	$Tan\delta$				Storage modulus E'	Loss modulus E"			
		$Tan\ \delta_{\mathrm{max}}$	Temperature at $tan\ \delta_{max}$ (℃)	$W_{\sqrt{2}}$	$Tan\delta_{25°\mathrm{C}}$	$E'_{25°\mathrm{C}}$ (GPa)	$E'_{-100°\mathrm{C}}$ (GPa)	$E''_{25°\mathrm{C}}$ (MPa)	$T_{\beta}^{E''}$ (℃)	E''_{max} (MPa)
LDPE	-	0.16	39.1	74.1	0.15	0.26	4.0	40.0	-24.6	140.1
LDPE/W$_{\mathrm{UN/9/0}}$	-	0.16	42.5	72.7	0.15	0.30	4.1	40.0	-19.9	170.3
LDPE/W$_{\mathrm{180/9/0}}$	180.0	0.15	43.2	73.4	0.15	0.35	3.8	51.9	-20.1	160.2
LDPE/W$_{\mathrm{200/9/0}}$	200.0	0.16	44.1	73.5	0.15	0.31	3.7	50.0	-19.2	130.4
LDPE/W$_{\mathrm{UN/20/0}}$	-	0.15	45.9	70.5	0.14	0.57	3.9	80.0	-19.1	200.1
LDPE/W$_{\mathrm{180/20/0}}$	180.0	0.16	47.4	66.0	0.13	0.56	3.6	60.0	-19.8	143.3
LDPE/W$_{\mathrm{200/20/0}}$	200.0	0.16	49.7	63.1	0.13	0.51	3.8	69.1	-18.1	150.3
LDPE/W$_{\mathrm{UN/37/0}}$	-	0.14	43.7	66.0	0.13	0.97	5.3	124.0	-16.7	249.1
LDPE/W$_{\mathrm{180/37/0}}$	180.0	0.14	48.1	66.6	0.12	0.96	5.6	126.9	-17.4	181.0
LDPE/W$_{\mathrm{200/37/0}}$	200.0	0.15	50.3	58.7	0.12	1.07	5.7	130.0	-15.9	220.3
LDPE/W$_{\mathrm{UN/20/2}}$	-	0.16	47.4	67.3	0.13	0.46	3.6	61.4	-19.3	141.4
LDPE/W$_{\mathrm{180/20/2}}$	180.0	0.16	50.3	64.9	0.14	0.58	4.0	80.0	-17.7	162.3
LDPE/W$_{\mathrm{200/20/2}}$	200.0	0.16	50.3	61.7	0.14	0.52	3.9	81.2	-18.7	150.1
LDPE/W$_{\mathrm{UN/37/2}}$	-	0.15	51.6	68.7	0.12	0.74	4.5	88.0	-17.9	171.0
LDPE/W$_{\mathrm{180/37/2}}$	180.0	0.15	52.6	52.9	0.12	1.08	5.6	125.0	-16.1	202.0
LDPE/W$_{\mathrm{200/37/2}}$	200.0	0.15	53.0	62.3	0.13	1.02	5.8	130.0	-16.8	220.4
LDPE/W$_{\mathrm{UN/20/4}}$	-	0.17	51.6	63.4	0.14	0.54	3.9	73.8	-19.9	153.3
LDPE/W$_{\mathrm{UN/37/4}}$	-	0.15	49.8	57.4	0.12	1.06	5.8	125.0	-18.3	211.4
LDPE/W$_{\mathrm{UN/20/6}}$	-	0.17	52.1	63.6	0.14	0.55	4.0	77.5	-19.9	157.1
LDPE/W$_{\mathrm{180/20/6}}$	180.0	0.17	52.2	66.4	0.14	0.49	3.7	69.4	-19.5	146.3
LDPE/W$_{\mathrm{200/20/6}}$	200.0	0.17	55.0	69.0	0.14	0.49	3.7	66.8	-20.7	150.4
LDPE/W$_{\mathrm{UN/37/6}}$	-	0.16	51.0	58.3	0.13	1.03	5.7	131.0	-19.3	220.2
LDPE/W$_{\mathrm{180/37/6}}$	180.0	0.16	51.8	66.4	0.14	0.71	4.6	96.6	-18.3	181.0
LDPE/W$_{\mathrm{200/37/6}}$	200.0	0.17	55.1	59.0	0.13	0.82	4.9	106.0	-19.2	190.2

Table 4.4 cont’d

Sample	Wood treatment temperature (°C)	$Tan\delta$				Storage modulus E'	Loss modulus E"			
		$Tan\ \delta_{max}$	Temperature at $Tan\ \delta_{max}$ (℃)	$W_{\sqrt{2}}$	$Tan\delta_{25°C}$	$E'_{25°C}$ (GPa)	$E'_{-100°C}$ (GPa)	$E''_{25°C}$ (MPa)	$T_{\beta}^{E''}$ (℃)	E''_{max} (MPa)
LDPE/$W_{UN/20/8}$	-	0.17	53.7	68.8	0.14	0.59	4.2	82.2	-20.1	164.2
LDPE/$W_{UN/37/8}$	-	0.16	54.1	63.1	0.13	0.94	5.5	122.0	-18.6	210.1
LDPE/$W_{UN/20/10}$	-	0.17	54.2	53.1	0.13	0.64	4.2	79.1	-19.9	157.5
LDPE/$W_{180/20/10}$	180.0	0.17	55.3	72.9	0.14	0.49	3.8	66.0	-21.3	145.7
LDPE/$W_{200/20/10}$	200.0	0.17	54.8	69.4	0.14	0.50	3.8	66.5	-21.6	151.8
LDPE/$W_{UN/37/10}$	-	0.16	55.2	62.0	0.13	1.02	5.6	128.0	-18.1	201.0
LDPE/$W_{180/37/10}$	180.0	0.16	57.0	59.7	0.12	0.85	5.0	104.0	-19.9	185.6
LDPE/$W_{200/37/10}$	200.0	0.17	55.3	65.1	0.14	0.76	4.8	102.0	-20.4	180.7

a)



b)

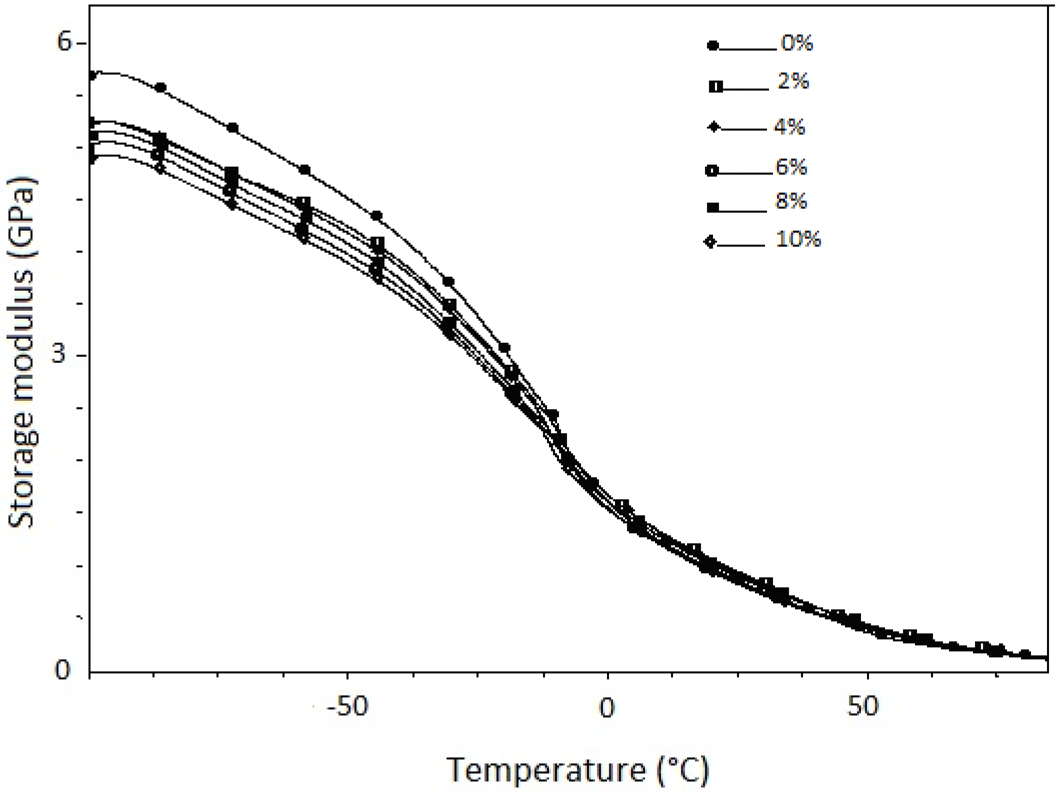


Figure 4.12: Storage modulus of LDPE and 37 wt% composites as a function of: a) heat treatment and b) MAPE content

4.2.3.3 Loss modulus, *E″*

It is also referred to as the imaginary (out-of-phase) modulus and is a measure of the viscous character or liquid-like nature of the material. It relates the ability of the material to dissipate energy and it is given by the equation;

$$E'' = \frac{\sin(\delta_0)}{\varepsilon_0} \tag{4.7}$$

Effect of wood content

Loss modulus, E'' curves for LDPE and composites containing untreated wood flour at different filler loadings are shown in Figure 4.13. Only the β relaxation peak is observed for the neat LDPE and the composites throughout the experimental temperature range. It has been suggested that in LDPE, which is a branched polymer, a clear β relaxation peak which is associated with the relaxation of the branched points and attributed to the segmental motions in the non-crystalline phase, can be detected [139].

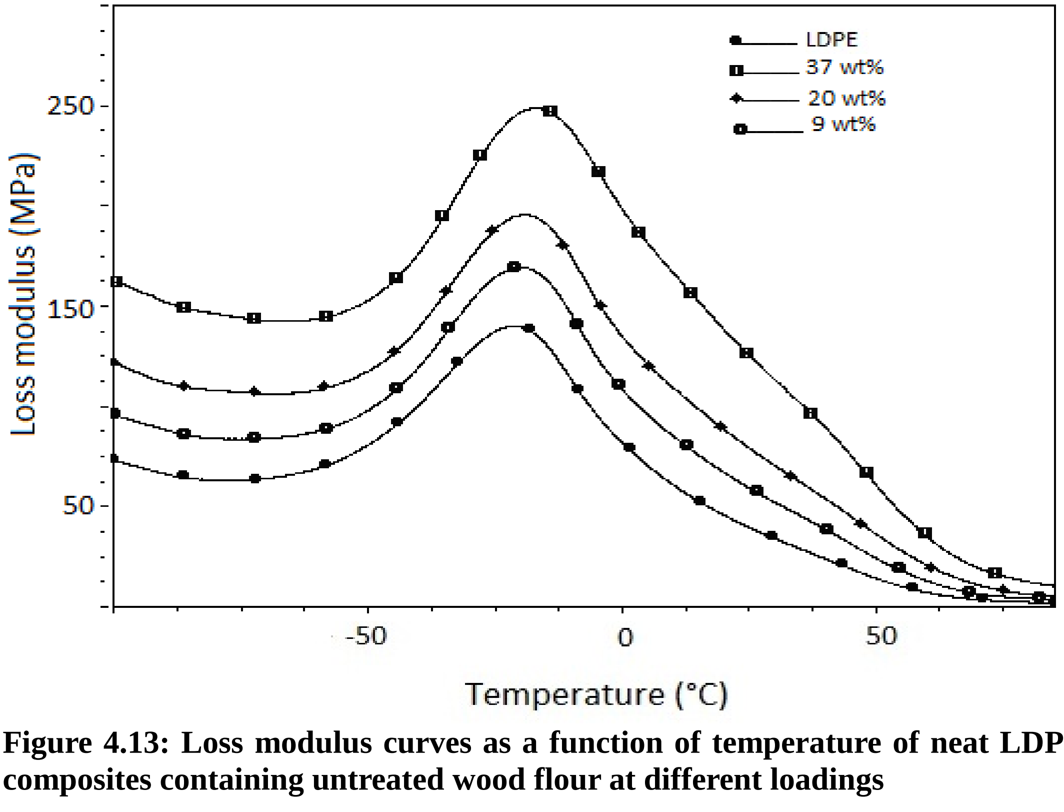


Figure 4.13: Loss modulus curves as a function of temperature of neat LDPE and composites containing untreated wood flour at different loadings

This peak, $T_\beta^{E''}$, referred to as the temperature at maximum value of E'', appeared at -25°C for the neat matrix and shifted to -19°C in 9 wt% and 20 wt%, then -16°C as the wood content increased to 37 wt% (Table 4.4, page 80). This T_β value is associated with the motion of the long chain segments in the amorphous region of LDPE. The higher temperature transition of E'' as the wood content increased may indicate the restriction of the segmental motion of the amorphous LDPE chains, as more wood flour was added. However, low temperature, γ- and high temperature, α- transitions could not be observed within the range of temperature used in this study. In addition, the peak maximum, $E''_{\max}$ and the value of E'' at 25°C ($E''_{25^\circ\mathrm{C}}$) increased with filler loading (Table 4.4, page 80). An increment of 44% is observed for composites loaded with 37 wt% wood when compared to the neat matrix. The higher modulus at this temperature is due to the presence of wood fillers which reduced the flexibility of the material by introducing constraints on the segmental mobility of the polymer chains at the relaxation temperatures [140]. Mohanty *et al*. [141] and Joseph *et al.* [136] also reported a similar trend for PP reinforced with jute and sisal fibre composites respectively. Similarly, Kalaprasad *et al*. [142] observed that the incorporation of short sisal fibre into LDPE resulted in an increase in loss modulus.

Effect of heat treatment

The effect of heat treatment on the loss modulus of composites loaded with 37 wt% wood flour is presented in Figure 4.14a. As was observed earlier, $T_\beta^{E''}$ shifted to higher temperature with the incorporation of wood flour. However, loading heat-treated wood flour seems to have no effect on $T_\beta^{E''}$ as no appreciable shift in $T_\beta^{E''}$ is observed with addition of wood flour treated at 180°C and 200°C. $T_\beta^{E''}$ values of -16°C, -17°C and $-16^\circ\mathrm{C}$ were observed for untreated, 180°C and 200°C treated WTC, respectively (Table 4.4, page 80). Furthermore, $E''_{\max}$ values are generally lower in heat-treated WTC when compared to those containing the untreated wood flour, with a percentage decrease of

27% in 180°C treated WTC and a 12% drop in composites made from wood treated at 200°C relative to the untreated ones. This drop in $E''_{\max}$ in heat-treated WTC may indicate the presence of genuine interphase [143] between heat-treated wood and LDPE as a result of better compatibility resulting from good wetting of the wood particles by the matrix. In addition, $E''_{\max}$ of composites made from wood treated at 180°C are lower than that from wood treated at 200°C. Although no pulsable explanation can be adduced for this trend, it is likely that treating wood at 180°C impacted more on the compatibility with the matrix than at 200°C. At room temperature, $E''_{25°\mathrm{C}}$ presents no identifiable trend apart from the general increase with respect to the matrix. There is a possiblity that at room temperature which is higher than the $T_\beta^{E''}$, further interactions between the filler and the matrix may manifest in the heat-treated wood composites that resulted in the trend observed.

Effect of MAPE content

Figure 4.14b shows the effect of MAPE content on the loss modulus of composites. The peak temperature, $T_\beta^{E''}$ decreased marginally with MAPE content (Table 4.4). $T_\beta^{E''}$ values decreased from -16°C in the uncoupled composites to -19°C in the coupled samples. Contrary to expectations, the $E''_{\max}$ value increased generally with MAPE loading. However, at 2% MAPE content, $E''_{\max}$ values droped by about 31%, relative to the uncoupled composites. This drop, as mentioned before, seems to indicate an improvement in the fibre/matrix interphase. Thereafter, a decrement was observed as the MAPE content increased. This behaviour may be attributed to the migration of excess MAPE around the wood particles, resulting in self entanglement among MAPE molecules rather than the matrix [144].

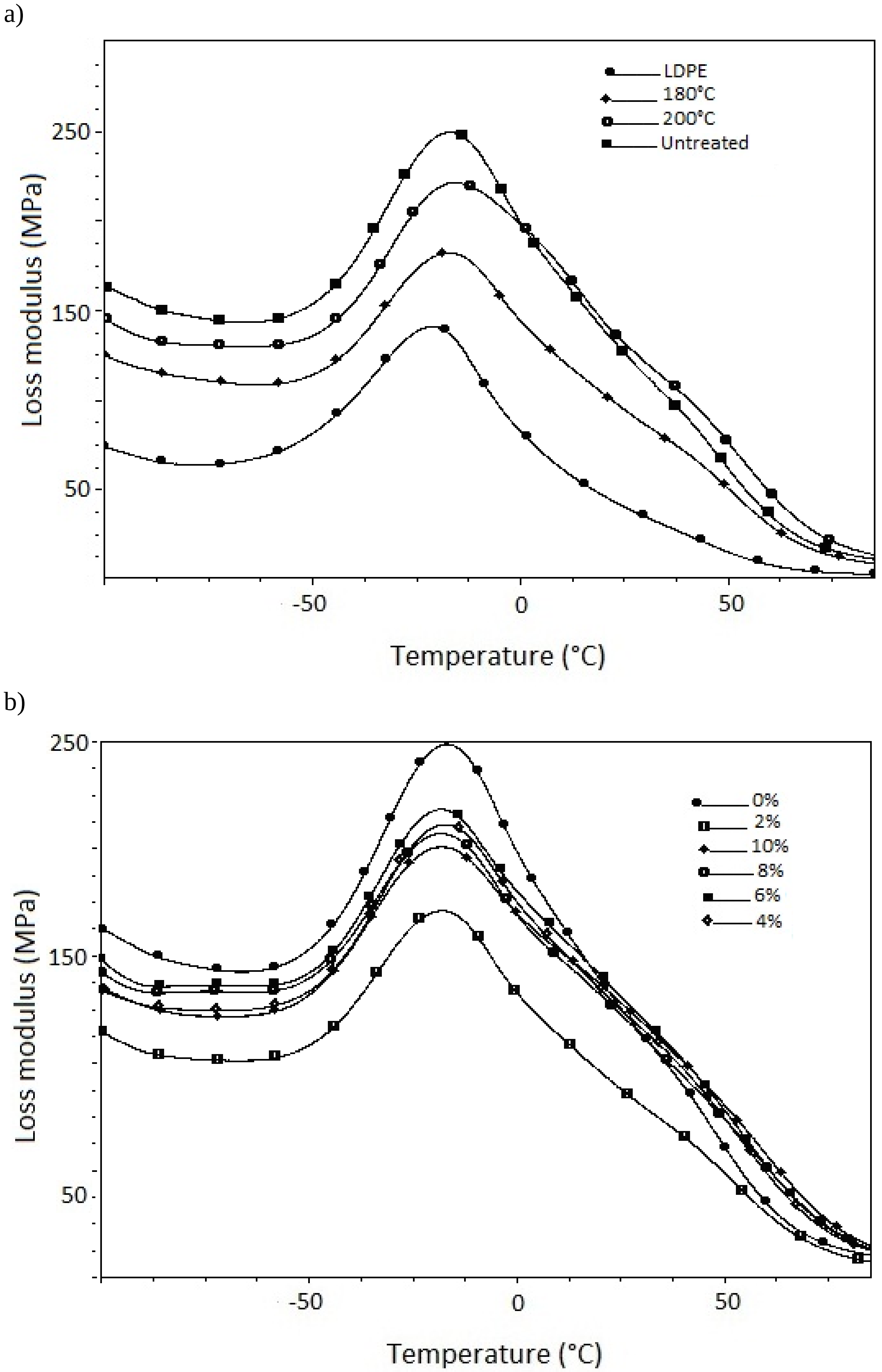


Figure 4.14: Loss modulus curves of LDPE and 37 wt% composites as a function of: a) heat treatment and b) MAPE content

Similarly, with increase in MAPE content, the values of $E''_{25°C}$ showed the same trends as that of $E''_{\max}$.

4.2.3.4 Tan delta, tan δ

The ratio of the loss modulus to the storage modulus is the mechanical loss factor also known as tan δ,

$$\tan\delta = \frac{E''}{E'} = \frac{\sin(\delta)}{\cos(\delta)} \tag{4.8}$$

It represents the ratio of the energy dissipated to the energy stored per cycle of deformation and indicates the damping characteristics of the material.

Effect of wood content

The dependence of tan δ on temperature for untreated wood composites at different filler loadings is presented in Figure 4.15. The $\tan\delta$ peak decreased with increasing wood content in comparison with the neat matrix (Table 4.4). This is because; as the wood content increases, less amount of LDPE matrix is available to dissipate the vibrational energy [137]. In addition, it is possible that there is an immobilisation of the LDPE matrix by the wood particles during the relaxation process. Tan $\delta_{\max}$ values of 0.16 (obtained for the LDPE) matrix droped to 0.15 and 0.14 at 20 wt% and 37 wt% wood contents, respectively. Although filler loading is a key parameter in determining the damping properties of composites, other factors, such as: the interaction between the filler and the polymer matrix will influence damping. The reduction in tan δ values denotes an improvement in the hysterisis of the system and a reduction in the internal friction [136]. The temperature at $\tan\delta_{\max}$ increased marginally as the wood content increased up to 20 wt% and then droped slightly at 37 wt% filler loading (Table 4.4).

This may be attributed to the reduced free volume available for segmental motion in the matrix as filler content increased, which resulted in higher energy demands for the transition to take place. As with $\tan\delta_{\max}$ value, the value of $\tan\delta$ at 25°C reduced with filler loading. Furthermore, the width of the transition region, $W_{\sqrt{2}}$, decreased generally with filler loading, with composites containing 37 wt% wood content exhibiting the highest decrement, indicating reduced damping [135] (Table 4.4).

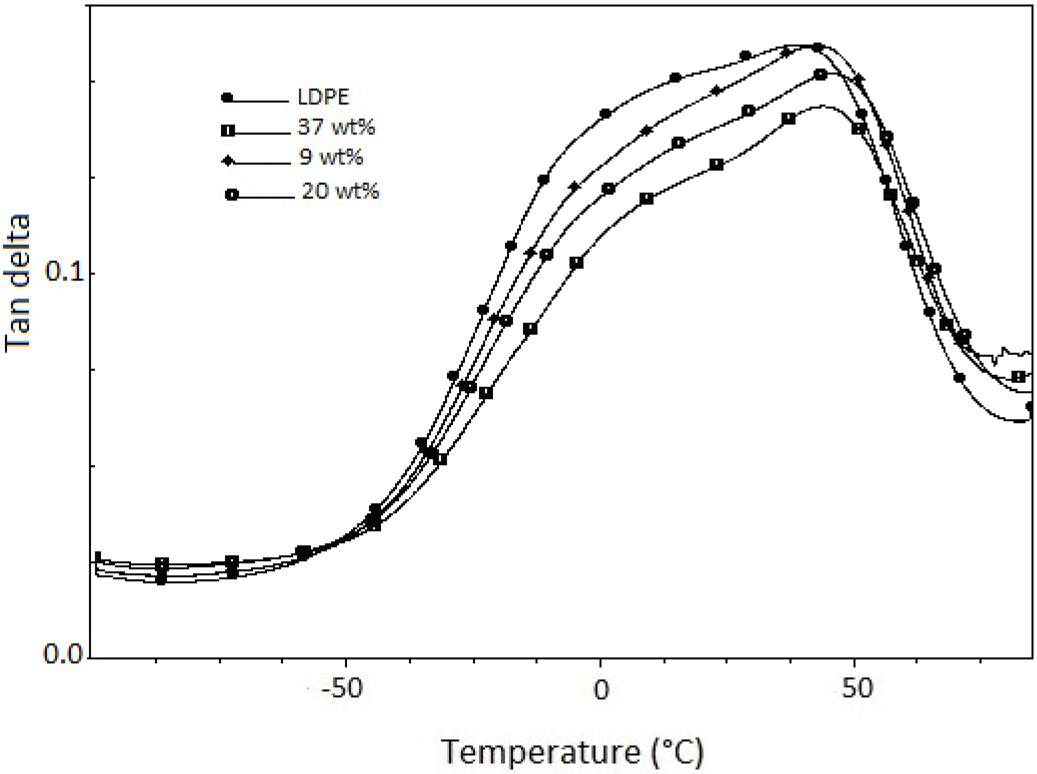


Figure 4.15: Variation of tan δ with temperature for LDPE and untreated wood composites at different filler loadings

Effect of heat treatment

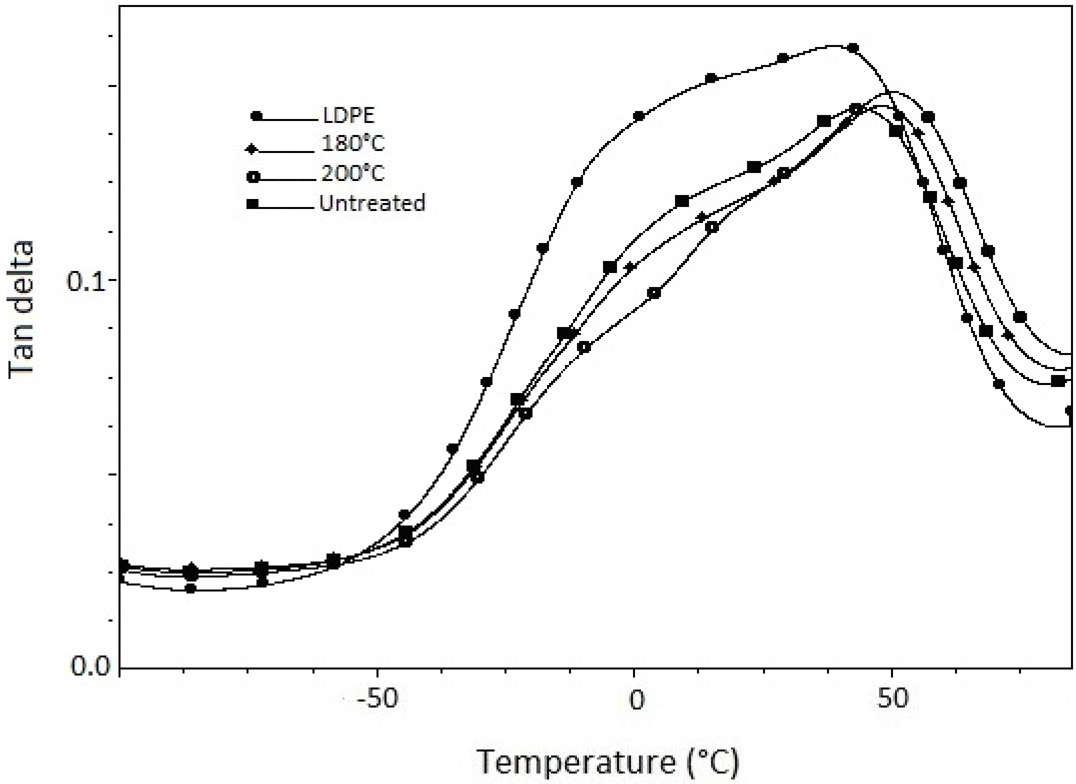
Figure 4.16a presents the dependence of $\tan\delta$ on temperature for LDPE and composites made from 37 wt% untreated and heat-treated wood flours. In comparison with the neat LDPE, $\tan\delta_{\max}$ values of untreated and heat-treated wood composites exhibited a lower magnitudes. However, no definite trend can be seen in the composites made from untreated and heat-treated wood flours with respect to $\tan\delta_{\max}$ values. Furthermore, temperature at $\tan\delta_{\max}$ increased with heat treatment for the composites studied (Table 4.4 page 80).

Better interaction between the heat-treated wood flour and LDPE may have resulted in reduced free volume available for segmental motion which may have shifted the $\tan\delta_{\max}$ temperatures to higher values, as higher energy is required for the transition to take place. In addition, at 25°C, $\tan\delta$ values are lower in the heat-treated wood composites than the untreated samples (Table 4.4, page 80). This envisages that a composite material with poor interfacial bonding between the wood particles and the matrix will tend to dissipate more energy, showing high magnitude of damping peak in comparison with strongly bonded interface [141] as expected for the heat-treated wood composites. Also, composites made from 180°C and 200°C treated wood flour showed the same values of $\tan\delta$ at 25°C, indicating that the wood flour from the two treatment temperatures, have probably exerted similar influence on $\tan\delta$ at ambient conditions. The transition width, $W_{\sqrt{2}}$, also decreased with heat treatment, with composites made from 200°C exhibiting the lowest value, implying reduced damping.

Effect of MAPE content

Tan δ curves, as a function of temperature for composites containing 37 wt% wood flour with varying MAPE contents, are presented in Figure 4.24. From this figure, it can be seen that the magnitude of $\tan\delta_{\max}$ increased with MAPE content (Table 4.4). Apart from a decrease in $\tan\delta_{\max}$ observed in the uncoupled composites, relative to the neat matrix, incorporation of MAPE at 2% and 4% loadings increased the $\tan\delta_{\max}$ value by the about 6%. Further addition of MAPE from 6% to 10% loading led to additional increase in $\tan\delta_{\max}$ values. As mentioned earlier, self-entanglement of excess MAPE molecules among themselves which led to increased damping of the composites, may be responsible for the observed trend. This finding disagrees with the work of Nayak and Mohanty [137], who reported decreased $\tan\delta_{\max}$ values for sisal/glass fibre hybrid PP composites, compatibilised with 2% MAPP. On the other hand, a positive impact of MAPE is seen at 25°C where $\tan\delta$ values of uncoupled composites decreased with MAPE contents at 2% and 4%. At this temperature, addition of MAPE at 6%, 8% and 10% levels increased the $\tan\delta_{25°C}$ further. In addition, the temperature at $\tan\delta_{\max}$ and $W_{\sqrt{2}}$ presented no particular trend.

a)



b)

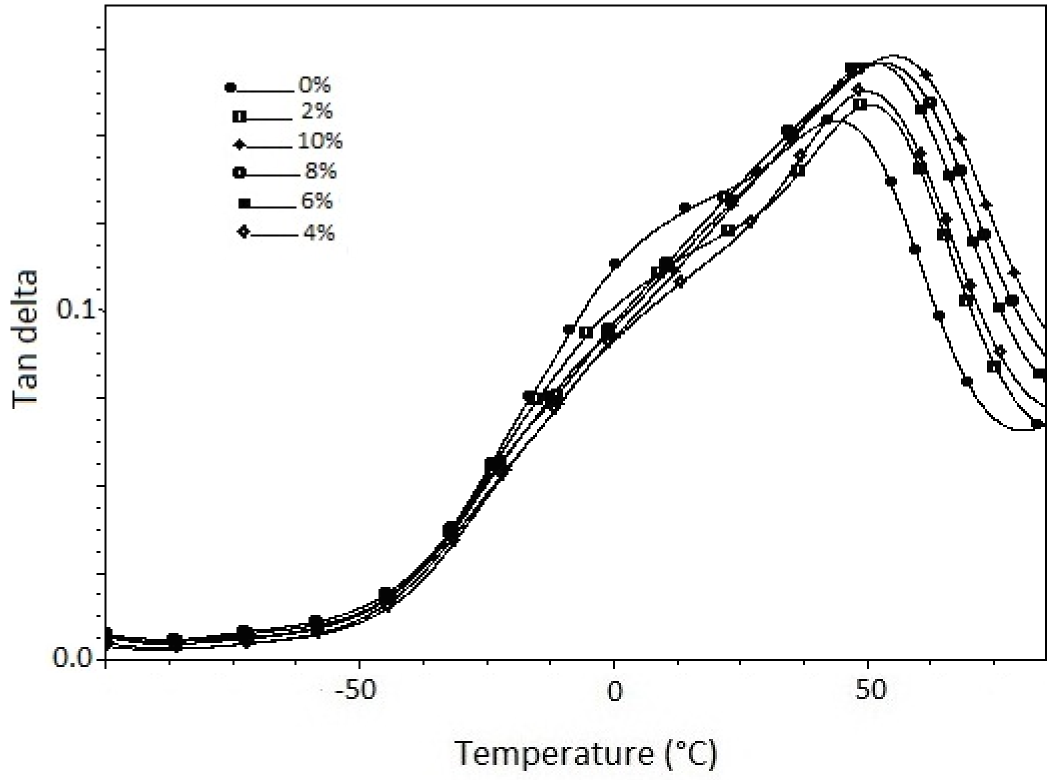


Figure 4.16: Tan δ curves of LDPE and 37 wt% composites as a function of: a) heat treatment and b) MAPE content

4.2.4 Mechanical properties

Most plastic materials are used because of their desirable mechanical properties at an economical cost. Therefore, the mechanical properties may be considered the most important of all the physical and chemical properties of polymers for most applications. Thus, to use such materials, at least, an elementary knowledge of their mechanical behaviour and how this behaviour can be modified by the numerous structural factors that can be varied in polymers [145] is of essence. Physical property testing involves the determination of a sample’s response to mechanical deformation under a variety of testing regimes. Tests may determine the relationship of deformation to applied force, stress as a function of applied strain, or the energy required to fracture a sample under specified conditions [25]. The mechanical properties of untreated and heat-treated wood composites were conducted in order to establish the mechanical behaviour of the materials under defined conditions.

4.2.4.1 Tensile properties.

Tensile properties are used in selecting materials for different applications. Material specifications often include minimum tensile properties to ensure quality, therefore, tests must be made to guarantee that the materials meet these requirements. Tensile properties are also used in research and development to compare new materials or processes [146]. Tensile tests were carried out on the composites in order to assess the effect of wood content, heat treatment and MAPE content, on the tensile properties.

Tensile modulus

It is a measure of the resistance of a material to deformation when external forces are applied in tension. It is the initial slope of the stress vs strain curve and is referred to as Young’s modulus. It is, effectively, a measure of the materials stiffness. Ideally, it is defined as the stress required to effect unit strain in the elastic portion of the force versus elongation curve. In practical terms, it is the slope of the graph of stress as a function of strain in the region prior to yielding [25].

Effect of wood content

The effect of untreated and heat-treated wood flour contents on the tensile modulus of the composites are presented in Figure 4.17. Generally, the tensile modulus increased with filler loading. Increases of 69%, 100% and 309% in tensile modulus are obtained for 9 wt%, 20 wt% and 37 wt% untreated wood composites, respectively relative to the pure matrix (0.23 GPa). This is be an indication of the reinforcing effect of the wood flour, which tended to stiffen the polymer matrix. As can be seen in Figure 4.18, pure LDPE is flexible, displaying a ductile mode of failure under tension. However, on addition of wood flour, a more or less brittle failure is observed (Figure 4.19).

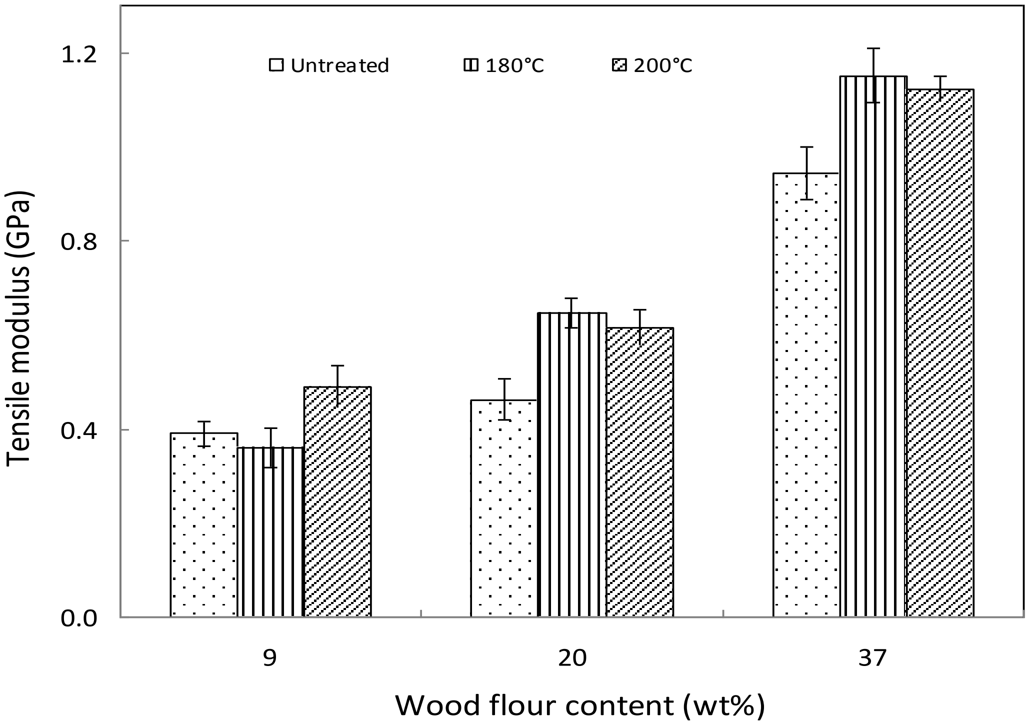


Figure 4.17: Tensile modulus of composites as a function of wood content and heat treatment

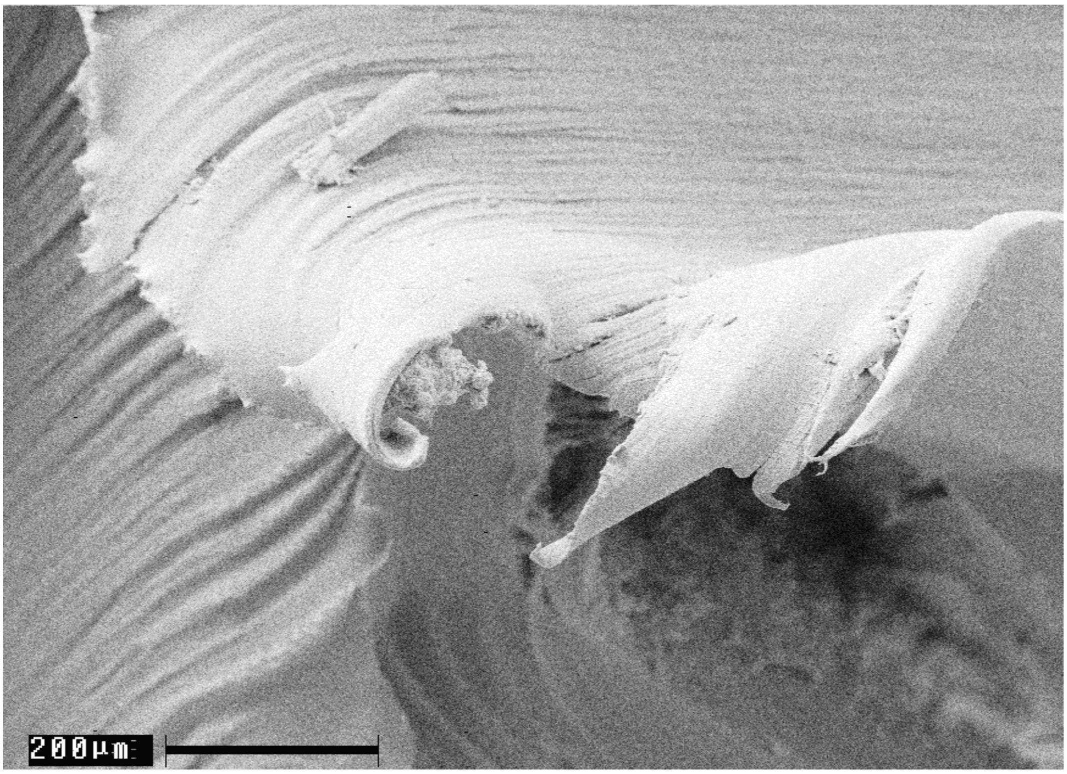


Figure 4.18: SEM micrograph of tensile fractured surface of pure LDPE

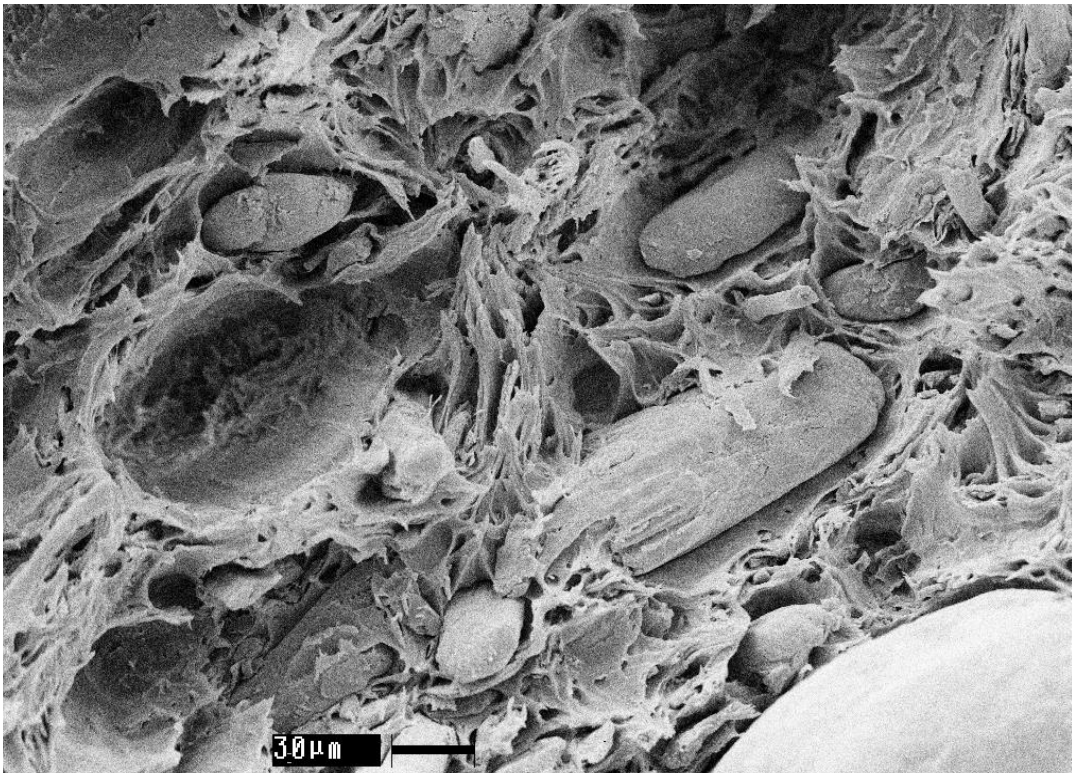


Figure 4.19: SEM micrograph of tensile fractured surface of composites containing 37 wt% untreated wood

The stiffening effect of high modulus wood flour particles on the flexible LDPE believed to be responsible for this failure mode. Composites made from 37 wt% exhibited the highest tensile modulus values.

Effect of heat treatment

The effect of heat treatment on the tensile modulus of the composites is also shown in Figure 4.17 (page 94). Heat treatment of wood flour increased the tensile modulus of the composites more than their untreated counterparts. At treatment temperature of 180°C, percentage increases in tensile modulus from 57% for 9 wt%, through 183% for 20 wt% to 400% for 37 wt% were observed when compared to the neat LDPE. This is attributed to better wetting of the heat-treated wood particles by the matrix, brought about by the reduced hydrophilicity (Figure 4.2, page 55) of the heat-treated wood flour, which facilitated the improved interfacial adhesion between the wood particles and the neat matrix [147, 148]. This can also be seen from the tensile fractured surfaces, as shown in Figures 4.19 and 4.20. Portions of LDPE are seen adhering to the surface of the heat-treated wood particles after fracture (Figure 4.20), indicating a good interfacial adhesion, unlike in Figure 4.19, where clean untreated wood particle surfaces are observed. Composites made from wood flour treated at 200°C influenced their tensile modulii to a lesser extent than that from180°C treated wood flour. It is possible that treating wood flour at 200°C must have caused some structural damages, such as char formation to the wood particles, thereby reducing its reinforcing efficiency.

Effect of MAPE content

The effect of MAPE content on the tensile modulii of composites is presented in Figure 4.21. Tensile modulus increased with MAPE content. Steady improvement in modulus is observed in 37 wt% filled wood composites up till 8% MAPE content. This improvement is expected because of the ability of a compatibiliser to induce an enhanced interfacial adhesion between the wood particles and the polymer matrix [149]. Further addition of MAPE, up to 10%, resulted in reduced modulus values. As mentioned earlier, excess MAPE molecules at the filler-polymer interphase tend to entangle themselves rather than the wood particles, resulting in slippage thereby reducing the modulus values [144]. It has been reported [145] that the interactions between non-polar thermoplastics such as PE and any coupling agents such as MAPE are predominantly those of chain entanglement. Stresses applied to one chain can be transmitted to other entangled chains, and stress is distributed among many chains. These entanglements function essentially like physical cross-links that provide some mechanical integrity to the material. When polymer chains are very short, there is little chance of entanglement between chains and they can easily slide past one another.

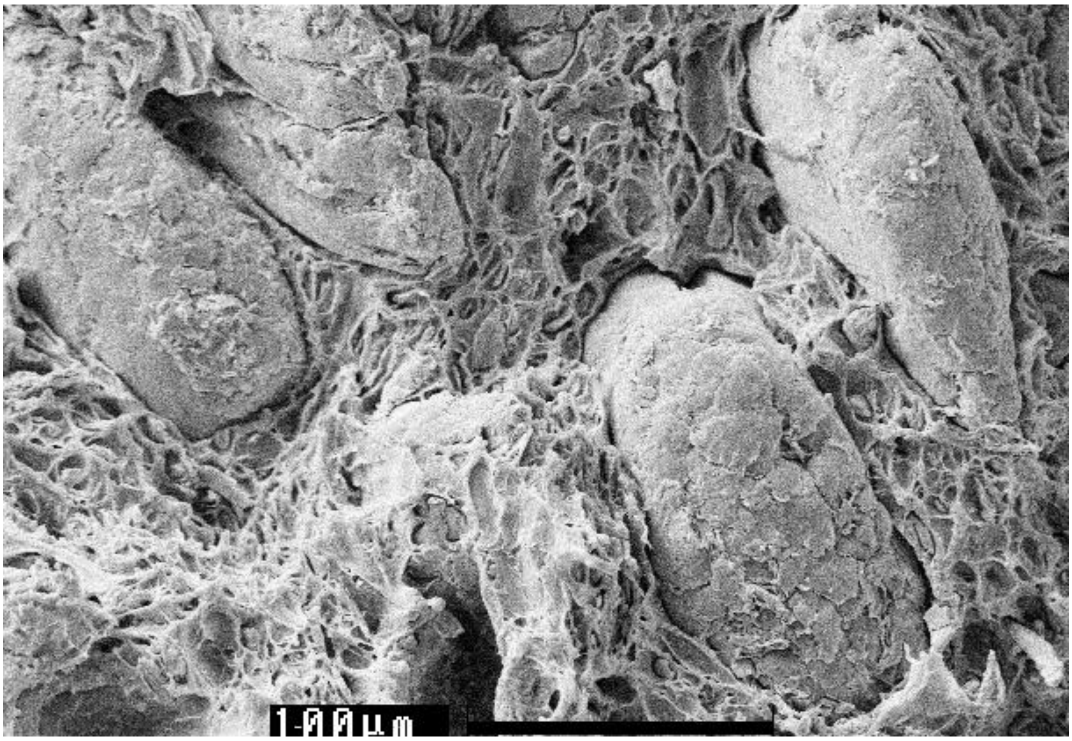


Figure 4.20: SEM micrograph of tensile fractured surface of 37 wt% composite made from wood flour treated at 180°C

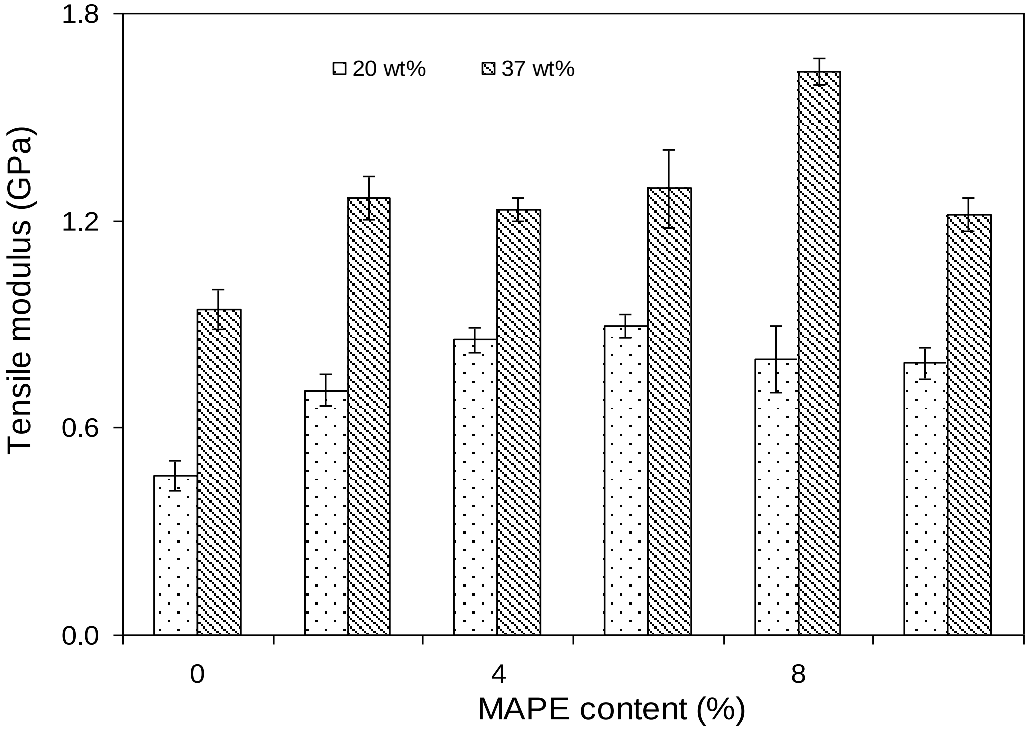


Figure 4.21: Tensile modulus of 20 wt% and 37 wt% composites containing untreated wood flour and different MAPE content

When the polymer chains are longer, effective entanglements between the chains occur that will influence the material properties [150]. However, at 20 wt%, 6% MAPE seems to provide the best coupling required for the enhancement of the tensile modulus. Beyond this MAPE content, a reduction in modulus is seen. This value is lower than that for 37 wt% filled composites. This is expected because of the lower content of wood and by implication, lower O-H groups available for coupling.

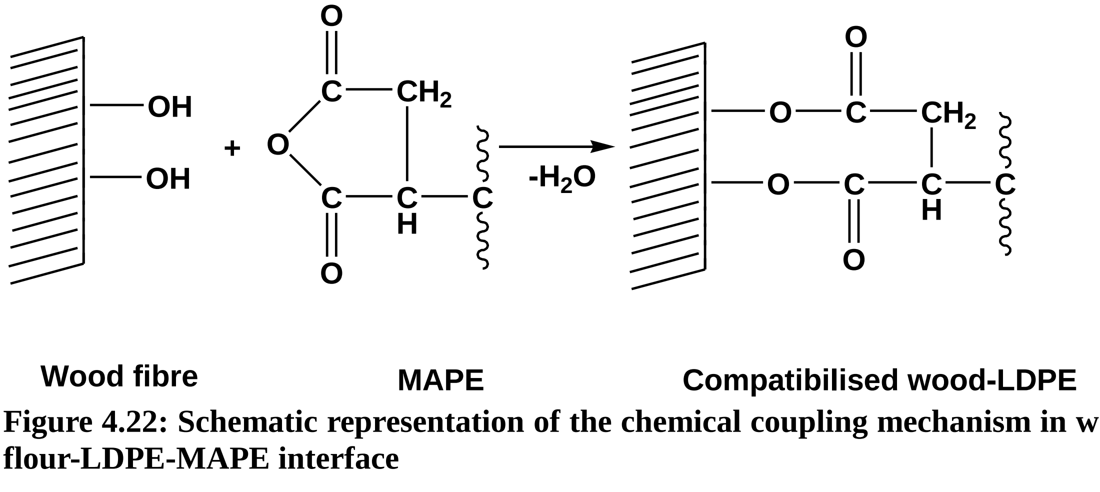


Figure 4.22: Schematic representation of the chemical coupling mechanism in wood flour-LDPE-MAPE interface

It is also important to note that the nature of the fibre surface is likely to restrict the mobility of the polymer chains and the minimum entangled lengths will vary according to the fibre surface characteristics. Therefore, in order to develop enough mechanical integrity of the interphase region, so that there is sufficient stress transfer property between the non-polar matrix and the polar fibre, the functional additive present near the fibre surface should be strongly interacting with the fibre surface through covalent bonding and/or acid-base interactions (Figure 4.22). This implies that enough functional groups should be present in the functional additive so that interactions can occur with the O-H groups on the fibre surface. In addition, the polymer chains of the functional additive should be long enough to permit entanglements with the LDPE at the interphase [7]. On the other hand, there is no appreciable influence of MAPE on heat-treated wood flour composites (Figure 4.23). This is anticipated because of the reduction of O-H groups on the wood surface as a result of heat treatment.

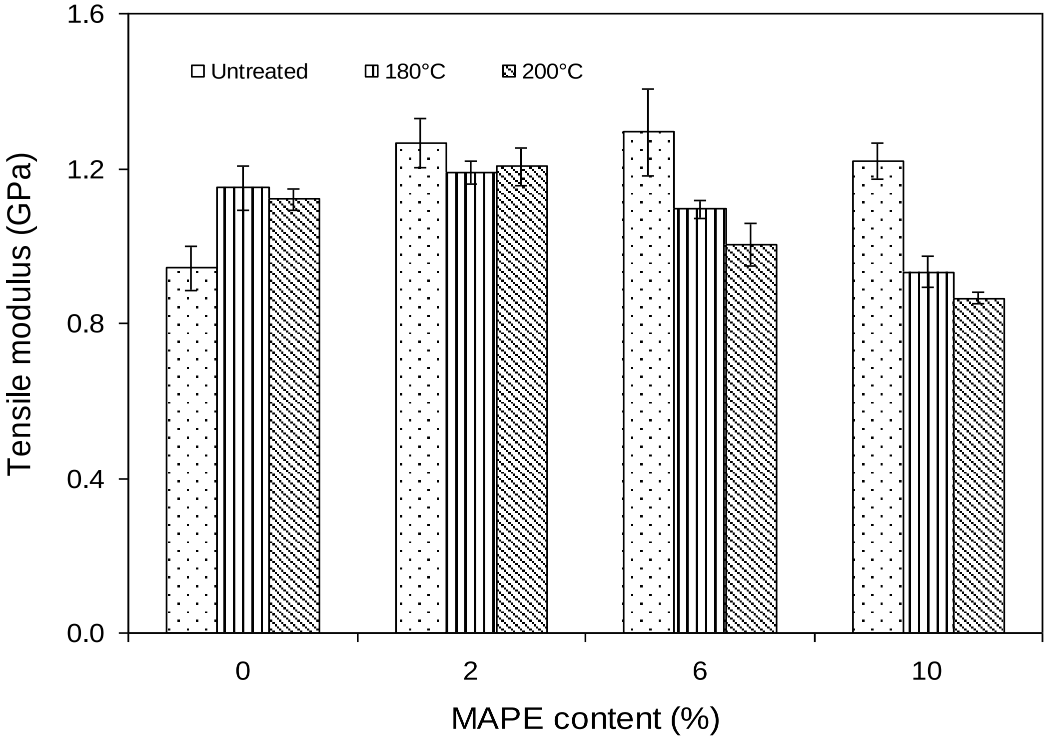


Figure 4.23: Tensile modulus of composites made from 37 wt% untreated and heat-treated wood flour with varying amounts of MAPE

Tensile strength

This is the force required to break a sample divided by its cross-sectional area. The tensile strength of a material is of great interest from a practical point of view. In many cases, it represents the maximum permissible load that a sample can withstand while still performing its assigned role. Once a sample has yielded, its dimensions are irrevocably changed and it may no longer meet the requirements for continued service [25]. The tensile strength of composites was assessed as a function of wood content, treatment temperature and MAPE content.

Effect of wood content

The tensile strength of composites as a function of wood content and heat treatment temperature is shown in Figure 4.24. The tensile strength of the composites decreases with increasing filler loading relative to the neat matrix (9.14 MPa). As reported by previous authors [151, 152], this is due to the weak interfacial adhesion and low compatibility between the polar wood particles and the non-polar polymer matrix. In addition, as the wood content increased, especially at 37 wt%, wetting problems became more pronounced and the probability of wood-wood contact was higher. During testing, especially in the tensile mode, the unwetted wood particles could become stress concentration areas, leading to premature failure and consequently, low strength [18]. Furthermore, poor interfacial bonding causes partially separated micro-spaces between the filler and the matrix polymer. This obstructs stress propagation and induces reduced strength [153].

Effect of heat treatment

The effect of heat treatment of wood flour on the tensile strength of composites is also presented in Figure 4.24. Heat treatment of wood flour at 180°C improves the tensile strength of the composites relative to the untreated composites. Despite the general decreasing trend with increasing filler loading observed earlier, wood-treated at 180°C maintained a consistently higher tensile strength at all filler contents, indicating that heat treatment at 180°C has improved the compatibility between the hydrophilic wood flour and the hydrophobic polymer matrix, to a certain degree. In addition, wood treated at 200°C seemed to have the least influence on tensile strength. It is worth noting that wood treated at 200°C also exhibited a significantly decreasing trend in degree of crystallinity for the various compositions (Table 4.3). It has been reported [154] that in semi-crystalline thermoplastic composites, degree of crystallinity is an important parameter influencing the mechanical properties. Therefore, it is not surprising that it presented the least tensile strength.

Effect of MAPE content

The decreasing trend in tensile strength of composites as the wood content increased can be assuaged by the use of coupling agents. Addition of MAPE increased the tensile strength of composites more than the neat LDPE (Figure 4.25). The compatibiliser chemically bonded the hydrophilic filler and wets the polymer chain (Figure 4.26), resulting in improved compatibility (enhanced interfacial bonding) between the filler and the matrix. This promoted efficient stress propagation between the filler and the matrix, resulting in higher tensile strength in response to stress [13]. As observed with tensile modulus, tensile strength increased up to 6% MAPE in composites loaded with 20 wt% filler, whereas, an increase was observed uptill 8% MAPE in 37 wt% wood composites. Beyond this MAPE content, indicated for the different filler levels, no appreciable improvement in tensile strength was further observed.

However, as seen in the tensile modulus, the response of composites made from untreated wood flour is higher than the heat-treated composites (Figure 4.27).

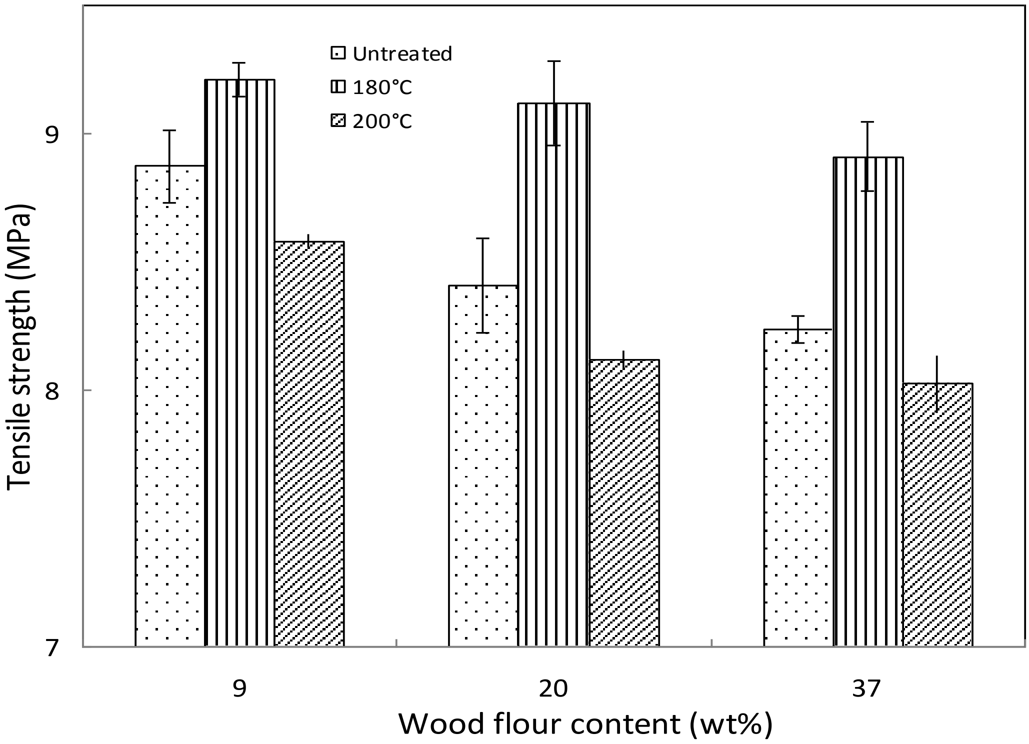


Figure 4.24: Tensile strength of composites as a function of wood content and heat treatment

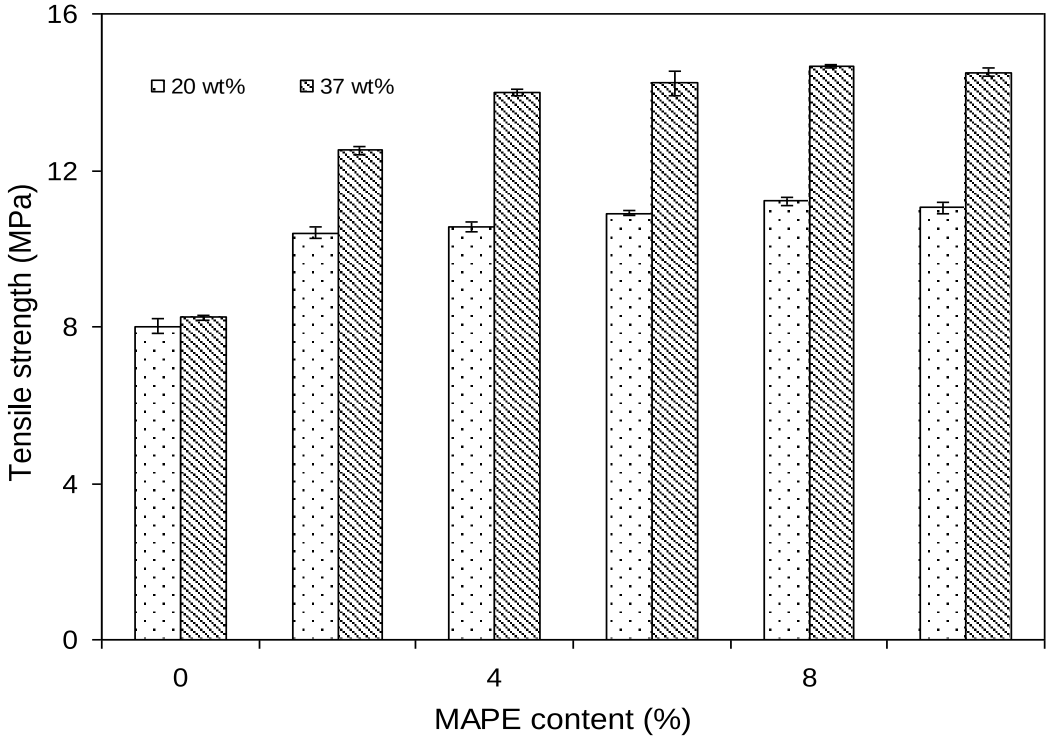


Figure 4.25: Tensile strength of 20 wt% and 37 wt% untreated wood composites as a function of MAPE content

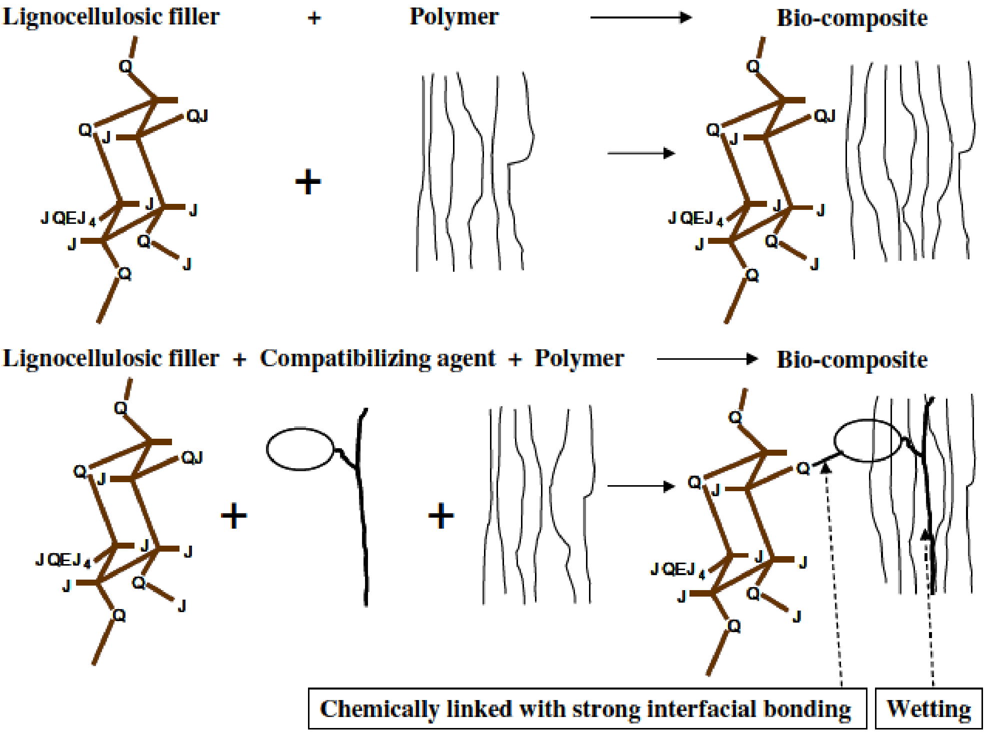


Figure 4.26: Schematic representation of wetting in compatibilised bio-composites [153]

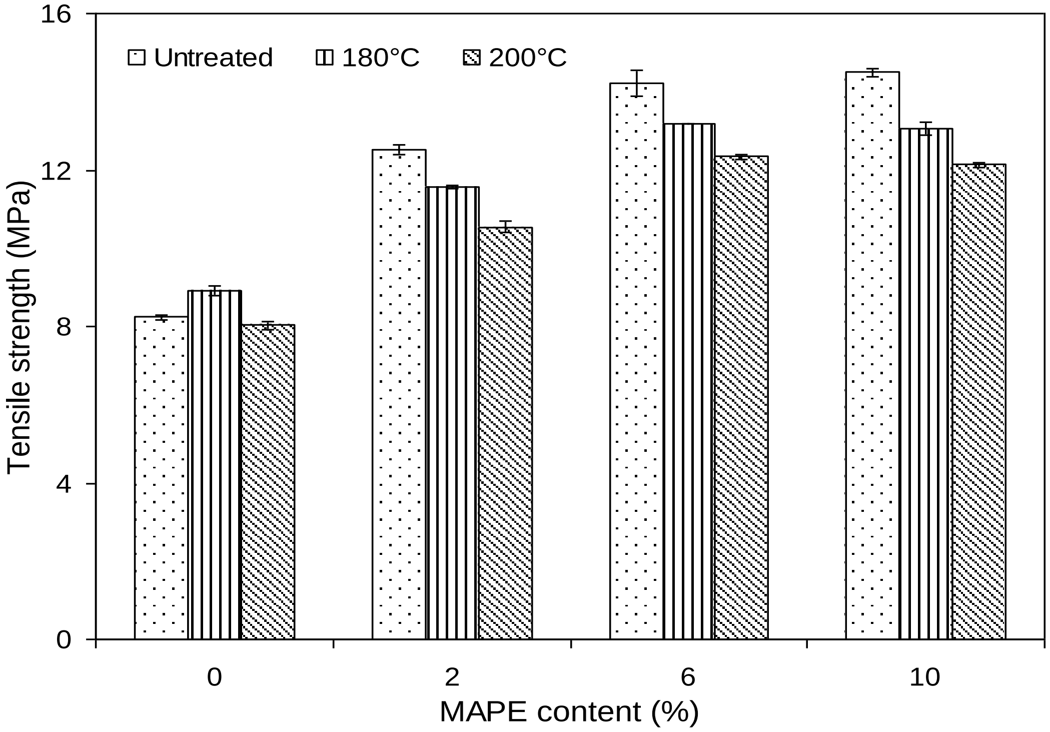


Figure 4.27: Tensile strength of composites made from 37 wt% untreated and heat-treated wood flour with varying amounts of MAPE

Tensile strain

The tensile strain of a sample is the strain corresponding to the yield point. It is routinely quoted in terms of percent strain relative to the undeformed (original) sample length.

Effect of wood content

The variation of tensile strain of composites with wood content and heat treatment is shown in Figure 4.28. Generally, the tensile strain of the composites decreased with increasing wood content. This observation can be related to increased rigidity of the matrix with the incorporation of fillers, as a result of restrained chain mobility, leading to drastic reduction of strain at failure [155].

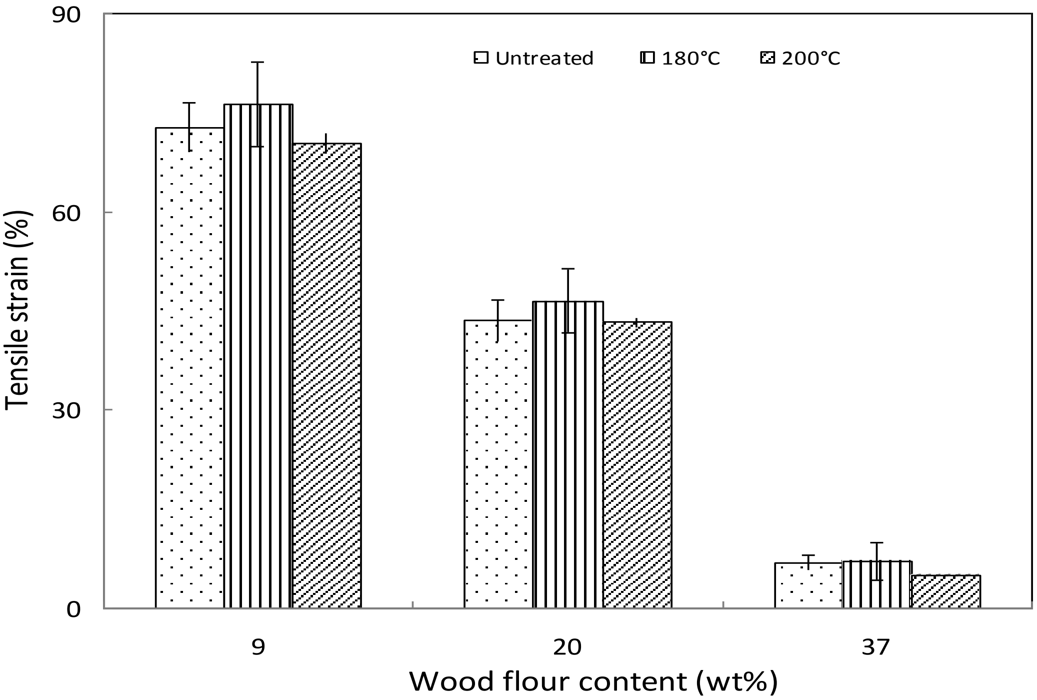


Figure 4.28: Tensile strain of composites at a function of wood content and heat treatment

However, the observed trend did not correlate with the tensile modulus and strength values. It was observed that in some of the specimens, extension took place outside the gauge length of the extensometer. Reports have shown that under ideal situations, the strain at break should be measured directly with an extensometer. In this case, it is assumed that all deformations occur within the gauge region of the sample and the elongation is calculated based on cross-head displacement as a function of the initial gauge length. In an event that deformation occurs in portions of the specimen outside the gauge region, unrealistically high values of elongation may result. In addition, tensile strain is also very sensitive to the manner in which the specimen is gripped. Strips held between planar jaw faces frequently break at much lower strains than those held in line grips. Premature break also reduces the tensile strain observed. The ultimate achievable strain for a specimen may be reduced by sample defects, overlaying its dependence upon material properties. This may account for the observed strain behaviour and the relatively larger error in the calculations for this property [25].

Effect of heat treatment

From Figure 4.28, a clear conclusion on the effect of heat treatment on the tensile strain of the composites cannot be drawn. It is expected that composites made from wood flour treated at 180°C should present the lowest strain value. However, this is not the case as this composite present the highest strain value. This, as has been explained before, may have resulted from some of the samples extending outside the set extensometer gauge length, giving unrealistic strain values.

Effect of MAPE content

Figure 4.29 shows the effect of MAPE content on the tensile strain of composites containing 20 wt% and 37 wt% untreated wood flour.

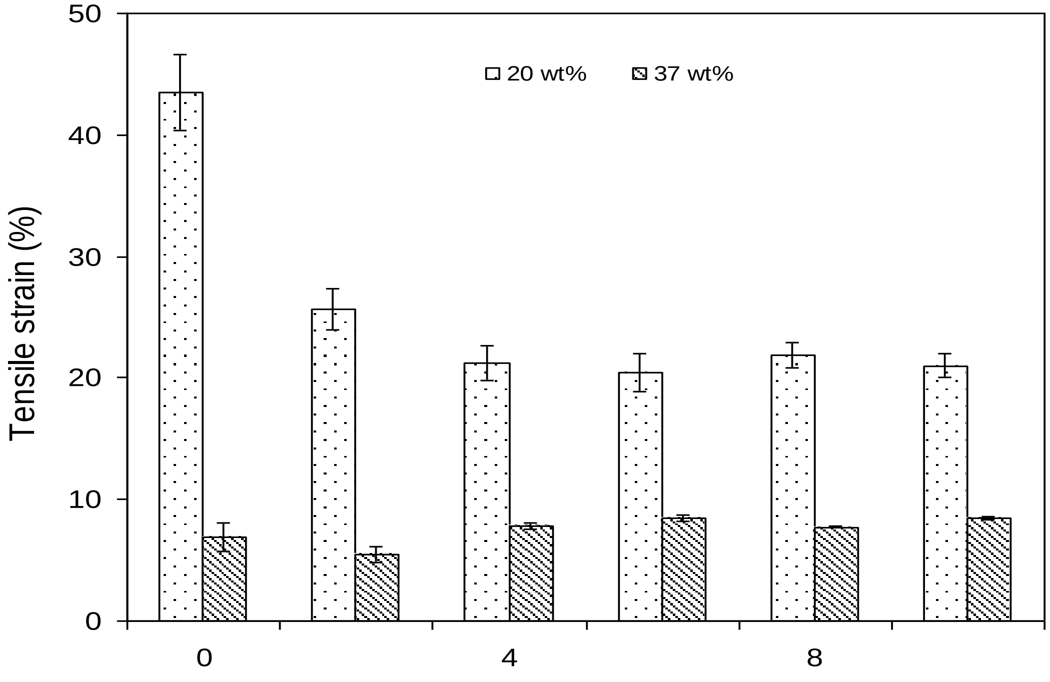


Figure 4.29: Tensile strain of 20 wt% and 37 wt% composites made from untreated wood as a function of MAPE content

Generally, addition of MAPE tends to reduce the tensile strain of composites relative to the uncoupled composites due to the improved adhesion on the filler-matrix interface.

At 20 wt% filler loading, tensile strain decreased up to 6% MAPE content. Thereafter, an increase is seen at 8% MAPE and levels off at 10 % MAPE content. The plasticization effect of excess MAPE at the interface could be responsible for this trend. Nevertheless, for the 37 wt% composites, a clear trend could not be established as the MAPE content increased.

Considering the effect of MAPE content on the tensile strain of heat-treated wood composites (Figure 4.37), an irregular trend was seen at 0% MAPE. As the MAPE content increased, a consistently higher tensile strain was observed as the treatment temperature increased. This indicate that with the heat-treated wood, the softening effect of excess MAPE was more pronounced, possibly, because of the reduction of the O-H groups on the surface of the heat-treated wood, which should have provided an avenue for the esterification reaction that resulted in the coupling effect.

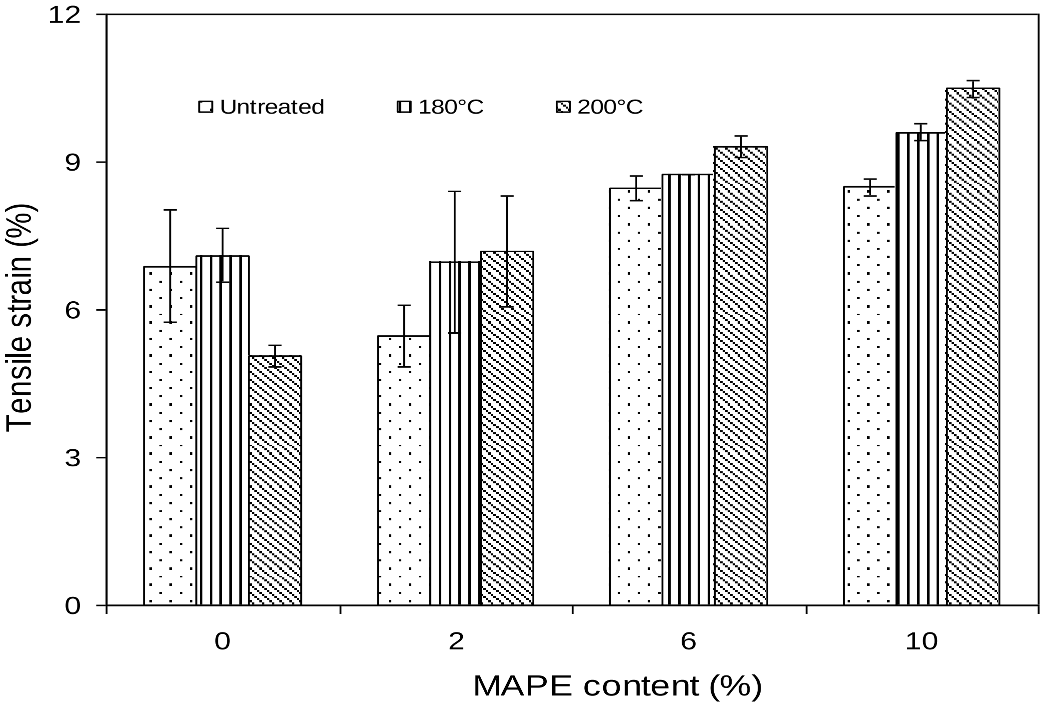


Figure 4.30: Tensile strain of 37 wt% untreated and heat-treated wood composites with varying amounts of MAPE

Consequently, the higher the MAPE content in the heat-treated wood composites, the higher is the softening, leading to higher strain values. In addition, it has been reported

[25] that the value of the elongation-at-yield is rather less important than the yield stress in practical applications of PE, because in typical use, specimens have to withstand applied stress rather than applied strain.

4.2.4.2 Flexural properties

The flexural properties of a material depict its resistance to bending. The flexural characteristics are commonly measured, in almost the same way, as the tensile properties. This is not surprising, considering the fact that in practical use, most components are subjected to a combination of loading modes, including flexing or bending, which often occur by intent or accident. Flexural stress-strain characteristics are derived by monitoring the force required to flex a material and the displacement that the material undergoes as a result of the applied force, at a constant deformation rate. In flexural testing, a maximum tensile force is applied on one side of the test piece, translating to a compressive force on the other. Therefore, the stress and strain that are calculated are the maximum outer fibre stresses and strains up to a maximum fibre strain of 5%. Hence, even though, in principle, the same parameters are measured as in a tensile test, it is the outer layer of the material, rather than the bulk that is referred to in flexural testing [156].

Flexural modulus

Effect of wood content

The variation of the flexural modulus of composites with wood content and treatment temperature is given in Figure 4.31. The flexural modulus of the composites increased with wood content. An increase of 308% is observed for the untreated wood composites at 37 wt% relative to the neat matrix (0.121 GPa). Loading LDPE with 9 wt% wood flour increased the flexural modulus to the tune of 42%, while 20 wt% loading resulted in a 118% increment in flexural modulus. This is due to the reinforcing effect of the wood flour on the matrix which resulted in increased stress transfer from the fillers to the matrix. This is in agreement with earlier reports [137].

Effect of heat treatment

The effect of heat treatment on the flexural modulus of composites is also shown in Figure 4.31. All the types of wood flour used have a positive influence on the flexural modulus of the neat LDPE matrix. Loading 37 wt% of wood flour treated at 180°C increased the flexural modulus by 284% relative to the neat matrix. At lower filler loading (9 wt% and 20 wt%), wood flour treated at 200°C seemed to impact more on the flexural modulus of the composites. Whereas, as the wood content increased, 37 wt% wood flour treated at 180°C enhanced the flexural modulus further.

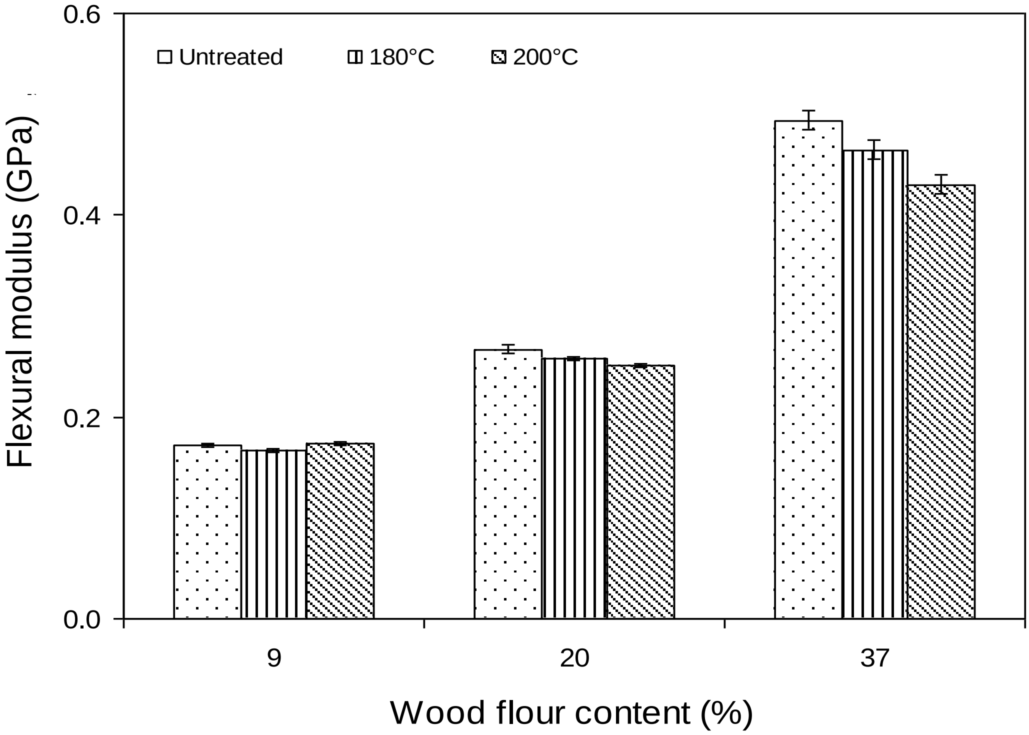


Figure 4.31: Flexural modulus of composites as a function of wood flour content and treatment temperature

This is in line with earlier finding where wood flour treated at 190°C produced composites with better flexural modulus than that treated at 205°C [74]. From Figure 4.31, it is clear that the flexural modulus of composites made from untreated wood flour is higher than those from heat-treated composites. This disagrees with earlier reports where heat-treated wood flour were found to have improved the flexural modulus of composites more than the untreated samples [74]. The lower flexural modulus of composites made from heat-treated wood (compared to the untreated composites) may result from the fact that heat treatment of wood flour could lead to decreased mechanical properties of wood [74]. Furthermore, as mentioned earlier, because of the mechanism of flexural deformations, parameters are measured for the outer layer of the material instead of the bulk as happens in tensile testing. Consequently, it is possible that the untreated wood particles are better able to withstand the compressive force on the outer layer than the heat-treated samples. This may have been responsible for the trend observed.

Effect of MAPE content

The variation of flexural modulus of 20 wt% and 37 wt% untreated wood composites with MAPE content, is presented in Figure 4.32. From the figure, addition of MAPE increased the flexural modulus of the composites. However, addition of 2% MAPE seems to have marginal effect on the flexural modulus of the composites at 20 wt% wood loading (4% increase), whereas at 37 wt% filler level, composites showed a significant improvement in modulus at 2% MAPE loading (10% increase). At 20 wt%, 4% MAPE loading displayed the highest modulus value. As the MAPE content increased from 4% to 6% loading in 37 wt% wood composites, a steady improvement in flexural modulus was observed. The fact that more O-H groups were present on the surface of the wood with higher filler loading for enhanced coupling, may have accounted for this observation. Incorporation of MAPE content up to 8% and 10% did not seem to effect further improvement in flexural modulus. From Figure 4.33, it is clear that untreated WTC responded more positively to the presence of MAPE than the heat-treated WTC. This finding disagrees with earlier reports in which composites made from heat-treated wood flour was reported to exhibit higher flexural modulus values in the presence of MAPE than their untreated counterparts [74]. However, a marginal improvement was observed in the flexural modulus of the coupled and heat-treated composites relative to the uncoupled composites.

Flexural strength

Effect of wood content

The effect of wood content on the flexural strength of composites is presented in Figure 4.34. The flexural strength of the composites increased with wood content. An increment of 27%, 53% and 104% were obtained for 9 wt%, 20 wt% and 37 wt% respectively, relative to the neat matrix (7.13 MPa). Incorporation of wood particles rendered the flexible LDPE matrix more rigid, thereby increasing the flexural strength.

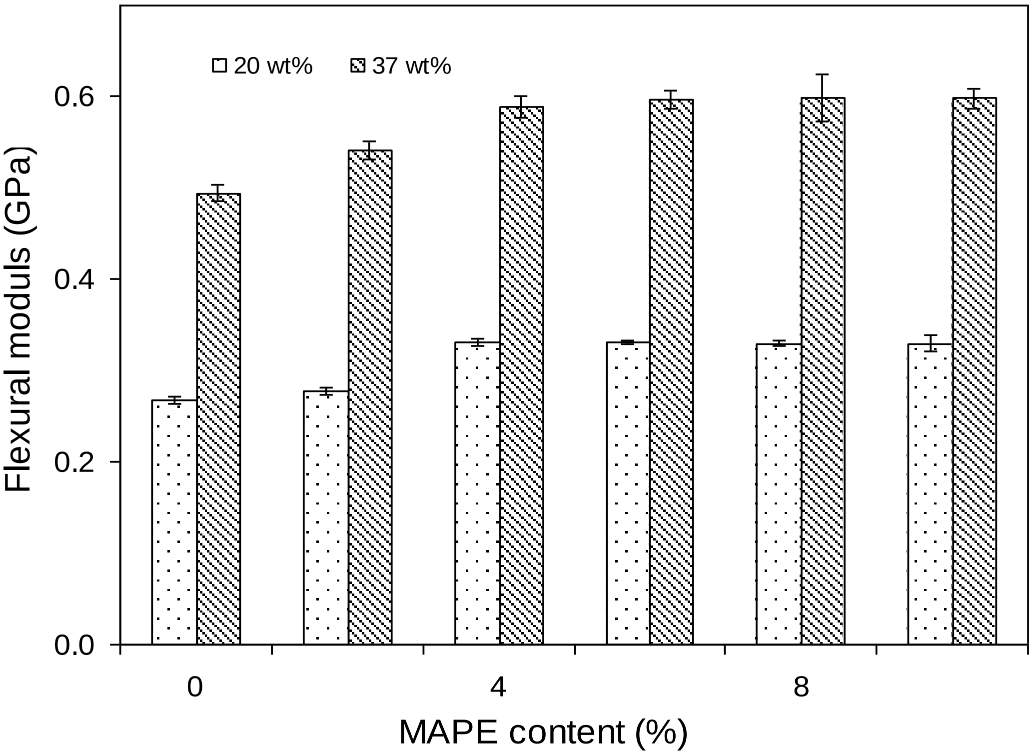


Figure 4.32: Flexural modulus of composites from untreated wood as a function of MAPE content

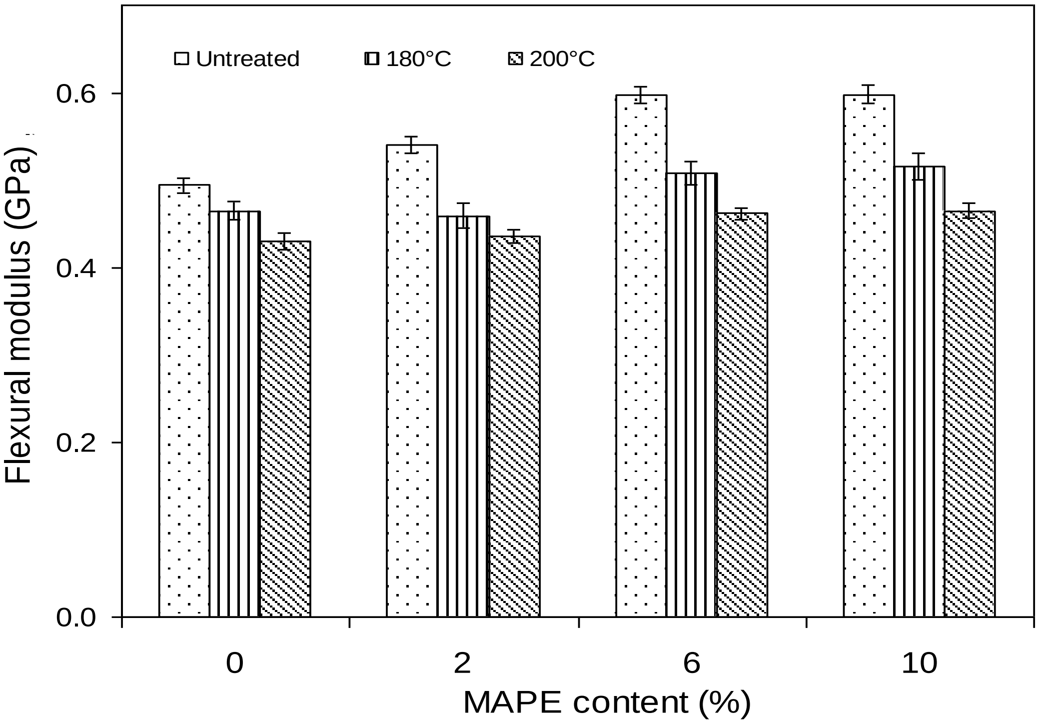


Figure 4.33: Flexural modulus of 37 wt% composites as a function of MAPE content and treatment temperature

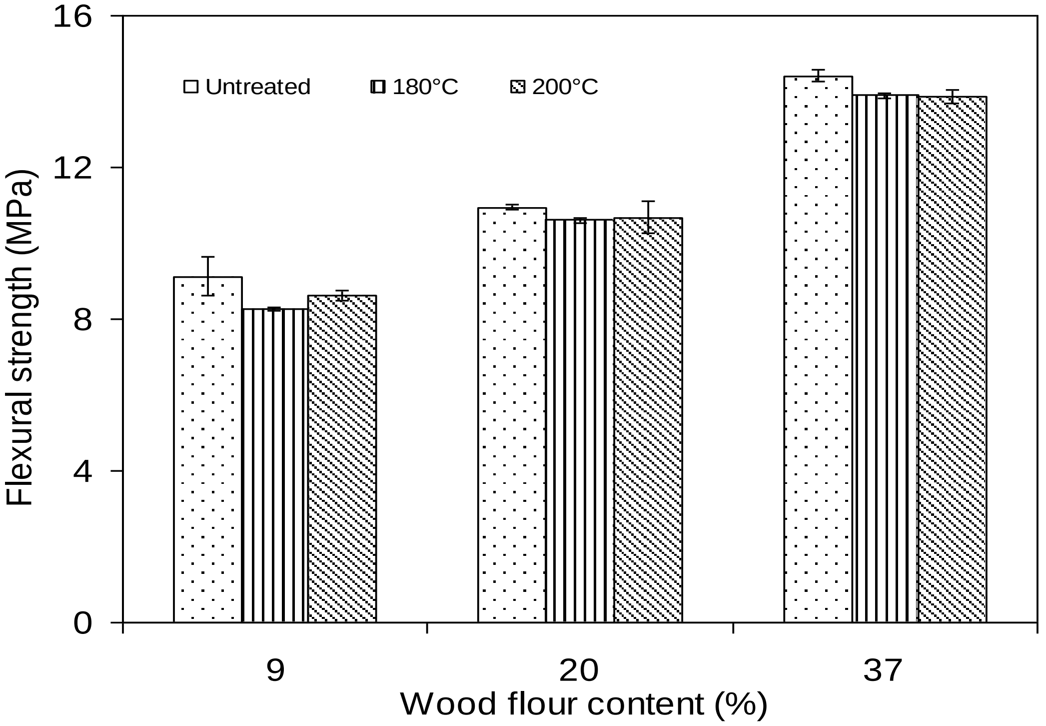


Figure 4.34: Flexural strength of composites as a function of wood flour content and treatment temperature

Effect of heat treatment

Also, in Figure 4.34, the influence of heat treatment on the flexural strength of the composites is shown. As with the flexural modulus, the flexural strength of the composites decreased with heat treatment. Composites made from wood flour treated at 200°C have higher flexural strength at lower filler loading than that from 180°C treated wood flour. However, as the wood content increased, the influence of heat treatment seemed to have levelled-off with wood flour treated at 180°C and 200°C, showing almost the same values of flexural strength.

Effect of MAPE content

Flexural strength increased steadily throughout the range of MAPE content used in this study (Figure 4.35). Better interfacial adhesion between the wood particles and the matrix could be responsible for this behaviour. At 20 wt% filler loading, the effect of loading 2% MAPE is negligible, relative to the uncoupled composites.

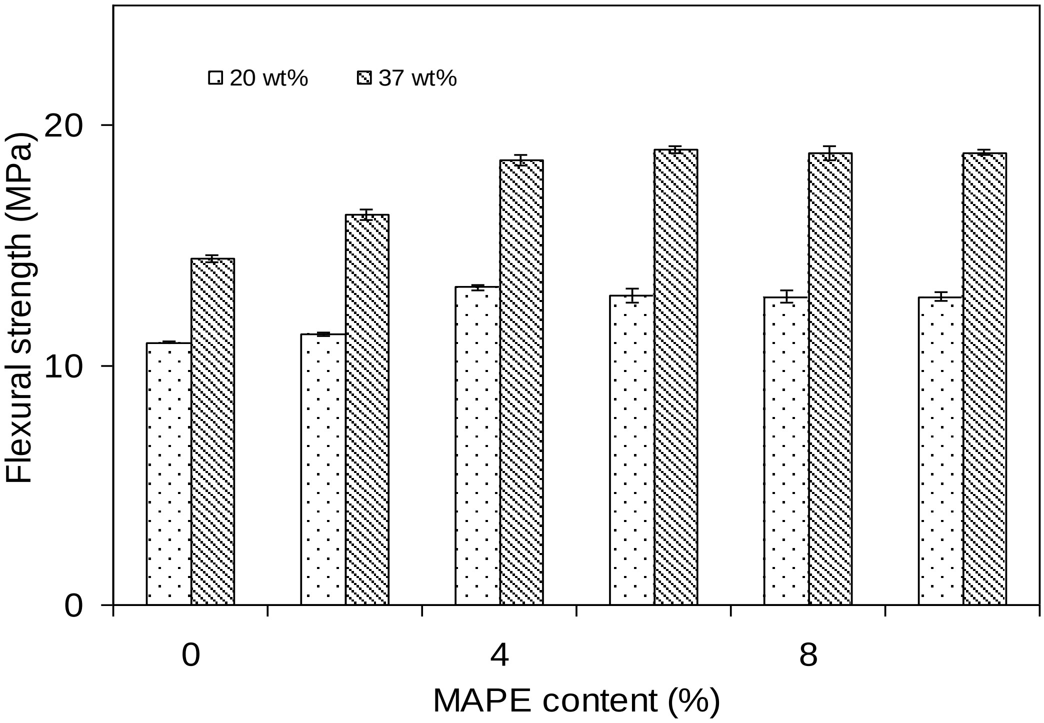


Figure 4.35: Flexural strength of composites from untreated wood as a function of MAPE content

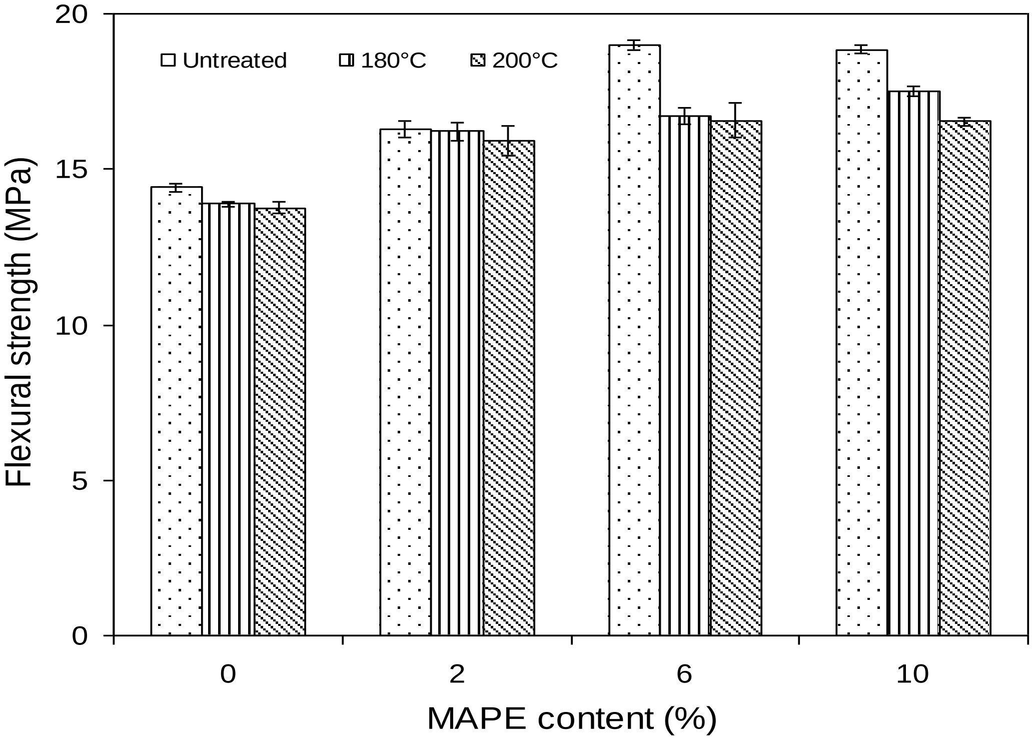


Figure 4.36: Flexural strength of 37 wt% composites as a function of MAPE content and heat treatment

Incorporation of 4% MAPE recorded the highest influence on the flexural strength. Beyond this MAPE level, no appreciable improvement could be seen. Composites made from loading different MAPE levels onto 37 wt% exhibited a significant increases between 0% and 6% MAPE. Beyond this MAPE content, the extent of improvement in strength was observed to be marginal, up to 10% MAPE. These observations of maximum levels of MAPE required for the different compositions may indicate that excess MAPE on the surface of the wood particles did not lead to enhanced properties. Figure 4.36 presents the effect of MAPE content on the flexural strength of composites with 37 wt% untreated and heat-treated wood flour. As observed earlier, the untreated wood composites seemed to respond to the presence of MAPE than the heat-treated composites. However, among the heat-treated wood composites, wood flour treated at 180°C showed better response to the presence of MAPE, than that treated at 200°C.

Flexural displacement

Effect of wood content

The effect of wood content on the flexural displacement of the composites is shown in Figure 4.37. Decrease in displacement at yield has been attributed to the fact that natural fillers have less strain at break than the matrix. Therefore, addition of brittle natural fillers renders the matrix more rigid by decreasing the flexibility of the polymer chain leading to reduced flexural displacement [157].

Effect of heat treatment

In Figure 4.37, the flexural displacements of the untreated and heat-treated WTC are displayed. There is no clear trend on the effect of heat treatment on the flexural displacement of composites at 9 wt% and 20 wt% wood flour loadings. However, at 37 wt% wood content, the flexural displacement increased with heat treatment, with the untreated wood composites displaying the lowest value, followed by composites made from the 180°C treated wood flour and finally, that from the 200°C treated wood flour. Again, as in flexural modulus, the weaker mechanical properties of heat-treated wood particles may be responsible for this trend.

Effect of MAPE content

Figure 4.38 presents the effect of MAPE content on the flexural displacement of the composites. The flexural displacement reduced generally with MAPE loading. This might have resulted from improved adhesion between the filler and the matrix which tends to stiffen the composite system.

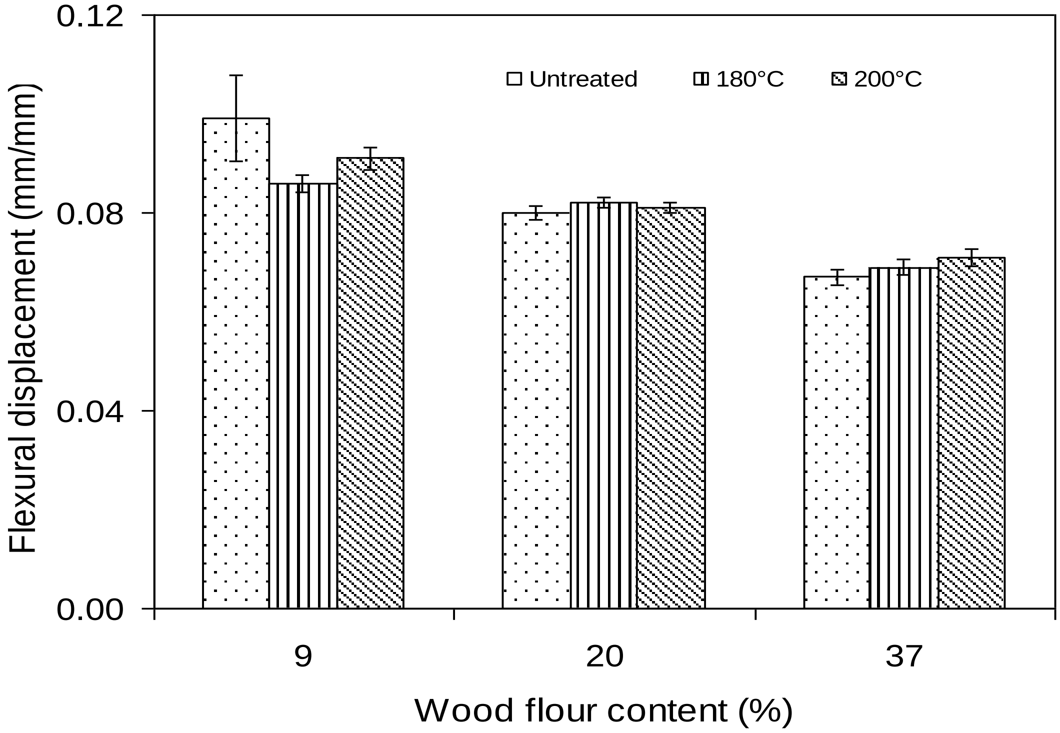


Figure 4.37: Flexural displacement of composites as a function of wood flour content and treatment temperature

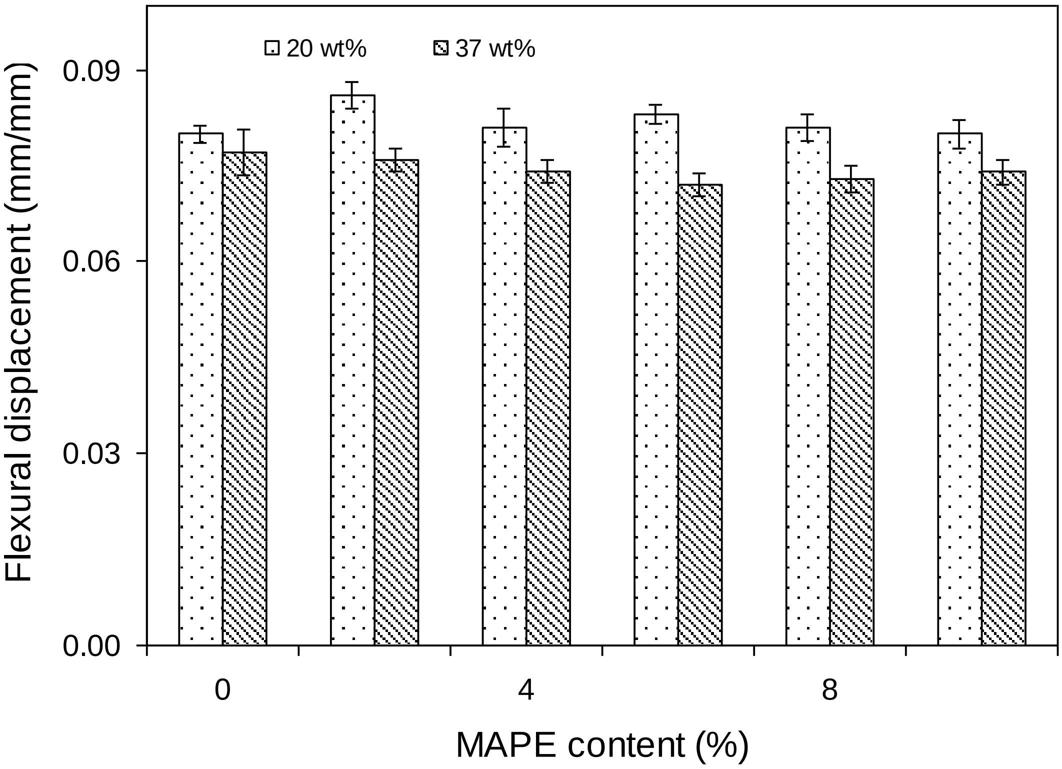


Figure 4.38: Flexural displacement of composites from untreated wood as a function of MAPE content

A clear trend could not be established in composites containing 20 wt% wood flour. Nevertheless, at 37 wt% wood flour loading, composites showed a decrement in flexural displacement as the MAPE content increaseed up to 6%. Better compatibility between the wood particles and the LDPE must have resulted in the embrittlement of the matrix, leading to reduced displacement at yield. Thereafter, an increment is observed for the 8% and 10% MAPE loadings. Again, it is possible that the excess MAPE on the surface of the wood particles plasticised the system, thereby increasing the flexural displacement.

In Figure 4.39, the effect of MAPE content on the flexural displacement of untreated and heat-treated wood composites at 37 wt% wood loading is shown. At lower MAPE content (0% and 2%), there is no clear trend relating the effect of MAPE content and wood flour treatment on the flexural displacement of the composites. However, as the MAPE content increased, from 6% to 10%, flexural displacement increased with heat treatment, with the coupled untreated wood composites showing lower values. As observed previously, it could be that better coupling has taken place in untreated wood composites relative to the heat-treated composites, probably because of the higher amount of O-H groups available for coupling with MAPE. This could mean that there is a higher tendency for excess of MAPE on the surface of heat-treated wood composites than the untreated composites, which might have led to the softening of the system, resulting in higher flexural displacement.

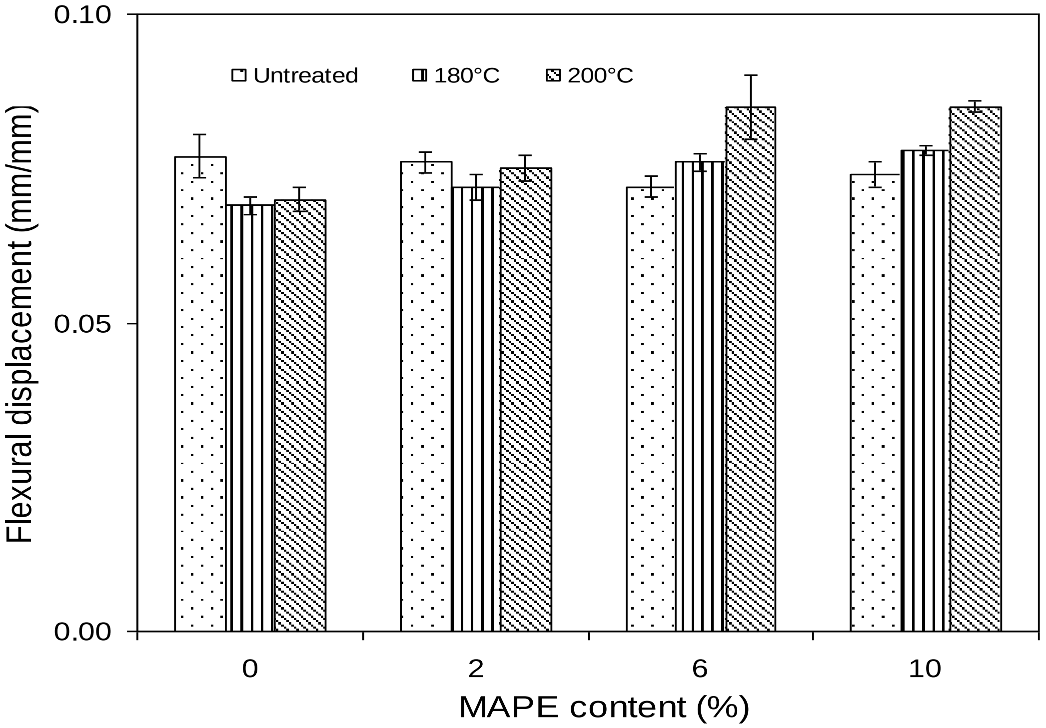


Figure 4.39: Flexural displacement of 37 wt% composites as a function of MAPE content and treatment temperature

4.2.4.3 Impact properties

Impact may be defined as the sudden application of an impulsive force to a limited volume of material or part of a structure [158]. During the service life, plastic products are exposed to many impact encounters that could lead to failure. It is therefore necessary to know, among other things, what maximum loads they can sustain without failing. Brittle failure in materials is caused by the presence of very small, microscopic flaws or cracks that exists under normal conditions at the surface and within the body of the material. They are referred to as stress concentrators because of their ability to magnify the applied stress. Any brittle fracture process involves two steps; crack formation and propagation in response to an applied stress. Using the principles of fracture mechanics, an expression has been developed that relates the critical stress for crack propagation, σ_c and the notch or crack length, *a*, as follows:

$$K_c = Y\sigma_c\sqrt{a} \tag{4.9}$$

where K_c is the fracture toughness or stress intensity factor, a property that is a measure of the material's resistance to brittle fracture when a crack is present. It is an indication of the energy per unit area needed to give a new crack surface and it characterises the severity of a crack situation as affected by crack size, stress and geometry. *Y* is a constant that depends on the crack length, *a* and the specimen sizes and geometries as well as the manner of load application [159]. In a three-point bend test, σ is given by simple bending theory as:

$$\sigma = \frac{6PS}{4BD^2} \tag{4.10}$$

For the three-point test specimen, where S/D is equal to 4, *Y* is given by:

$$Y = 1.93 - 3.07\left(\frac{a}{D}\right) + 14.53\left(\frac{a}{D}\right)^2 - 25.11\left(\frac{a}{D}\right)^3 + 25.80\left(\frac{a}{D}\right)^4 \tag{4.11}$$

A plot of σY against $a^{0.5}$ gives a straight line, where the slope equals the K_c of the materials.

It is assumed that composite materials fail in a linear-elastic manner. Thus, linear elastic fracture mechanics (LEFM) theory is applied. The compliance of the specimen, *C*, is the displacement per unit load (a reciprocal of stiffness). Therefore, when the crack has a length *a*, the specimen is less compliant. Generally, the concept of compliance as a ratio of deformation to applied load is given by the equation:

$$C=\frac{\delta}{P} \tag{4.12}$$

Since energy is stored as strain energy when the material is under stress and the material's response is entirely elastic, the energy absorbed, W is given by:

$$W=\frac{P\delta}{2}=\frac{P^2C}{2} \tag{4.13}$$

The total strain energy, U, for a specimen with uniform thickness, B, can be written in terms of this compliance as:

$$U=\frac{W}{B}=\frac{CP^2}{2B} \tag{4.14}$$

When a crack of length, a, grows into the specimen by a small amount, ∂a, the material becomes more compliant. Thus, it stores less energy at a fixed displacement, but elastic energy is stored more at a fixed load. The rate of change of elastic energy with increase in crack area is defined as the strain energy release rate, G [159]:

$$G=\frac{\partial U}{\partial a}=\frac{P^2}{B}\frac{\partial C}{\partial a} \tag{4.15}$$

The energy release rate is related to the stress intensity factor as follows:

$$G=\frac{K^2}{E} \tag{4.16}$$

where E is the Young's modulus and K is given by Equation 4.9. Substituting Equation 4.9 for K^2 in Equation 4.16, G becomes:

$$G=\frac{Y^2\sigma^2 a}{E}=\frac{P^2}{2B}\frac{\partial C}{2B\partial a} \tag{4.17}$$

Therefore,

$$\frac{\partial C}{\partial a}=\frac{2BY^2\sigma^2 a}{P^2E} \tag{4.18}$$

From Equation 4.10,

$$P = \frac{4BD^2\sigma}{6S} \tag{4.19}$$

Substituting for P in Equation 4.18 gives:

$$\frac{\partial C}{\partial a} = \frac{9aY^2S^2}{2EBD^4} \tag{4.20}$$

Thus, the compliance, C, can be written as:

$$C = \frac{9S^2}{2EBD^4}\int Y^2 a.\partial a + C_{\circ} \tag{4.21}$$

Substituting Equations 4.19 and 4.21 for P and C respectively in Equations 4.13 gives;

$$W = \frac{B\sigma^2}{E}\left[\int Y^2 a.\partial a + \left(\frac{SD}{18}\right)\right] \tag{4.22}$$

The term σ^2 in Equation 4.22 can be eliminated by using Equations 4.9 and 4.16 thus;

$$W = \frac{GB}{Y^2 a}\left[\int Y^2 a.\partial a + \left(\frac{SD}{18}\right)\right] \tag{4.23}$$

$$W = GBD\phi \tag{4.24}$$

where B and D refer to the width and depth of the specimen respectively.

The parameter ϕ is a geometrical correction factor determined as a function of a/D given by:

$$\phi = \frac{1}{2}\left(\frac{a}{D}\right) + \frac{1}{18\pi}\left(\frac{S}{D}\right)\frac{1}{\left(\frac{a}{D}\right)} \tag{4.25}$$

where a and S are the notch depth (crack length) and the specimen support span respectively. At fracture, the energy release rate, G assumes a critical value, G_c. Equation 4.24 then becomes:

$$W = G_c BD\phi \tag{4.26}$$

A plot of W against $BD\phi$ gives a straight line with the slope as the G_c of the material [160].

Peak load, *P*

The peak load is the maximum force needed to cause the fracture of the sample. It depicts the maximum point on the load-deflection curve and is a function of the resistance to damage of the material.

Effect of wood content

Peak load of the composites as a function of notch depth at different filler loadings and treatment temperatures are presented in Figure 4.40. Generally, *P* decreased with notch to depth ratio, a/D. Increase in a/D reduces the available length for crack propagation. This in turn decreased the maximum load required for fracture. The neat polymer exhibited the highest *P* values of 266.6 N, 225.3 N, 184.5 N and 137.4 N for a/D ratios of 0.1, 0.2, 0.3, and 0.4 respectively because of its ductility (Figure 4.41). However, incorporation of wood fillers reduced the *P* of the neat matrix by introducing a measure of brittle behaviour (Figure 4.42). It has been said that in WTC, the wood particles are encapsulated in the flexible polymer matrix. Therefore, the average thickness of the polymer layer between two adjacent wood particles would depend on the amount of wood flour in the mixture. Higher wood content would generally result in thinner polymer layer between wood particles. With the application of an external force, separation or cracking along the weak polymer-wood interface results [161]. The initiation and propagation of the cracks due to debonding contributed to the weakening of the composites (Figure 4.42a). At lower filler content (9 wt% and 20 wt%), *P* values indicated that the samples could not sustain the maximum load and hence lower values were observed. However, as the wood content increase to 37 wt%, an increment in *P* values was observed. This is in agreement with the resistance to sliding offered by the wood filler which is expected to stiffen the neat matrix. The higher the wood content, the higher is the resistance.

Effect of heat treatment

The effect of heat treatment on the *P* values of the composites is also presented in Figure 4.40. *P* values of the neat LDPE is higher than both the treated and untreated wood composites, except for composites made from heat-treated wood at 200°C at 37 wt% filler loading. Higher values of *P* in heat-treated wood composites, relative to the untreated composites could be attributed to the reduced hydrophilicity in heat-treated wood flour compared to their untreated counterparts which had improved the interfacial interaction between the wood particles and the LDPE matrix. From the SEM micrograph in Figure 4.42a, it can be seen that the wood particles pulled out of the matrix, indicating poor bonding between the matrix and the fillers, resulting in lower *P* values of the untreated wood composites. However, Figure 4.42b showed portions of the matrix still adhering to the wood particles after fracture, indicating better adhesion and consequently, higher *P* in composites made from heat-treated at 200°C.

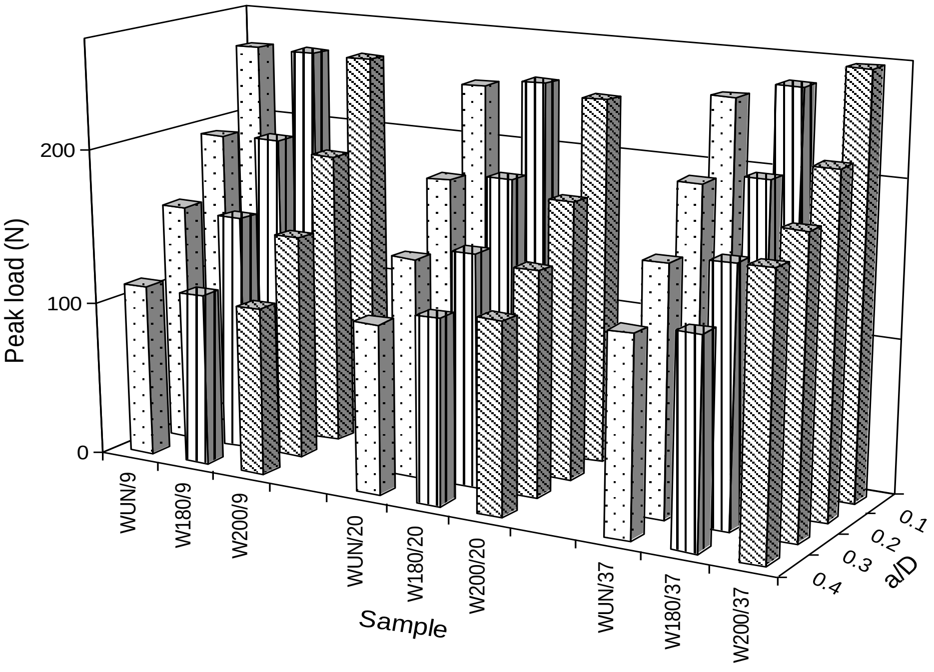


Figure 4.40: Peak load as a function of notch dept for different wood content and

heat treatments

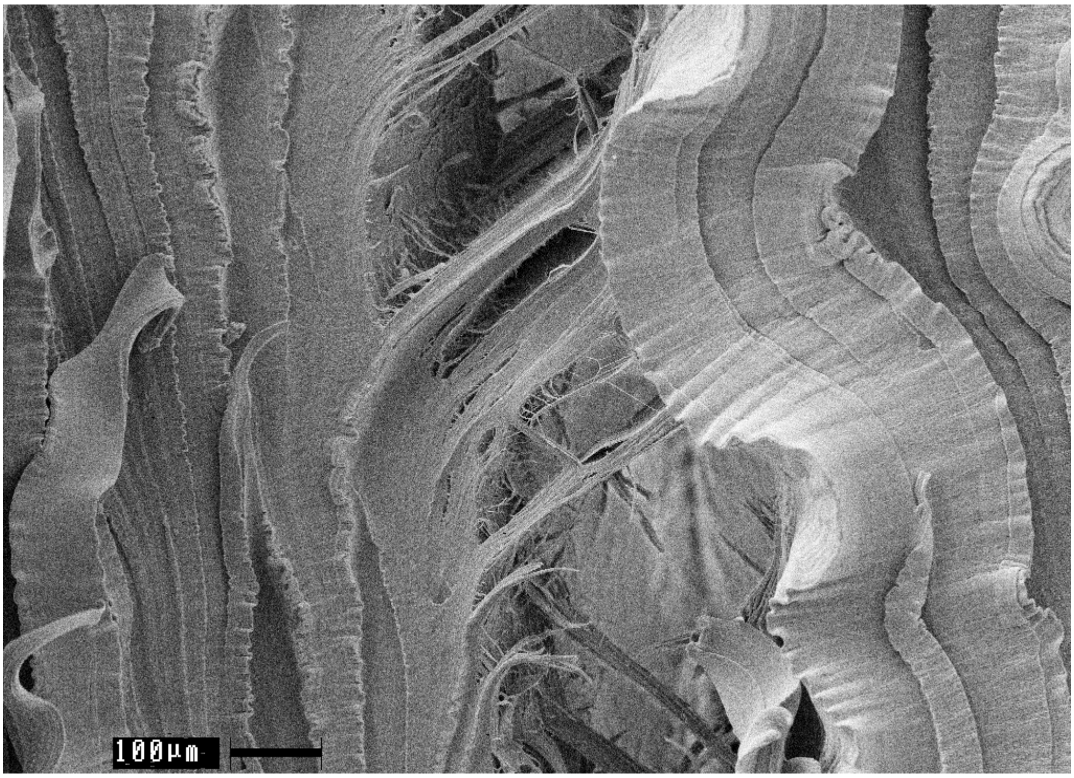


Figure 4.41: Impact fractured surface of neat LDPE showing signs of ductility

a)

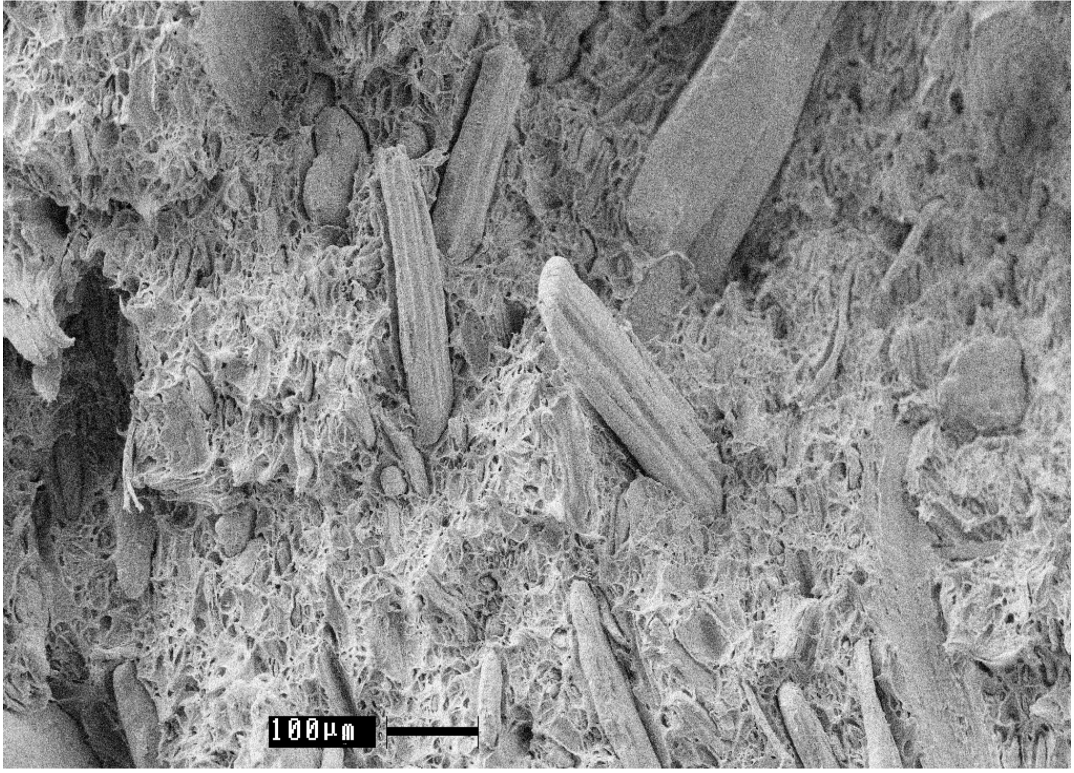


Figure 4.42 cont'd

b)

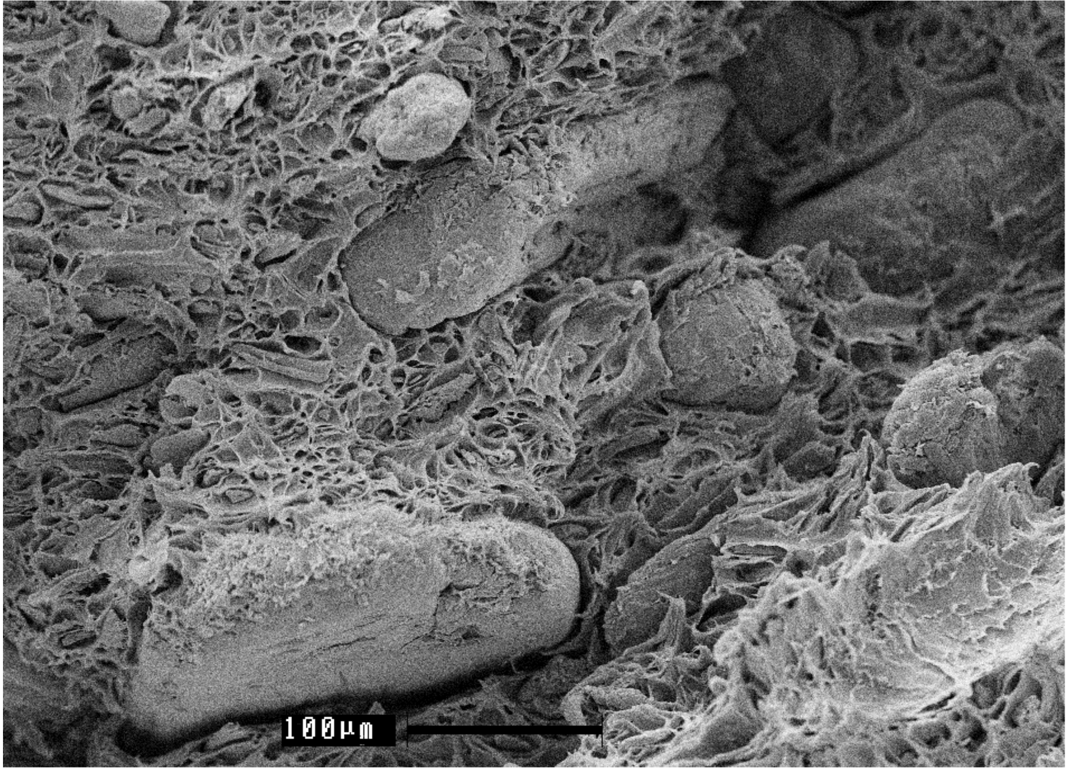


Figure 4.42: Impact fractured surface of composites containing 37 wt% a): untreated and b): 200°C treated wood flour

Effect of MAPE content

The effect of MAPE content on the *P* values of composites reinforced with 37 wt% filler at different treatment temperatures are given in Figure 4.43. Generally, *P* increased with MAPE content in all the categories of composites studied. Untreated wood composites showed more positive response to the presence of MAPE, exhibiting a higher *P* values than the heat-treated composites as the MAPE content increased. This is expected because MAPE improves the fibre-matrix adhesion by bonding with the hydroxyl groups of the wood particles and entangling its polymer chains in the bulk of the LDPE matrix [13].

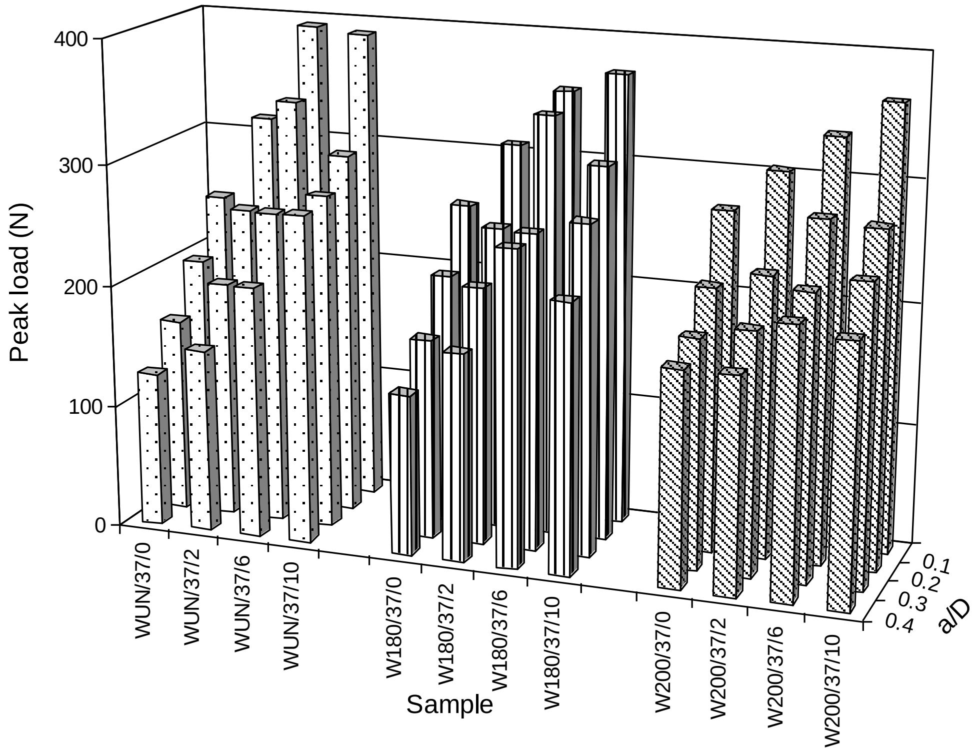


Figure 4.43: Peak load of different a/D as a function of MAPE content and heat treatment

The effect of the addition of MAPE in untreated wood composites was highest at 6% MAPE loading and levelled-up at 10% MAPE when a reduction in *P* was observed. As has been observed earlier, excess MAPE which migrated to the surface of the wood particles could led to self-entanglement among MAPE molecules rather than the polymer matrix, resulting in slippage and consequently, reduced *P* [144]. However, for the heat-treated WTC, although an improvement was observed and a levelling-off was not evident, the rate of improvement was lower than the untreated wood composites. The possibility of reduced O-H groups on the surface of the wood particles by heat treatment might have hindered effective coupling with MAPE, thereby resulting in the reduction in properties.

Critical stress intensity factor or fracture toughness, K_c

K_c represents the materials ability to withstand applied force (load).

Effect of wood content

The variation of K_c with wood content is presented in Figure 4.44. The neat LDPE has K_c value of 1.7 MPa.m$^{0.5}$. Again, this value was higher than that of the composites. Once more, the ductile nature of LDPE could account for this observation. As has been observed with P, K_c increased with wood content. Incorporation of stiff wood particles into the flexible LDPE matrix is expected, in principle, to stiffen the composites system, due to stress transfer between the wood particles and the matrix resulting in high modulus. From these results, the stiffening was higher with increasing wood content. The presence of wood particles tended to reduce the resistance to crack propagation, while at the same time, reducing crack propagation through the matrix by forcing crack lines around the particle ends [162]. As has been observed earlier, lower wood content did not contribute, appreciably, to the stiffening of the composite. This is because at low wood content, wood particle ends may act as notches, a possible reason for the low K_c values observed at 9 and 20 wt% and a relative improvement in K_c value seen in composites loaded with 37 wt% wood flour.

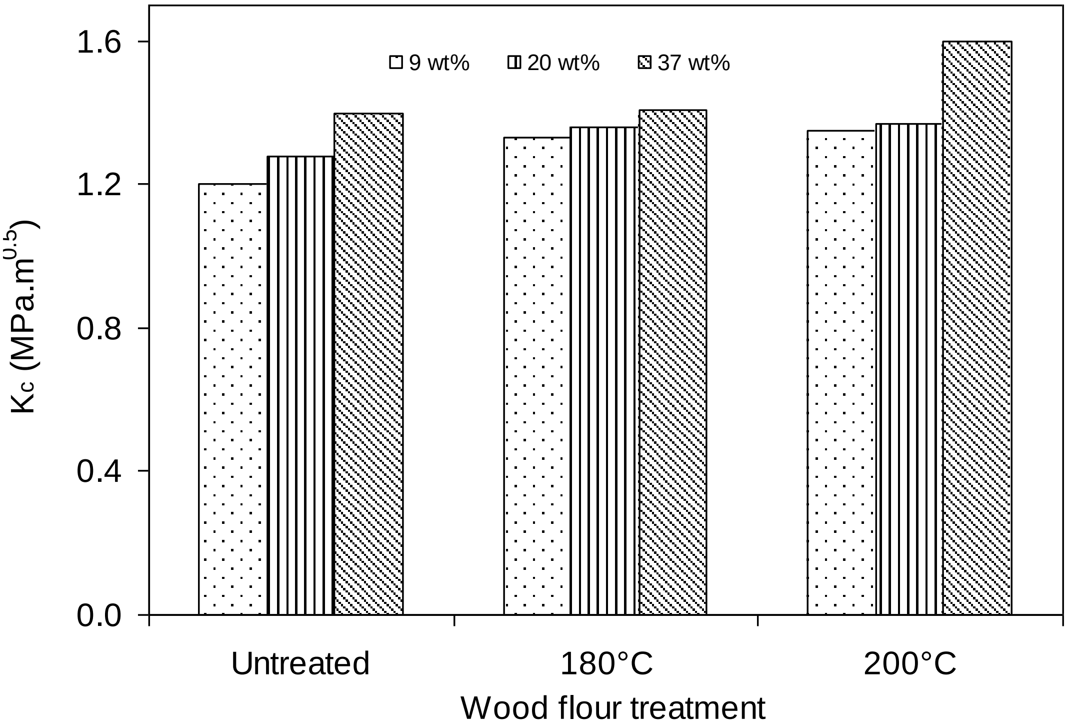


Figure 4.44: *K_c* of composites as a function of wood content and treatment temperature

Effect of heat treatment

The effect of heat treatment on the K_c values of the composites is also seen in Figure 4.44. K_c improved with heat treatment, relative to the untreated wood composites at all compositions. However, composites made from wood flour treated at 180°C had a marginal (5%) increase in the value of K_c when compared to the untreated wood composites, while composites made from wood flour treated at 200°C produced composites with the highest K_c value of 1.6 MPa.m$^{0.5}$ at 37 wt%, a 14% increase over the untreated wood composites at the same composition. Improved compatibility between the wood particles and the LDPE matrix, as a result of reduced polarity of heat-treated wood flour and a better dispersion of the fillers within the matrix, must have resulted in improved stiffness.

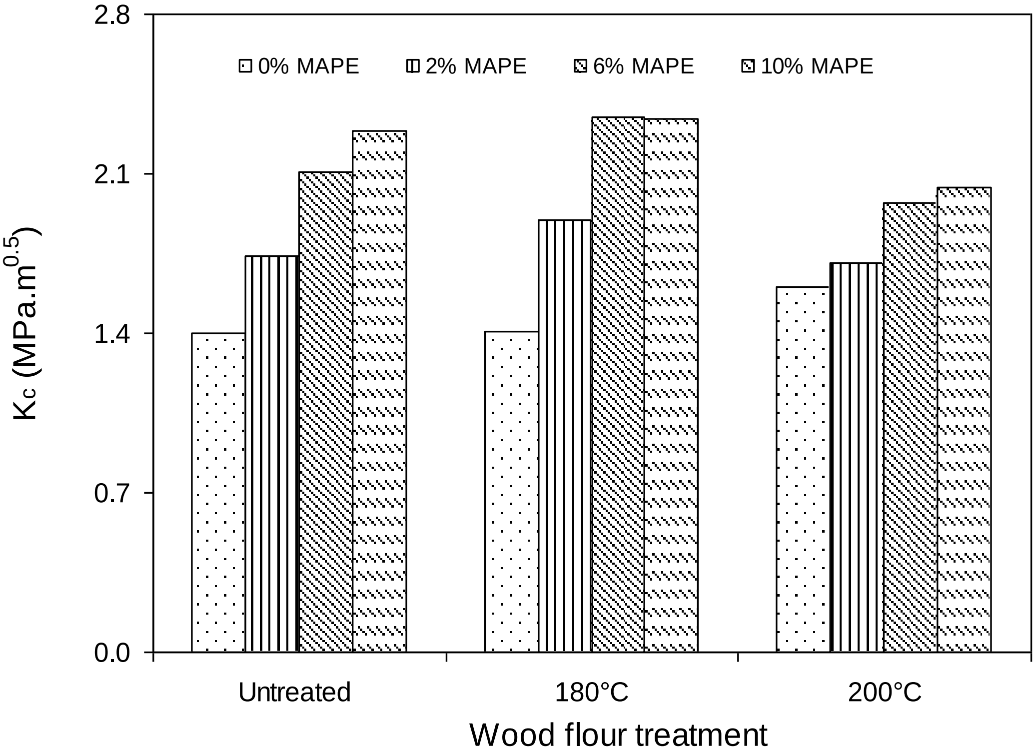


Figure 4.45: K_c of 37 wt% composites as a function of MAPE content and treatment temperature

Effect of MAPE content

Figure 4.45 shows the effect of MAPE content on the K_c values of the composites. K_c improved as the content of MAPE increased in all the composites studied. However, untreated wood composites exhibited a consistent increment with no levelling-off observed at all MAPE contents. Increase in K_c with increasing MAPE content can be attributed to improved interfacial adhesion between the wood flour and the polymer matrix which resulted in higher fracture toughness of the material. Composites made from wood flour treated at 180°C also showed an increment in K_c value as the MAPE content increased up to 6%. There was no further improvement in K_c at 10% MAPE content. This trend was also observed in the composites made from wood flour treated at 200°C, although an insignificant improvement was observed at 10% MAPE content. As observed earlier, a levelling-off in K_c between 6% and 10% MAPE levels in heat-treated wood composites may indicate an excess of MAPE on the surface of the wood particles which tended to soften the material.

Energy to failure, *W*

The energy to failure represents the total energy the material will absorb until full penetration of the impactor tup. It is the area under the force-deflection curve up to peak deflection where propagation of damage takes place until fracture.

Effect of wood content

The variation of *W* with filler loading at different a/D is presented in Figure 4.46. *W* decreased with a/D at the same composition. Values of 4.62 J, 3.48 J, 3.17 J and 2.12 J were obtained for a/D ratios 0.1, 0.2, 0.3 and 0.4 respectively for the neat LDPE. As mentioned before, this is as a result of the reduction in the fracture area as the notch depth increased. *W* of pure LDPE was higher than that of the composites. The ductile nature of the neat LDPE requires higher energy to break the specimen. However, as the wood content increased, a decrement in the values of *W* was observed. At high wood content, many wood particle ends exist within the composite, which could aid crack propagation and consequently, premature failure. Also, higher wood loading leads to agglomeration of the wood particles which, in addition to the already existing notches, could act as stress concentration points requiring lower failure energy [144]. This phenomenon increased with increase in wood content, with wood flour loading at 37 wt% showing the lowest value of *W*. In addition, poor interfacial bonding between the fillers and the matrix resulting from poor compatibility may also be responsible for the observed trend.

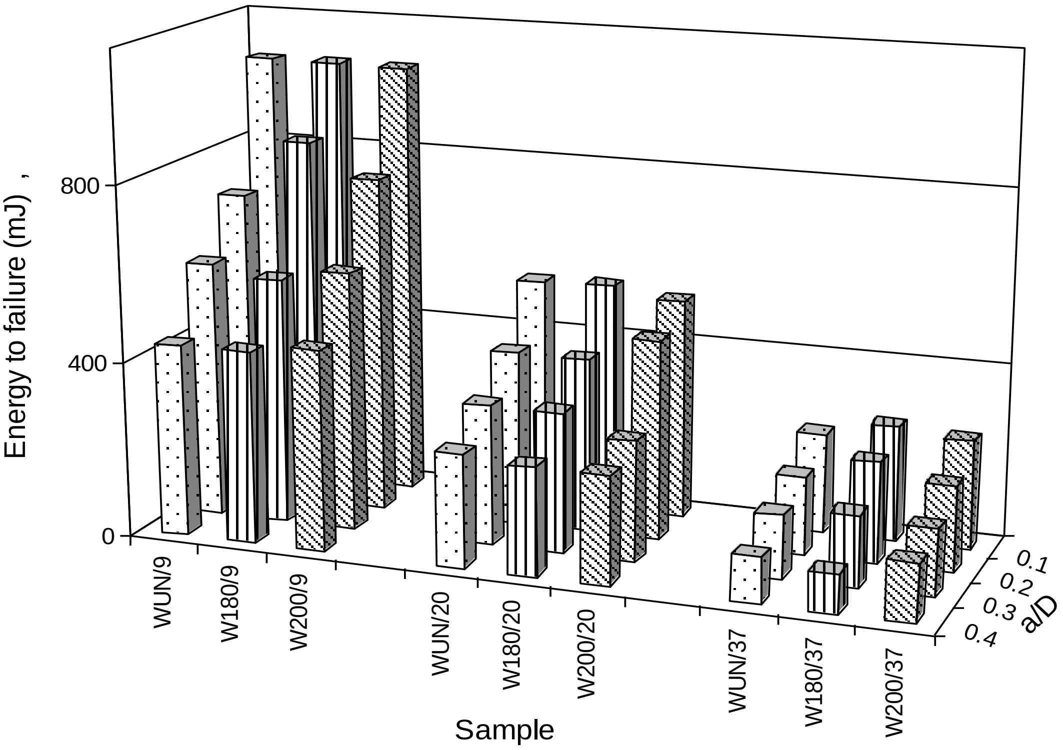


Figure 4.46: Energy to failure of composites as a function of wood content and treatment temperature for different a/D ratios

Effect of heat treatment

The effect of heat treatment on *W* of the composites is seen in Figure 4.46. At low wood content (9 wt%), a clear trend could not be established. At this composition, the reinforcing effect of wood flour was not pronounced and as such, the behaviour of the neat matrix dominated. Therefore, an inconsistent trend wais observed. However, as the wood content increased to 20 wt% and 37 wt%, the effect of heat treatment seemed evident. Composites made from wood flour treated at 180°C appeared to influence the *W* more that those from the untreated and wood flour treated at 200°C. This indicated that treating wood at 180°C had modified the wood flour to a certain degree, which enhanced better compatibility between the non polar LDPE matrix and the polar wood particles, relative to the untreated wood composites. This trend was also observed in previous sections where the tensile strength of composites from wood flour treated at 180°C was higher than that of untreated and 200°C treated wood composites. Heat treatment of wood flour at 200°C might have caused deterioration of the mechanical properties of the wood particles and lowered its stress transfer efficiency, resulting in reduced *W*.

Effect of MAPE content

The effect of MAPE content on *W* of 37 wt% untreated and heat-treated wood composites is given in Figure 4.47. Generally, addition of MAPE resulted in increases in the *W* values of the composites. Improved interfacial bonding between the wood particles and the LDPE matrix as a result of coupling actions of MAPE could have resulted in higher energy requirement to fracture. It has been reported [163] that the anhydride moieties of functionalised polyolefin-coupling agents undergo esterification reaction with the surface hydroxyl groups of wood particles, thereby exposing the polyolefin backbone chain of the coupling agent on the surface of the wood particles. It is believed that the exposed polyolefin chains diffuse into the LDPE matrix phase and entangle with LDPE molecules during processing, creating a bridge, at the interface, between the wood flour and the PP matrix. As the MAPE content increased from 0% to 2%, a significant increase in *W* was observed in the untreated wood composites at all a/D ratios. Nevertheless, as the MAPE content increased to 6% and 10% loading, *W* remained relatively unchanged. Similarly, composites made from heat-treated wood demonstrated the same trend, but the increase in *W* between 0% and 2% is lower. Between 2% and 6% MAPE level, a significant improvement in *W* was seen, beyond which, no further increment was observed. Increase in *W* at higher MAPE level may be a result of excess MAPE on the surface of the wood particles, resulting in self-entanglement among the molecules of the compatibiliser rather than the matrix, thereby softening the system.

Critical strain energy release rate, G_c

G_c, is a material property referred to as the toughness, critical strain energy release rate or crack extension force. It is effectively the energy required to increase the crack length by unit length in a piece of material of unit width [164].

Effect of wood content

The effect of wood content on the G_c of the composites is presented in Figure 4.48. The neat LDPE had a G_c value of 96.6 kJ.m^{-2}. The high value of the unreinforced LDPE is as a result of slow crack propagation because of the ductile nature of the neat LDPE. G_c decreased with incorporation of wood flour, with the highest G_c value observed in composites loaded with 9 wt% wood flour and the lowest in 37 wt% filled WTC (Figure 4.48). As has been observed for W, this decrement may have resulted from the presence of wood particle ends within the LDPE matrix which tends to aid crack propagation. Furthermore, at high wood content, the possibility of the wood particles agglomerating is high. This, as seen earlier, could act as stress concentrators, thereby enhancing crack growth.

Effect of heat treatment

The effect of heat treatment on G_c of the composites is also shown in Figure 4.48. From the Figure, it can be seen that G_c increased marginally with heat treatment at all filler loadings, with composites made from wood treated at 180°C exhibiting the highest value. A look at 37 wt% wood content revealed that a value of 4.85 kJ.m^{-2}, 5.47 kJ.m^{-2} and 5.08 kJ.m^{-2} were obtained for composites made from untreated, 180°C and 200°C treated wood, respectively.

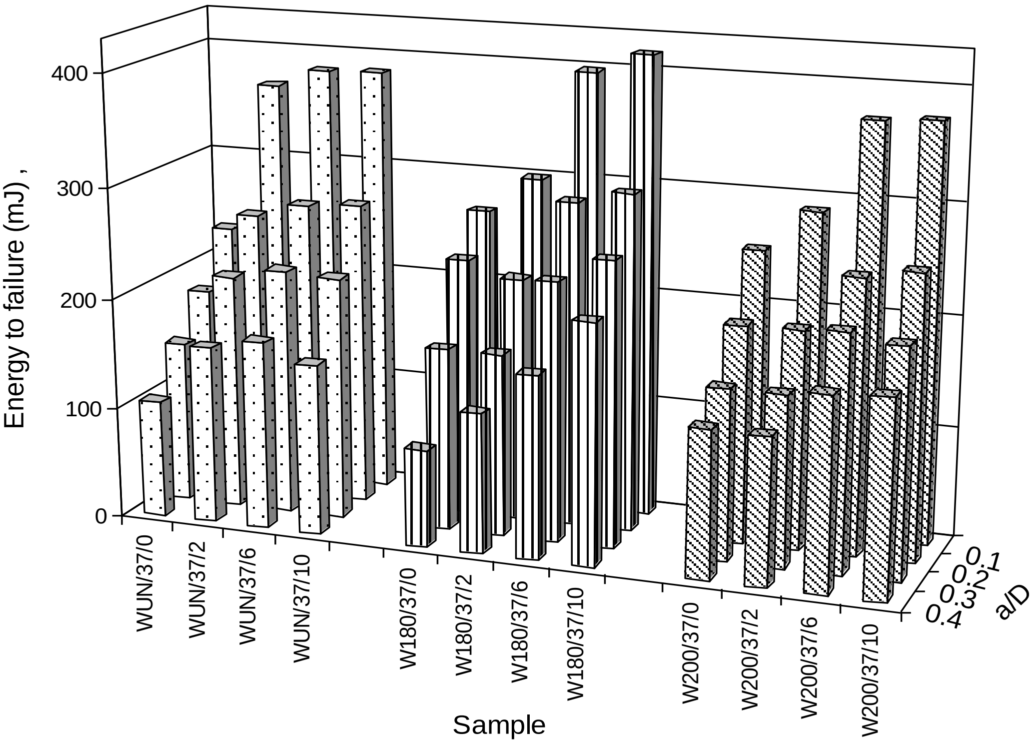


Figure 4.47: *W* of composites as a function of MAPE content and heat treatment for different a/D ratios

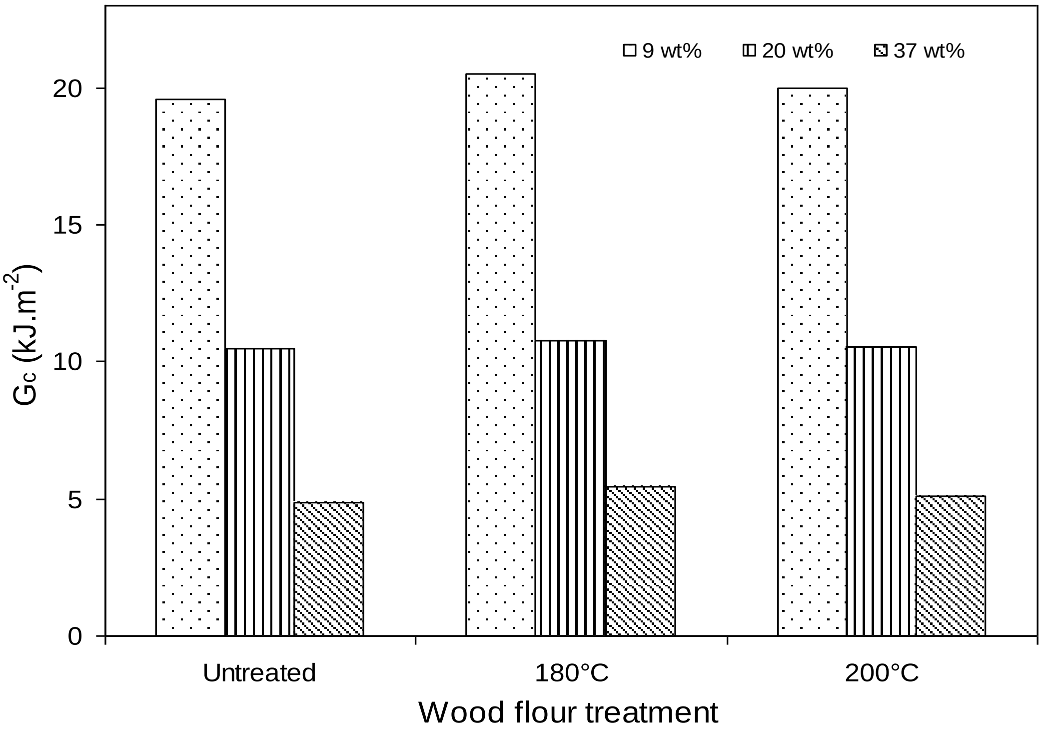


Figure 4.48: G_c of composites as a function of wood content and treatment temperature

The marginal increase in the G_c of heat-treated wood composites, relative to the untreated samples indicated some level of modification by heat treatment which rendered the wood more compatible with the non polar LDPE matrix, thereby showing some degree of resistance in crack propagation when the notched samples were subjected to impact testing.

Effect of MAPE content

Figure 4.49 shows the effect of coupling agent content and heat treatment on G_c of the composites. Increase in MAPE content increased G_c in the heat-treated and the untreated wood composites. This is expected, as mentioned before, because of the coupling action of MAPE between the polar O-H groups on the surface of the wood particles and the non polar LDPE matrix.

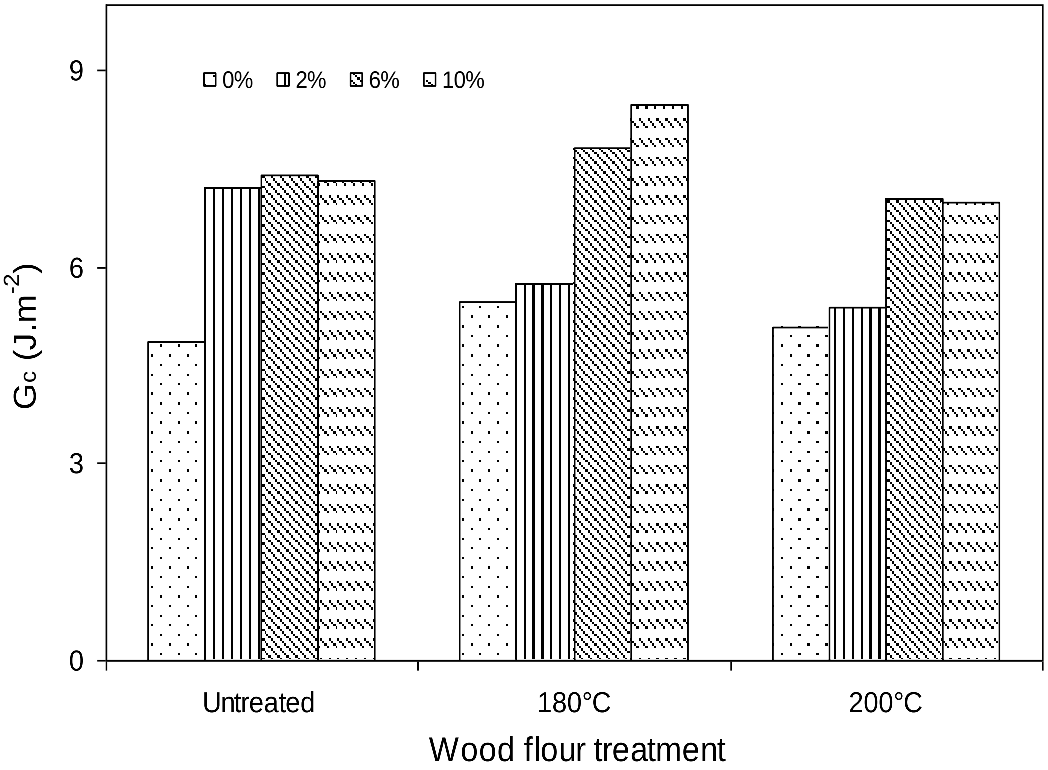


Figure 4.49: Variation of G_c of 37 wt% with MAPE content and treatment temperature

This enhanced better compatibility between the wood particles and the LDPE matrix, leading to improved interfacial adhesion needed for better stress transfer between the stiff wood particles and the flexible LDPE matrix. Consequently, the composites exhibited a relatively higher intensity in its resistance to crack growth on impact loading, leading to higher values of G_c. The untreated wood composites showed a marked improvement in G_c at 2% MAPE level. Further addition of MAPE from 6% to 10% did not show any additional improvement, rather, a decrement is observed. This indicated that effective coupling took place at 2% MAPE content. Higher levels of MAPE only acted to soften the system as explained earlier. However, for the heat-treated wood composites, 6% MAPE loading gave the highest G_c values. Additional MAPE content (10%) also resulted in lower G_c values.

4.3 Effect of different environmental conditionings.

Degradation of polymeric materials occurs in a wide variety of environments and service conditions and very often limits the service lifetime. It occurs as the result of environmentally-dependent chemical or physical attack, often caused by a combination of degradation agents and may involve several chemical and mechanical mechanisms [165]. In this section, the response of the composites on exposure to different environmental conditions is evaluated with respect to changes in their properties.

4.3.1 Water absorption behaviour

The hygroscopic nature of wood remains a shortcoming when WTC is used in outdoor or moisture related applications. In certain usage, the environmental conditions can be so unfavourable that the performance of these composites is negatively affected [6]. It has been observed that the absorption of water by non polar polymers containing fillers depends mainly on the nature of the filler [166]. Therefore, for hydrophilic fillers such as wood, increase in water absorption should be expected. Besides, many polymer matrices absorb moisture reversibly by Fickian diffusion. This is found to depend on the polarity of the molecular structure (presence of chemical groups that has the ability to form hydrogen bonds with water), degree of cross-linking, presence of residual monomer or other water attracting species and degree of crystallinity of the polymer (higher crystallinity leads to reduced water absorption). The presence of adventitious impurities is also a factor to reckon with. Consequently, non-Fickian processes may occur that may not necessarily lead to reversible effects. More so, the presence of aggregates of a second phase, such as natural filler, may complicate this phenomenon. Such been the case, the presence of fillers may modify the response of the resin in the presence of water, particularly, when the two components, each has appreciably different responses [166]. In this section, the effect of heat treatment of wood flour and MAPE content on the water absorption behaviour and kinetics of the composites are evaluated.

Effect of wood content

Water uptake, W_t, was calculated using the formula,

$$W_t = \frac{W_2 - W_1}{W_1} \times 100\ (\%) \qquad (4.27)$$

where W_1 and W_2 are the dry weight and weight after time t of immersion in water respectively.

A plot of moisture content against time for the different treatment temperatures and wood flour loadings is presented in Figure 4.50. The neat LDPE showed no water absorption as no weight increase was observed over the period of study. This is because LDPE is hydrophobic and has no tendency of absorbing water. However, the untreated and treated wood composites absorbed water to various extents. As the neat LDPE did not absorb water, it can be assumed that the wood flour is responsible for all the moisture absorbed by the composites. This is expected due to the hydrophilic nature of wood flour. It is sometimes believed that moisture is not an issue with WTC because wood is totally encapsulated by the matrix. If that was the case, the matrix would shield the wood from moisture because they are hydrophobic. Nevertheless, the composites still exhibit a degree of moisture absorption tendency [167]. This seems to indicate that wood must have been exposed on the surface of the samples which may be responsible for the various degree of water absorption exhibited by the composites. Also, it can be seen that water absorption increased with time of immersion, reaching a certain value (the equilibrium point), when the water content of the composite remains constant. Composites containing 20 wt% and 37 wt% untreated wood flour showed a saturation point of 3.48% and 6.02% respectively on the 119th day of immersion.

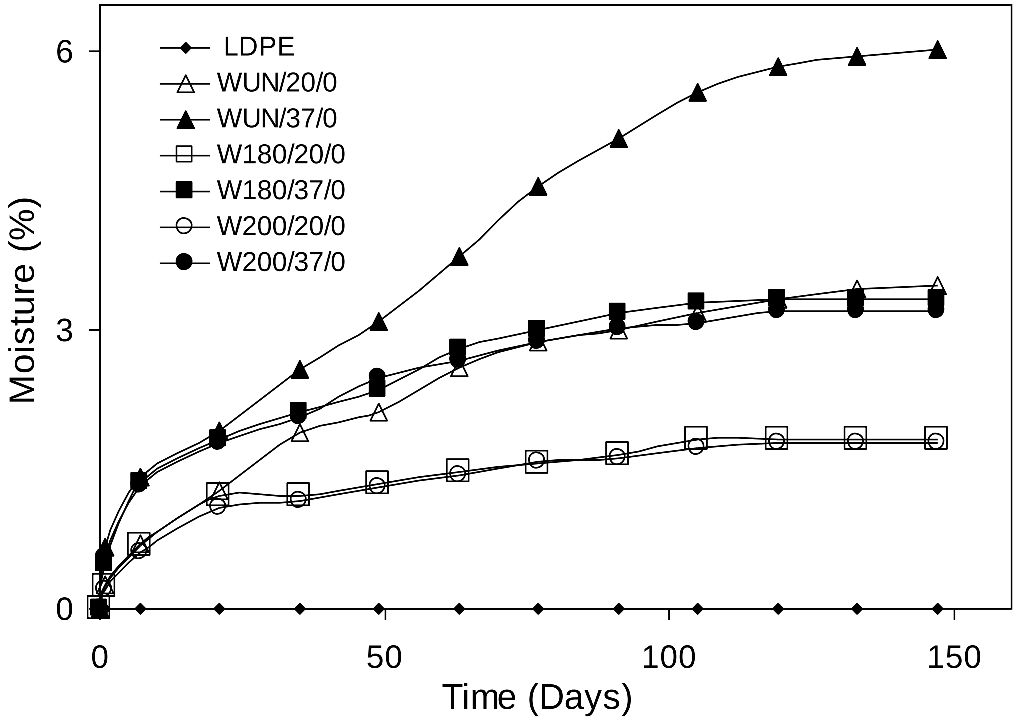


Figure 4.50: Moisture absorption of composites as a function of wood content and treatment temperature

This is likely because of the higher number of free O-H groups on the surfaces of untreated wood composites which interact with water via hydrogen bonding, leading to more ability to absorb water [168]. The higher the wood content, the higher was the water absorption tendency (Figure 4.50). It was also possible that at 37 wt%, the wood flour was not continuously distributed and most of the wood particles probably contacted one another directly, in which case, complete encapsulation was not achieved (Figure 4.19, page 94). This could result in the higher water absorption values recorded for composites at 37 wt% wood content.

Water absorption in WTC has been shown to not only depend on the filler particles and matrix structure, but also on the filler-matrix interface [169]. Hydrophilic fillers lead to lower filler-matrix interaction resulting in poor interface which facilitates the absorption process. This is supported by the SEM micrographs presented in Fig 4.19, (page 94). It has been reported that moisture can be absorbed into the composite by the dissolution of water into the polymer network, moisture sorption into the free volume, if present, in the glassy structure and by hydrogen bonding between water and the hydrophilic components of the composite. Micro-cracks can also allow moisture transportation involving flow and storage of water within the cracks [169].

Effect of heat treatment

Figure 4.50 presents the effect of heat treatment of wood flour on the water absorption of the composites. The initial rate and the equilibrium water uptake values decreased with heat treatment. 20 wt% composites made from 180°C and 200°C treated wood flour reached equilibrium (1.82% and 1.74% respectively) in 91 days while that containing 37 wt% attained equilibrium point (3.34% and 3.20% respectively) on the 105th day of immersion. Untreated wood composites generally show higher water absorption than the heat-treated composites. Composites containing 20 wt% untreated wood flour absorbed 92% more water when compared to that made from 180°C treated wood flour and 94% relative to those made from wood flour treated at 200°C, while composites made from 37 wt% untreated wood flour absorbed about 80% water higher than that made from 180°C and 89% water more than that containing 200°C treated wood flour. This could be attributed to the removal of the water-sensitive components, hemicellulose, in wood flour by heat the treatment, thereby rendering the composites more water resistant. Furthermore, free hydroxyl groups of the cellulose were reduced with heat treatment (Figure 4.2, Page 55) which could lead to a decrease in the water absorption of the wood flour and consequently, the composites. Follrich *et al.* [148], reported that at 200°C, hydrophilicity of spruce wood decreased appreciably. This was observed as an important result for WTC compounding and inferred that it is an alternative way of increasing the adhesion between wood and hydrophobic thermoplastics without the use of compatibiliser. Composites containing 20 wt% wood flour absorbed water and reached saturation faster than that made from 37 wt% wood flour, which attained saturation more gradually (Table 4.5). The fact that higher wood flour filler content means higher ability to absorb water may have resulted in delayed equilibrium moisture content attainment for the treated and untreated composites. Increase in water absorption of untreated wood composites relative to the treated, is due to the hydrophilicity of wood, imparted by the free O-H groups in the wood structure which has a high tendency for hydrogen bonding with water (Fig 4.2, page 55). It has also been reported that the untreated wood has higher hemicellulose content [18] which is responsible for moisture absorption. Previous reports [166] revealed that the absorption of water by non polar polymers containing fillers depends mainly on the nature and the amount of the fillers. Furthermore, the amount of accessible O-H groups that can form hydrogen bonds with water molecules is another factor responsible for the degree of water absorption by composites. The higher the amount of the O-H groups, the higher is the initial rate as well as the level of water uptake, explaining the trend observed.

Effect of MAPE content

The effect of MAPE content on the water absorption behaviour of the composites is shown in Figure 4.51. Incorporation of MAPE reduced the initial and the equilibrium water absorption of the untreated and heat-treated WTC, with the heat-treated WTC showing lower values. Incorporation of 2% MAPE in 37 wt% untreated WTC reduced the equilibrium water absorption by 51%, while 6% and 10% MAPE resulted in a 52% decrease. On the other hand, 20 wt% untreated WTC presented a decrease in water absorption to the tune of 76% on loading 2% MAPE and 77% when 6% and 10% MAPE were added. This reduction has been attributed to the improved interfacial adhesion between the wood flour filler and the matrix by the action of MAPE, which prevent easy penetration of water molecules into the modified composites [170].

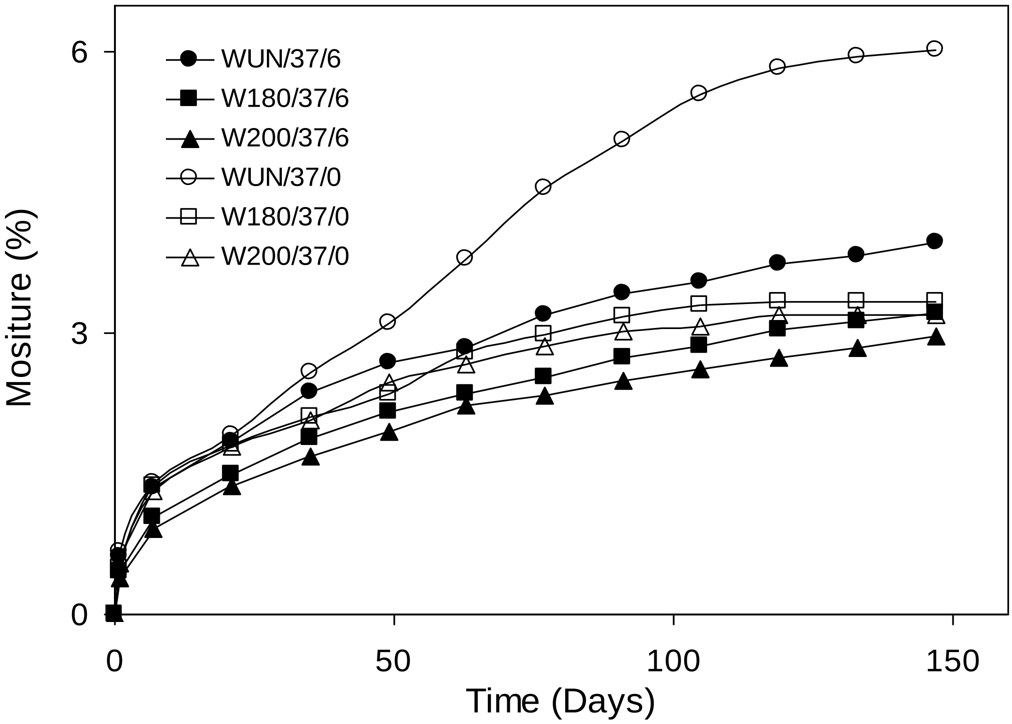


Figure 4.51: Water absorption of 37 wt% composites as a function of MAPE content and heat treatment

It can be seen from these results that for the untreated wood composite, a 2% MAPE content will achieve almost the same extent of moisture reduction as the 6% or the 10% MAPE level. The effect of MAPE on the water absorption of heat-treated WTC seems negligible as composites treated at 180°C and 200°C showed minimal decrease in equilibrium moisture. This finding is in line with recent reports [171]. The possibility of reduced number of surface O-H groups on heat-treated wood flour, with reduction in hydrophilicity, might have invalidated the use of MAPE in this category of composites. This confirms the findings from previous reports [148].

4.3.1.1 Kinetics of water absorption

Diffusion is the process through which matter is transferred from one part of a system to another as a result of random molecular movements. There are three different mechanisms through which moisture is absorbed into composites. The main process is the diffusion of water molecules into the microgaps between the polymer chains. Other prevalent mechanisms are movement of water molecules by capillary action into the gaps and flaws at the polymer-filler interface, due to incomplete wetting and the transport of water molecules by micro cracks formed during the extrusion process [172].

Generally, diffusion in glassy amorphous polymers can be classified by the relative mobility of the diffusing substance and the polymer chains. There are three categories of diffusion behaviour [173]: First case (case I), in which the rate of diffusion is significantly less than that of the polymer chain mobility. The equilibrium inside the polymer is readily reached and maintained with time. This is referred to as the Fickian diffusion. Second case (case II); the mobility of the diffusing substance is much higher than other relaxation processes within the polymer chain. In this case, there is the development of a boundary between the swollen outer part and the inner glassy core of the polymer. The boundary advances at a constant velocity and the core diminishes in size until an equilibrium concentration of the diffusing substance is reached in the whole polymer. Third, non-Fickian or anomalous diffusion, presents an intermediate property between cases I and II. It occurs when the mobility of the diffusing substance and the polymer chain relaxation are similar.

Theoretically, these three categories can be distinguished by the shape of the sorption curve represented by the equation,

$$\frac{M_t}{M_\infty} = k\,t^n \qquad (4.28)$$

where M_t is the moisture content of the specimen at time, *t*, M_∞ denotes the corresponding quantity after an infinite time while *n* and *k* are constants. The mechanism of water uptake and the values of the kinetic parameters *n* and *k* were obtained by adjusting the experimental values to Equation 4.28,

$$log\left(\frac{M_t}{M_\infty}\right) = log\left(k\right) + n\,log\left(t\right) \qquad (4.29)$$

The value of the coefficients *n* and *k* indicate the different behaviours of the three categories. For Fickian diffusion, $n = 0.5$, while for case II, $n > 1$. In the case of anomalous diffusion, *n* exhibits an intermediate value; $0.5 < n < 1$. The value of *k* gives an idea of the extent of interaction of moisture with the material.

4.3.1.2 Kinetic parameters, *n* and *k*

The values of *n* and *k* obtained from the fitting curves of the water absorption of heat-treated and untreated WTC is given in Table 4.5.

It can be seen that almost all the composites exhibited a deviation from the Fickian mode of diffusion as the values for *n* are either slightly lower or higher than 0.5. In general, *n* reduced with wood content and heat treatment. Values of *n* for composites filled with 20 wt% and 37 wt% untreated wood flour are 0.55 and 0.47 respectively. This trend was also observed in the heat-treated WTC although of a lower magnitude. Composites filled with 20 wt% untreated wood flour exhibited an anomalous non Fickian mode. The higher equilibrium moisture content (3.48%) at this composition relative to heat-treated counterparts with the same wood content may be due to voids which developed inside the material during processing. The water absorbed in the voids increased the water absorption pattern of the composite and resulted in the weight change profile being greater than the Fickian curve. This observation is in agreement with literature [78]. Deviations from Fickian behaviour has been considered to be associated with the finite rates at which the polymer structure may change in response to the sorption or desorption of penetrant molecules. Anomalous effects may be directly related to the influence of the changing polymer structure on solubility and diffusional mobility, or they may result from the internal stresses exerted by one part of the medium on another as diffusion proceeds [173]. Incorporation of 2% MAPE to 37 wt% untreated WTC reduced the values of *n* from 0.47 to 0.39 with no decrement on further addition of MAPE (6% and

10%). However, WTC made from wood flour heat-treated at 180°C exhibited no increase in *n* values with increasing MAPE content. On the contrary, an increase was observed as the MAPE content of WTC made from 200°C treated wood flour was increased.

The values of *k* increase with wood content in the treated and untreated WTC, indicating that as the wood content increased, the interaction of moisture with the material increased. This is expected because of the presence of O-H groups on the surface of the wood flour, which tended to attract water molecules. Strangely, *k* also increased with heat treatment. For instance, composites containing 37 wt% wood flour at different treatment temperatures, showed increment from 0.5 s^{-2} through 2.0 s^{-2} to 3.2 s^{-2} is obtained for composites containing untreated, 180°C and 200°C treated wood flour respectively. It was expected that with heat treatment of wood flour and the consequent reduction in hydrophilicity, *k* values should reduce as the treatment temperature was raised. This was not achieved in this investigation. It was possible that the presence of voids and cracks which was not captured in this study may have influenced the water absorption pattern of the composites. More so, the water absorption behaviour of the pure wood flour was not studied, hence it is difficult to state precisely what form the *k* values of the wood flour will take, vis-à-vis those of the composites. Similarly, *k* values increased with the incorporation of MAPE in the untreated WTC. Again, this result seemed odd since addition of MAPE should, in principle, lead to a reduction of the surface O-H groups of the wood flour and as a result, lower moisture interaction with the material. On the other hand, it was possible that with the esterification reaction between the O-H groups of the wood flour and the MAPE, carbonyl groups were formed. The carbonyl groups can as well interact with water molecules through hydrogen bonding. As a result, *k* values are raised with addition of MAPE [174]. On the contrary, adding MAPE to heat-treated WTC resulted in lower *k* values of the composites made from wood flour treated at 180°C and 200°C.

4.3.1.3 Diffusion coefficient

Diffusion coefficient, *D*, is the most important parameter of the Fick's model. It indicates the ability of solvent molecules to penetrate inside the composite structure [175]. It was evaluated using the following equations [173];

$$\frac{M_t}{M_\infty} = \frac{4}{h}\left(\frac{D_A}{\pi}\right)^{0.5} t^{0.5} \tag{4.30}$$

$$D_A = \frac{\pi}{16} h^2 \theta^2 \tag{4.31}$$

where θ is the slope of the linear portion of the plot of $\frac{M_t}{M_\infty}$ vs. $\sqrt{t}$, D_A is the apparent diffusion coefficient and *h* is the thickness of the specimen. The value of D_A obtained in Equation 4.31 does not account for the diffusion through the edges of the samples. A geometrical edge correction factor has been proposed to calculate the true diffusion coefficient D_T, taking into account moisture penetrating through the edges of the specimen using the following equation [176];

$$D_T = \frac{D_A}{\left[1 + \frac{h}{L} + \frac{h}{W}\right]^2} \tag{4.32}$$

where *L* and *W* are the length and width of the sample respectively.

Table 4.5 presents the apparent diffusion coefficient, D_A and true diffusion coefficient, D_T of treated and untreated wood composites. Untreated wood composites at 37 wt% filler loading showed lower values of D_T relative to the heat-treated ones. Since wood is hygroscopic, it is expected that a high diffusion coefficient in untreated wood composites is attained. However, wood by nature, possesses polar groups in its chemical structure. These represent a potential energy 'sink' that can attract and bind water molecules through hydrogen bonding. Consequently, hydrogen bonding becomes a limiting factor in the diffusion of water molecules into the wood particles and results in the immobilization of the diffusing species and contributes to delaying their transport [166]. Several authors have previously discussed this justification to be able to describe the behaviour of water molecules diffusing in polymer systems and attributed it to the structuralisation of water around the polar groups [78, 177, 178]. This may be responsible for the trend observed for untreated wood composites. It should be noted that it took the composite longer period (119 days) to attain equilibrium moisture saturation. On the other hand, D_T values observed for heat-treated wood composites were higher. On the contrary, this may mean that reduced O-H groups by heat treatment had resulted in decreased hydrogen bonding between water molecules and the wood polymers so that transport of water molecules within these composites was faster and might indicate higher diffusion rate and faster attainment of equilibrium (105 days, Fig 4.50, page 138). This trend is in line with earlier reports [78, 169]. Incorporation of MAPE had no significant effect on D_T.

4.3.1.4 Thickness swelling behaviour

The thickness swelling of the composites was evaluated using the following equation:

$$T_t = \frac{T_2 - T_1}{T_1} \times 100\ (\%) \qquad (4.33)$$

where T_1 and T_2 are the thickness of the dry samples and the thickness after time t of immersion in water, respectively. A plot of the percentage increase in thickness against time for the different treatment temperatures and wood flour loadings is presented in Figure 4.52. The thickness swelling of the composites increased with time of immersion until a point of equilibrium was reached when the thickness remained constant. From Figure 4.60, it can be seen that composites with higher wood content exhibited higher thickness swelling values. Wood flour is hygroscopic in nature and swells when immersed in water. The swelling of individual particle contributes to the overall swelling of the composites.

Table 4.5: Water absorption data of composites

Sample	Equilibrium moisture (%)	n	k (x 10^{-3} s^{-2})	D_A (x 10^{-9} $cm^2.s^{-1}$)	D_T (x10^{-10} cm^2s^{-1})
LDPE/$W_{UN/20/0}$	3.48	0.55	0.15	7.56	4.30
LDPE/$W_{UN/20/2}$	1.97	0.42	1.20	7.56	4.36
LDPE/$W_{UN/20/6}$	1.96	0.42	1.10	7.47	4.34
LDPE/$W_{UN/20/10}$	1.96	0.42	1.00	7.47	4.34
LDPE/$W_{UN/37/0}$	6.02	0.47	0.50	3.36	1.97
LDPE/$W_{UN/37/2}$	3.98	0.39	1.27	3.34	1.95
LDPE/$W_{UN/37/6}$	3.96	0.39	1.38	7.52	4.26
LDPE/$W_{UN/37/10}$	3.96	0.36	2.90	7.47	4.46
LDPE/$W_{180/20/0}$	1.82	0.41	1.50	7.56	4.39
LDPE/$W_{180/20/2}$	1.82	0.42	1.20	7.52	4.42
LDPE/$W_{180/20/6}$	1.82	0.43	1.00	7.47	4.30
LDPE/$W_{180/20/10}$	1.83	0.44	0.80	7.47	4.46
LDPE/$W_{180/37/0}$	3.34	0.39	2.00	7.56	4.43
LDPE/$W_{180/37/2}$	3.32	0.39	1.80	7.56	4.39
LDPE/$W_{180/37/6}$	3.22	0.40	1.60	7.47	4.26
LDPE/$W_{180/37/10}$	3.29	0.40	1.50	7.47	4.42
LDPE/$W_{200/20/0}$	1.79	0.43	1.00	7.56	4.35
LDPE/$W_{200/20/2}$	1.81	0.44	0.80	7.52	4.34
LDPE/$W_{200/20/6}$	1.67	0.44	0.80	7.42	4.33
LDPE/$W_{200/20/10}$	1.66	0.44	0.70	7.47	4.34
LDPE/$W_{200/37/0}$	3.20	0.36	3.20	7.61	4.36
LDPE/$W_{200/37/2}$	3.08	0.38	2.20	7.52	4.34
LDPE/$W_{200/37/6}$	2.97	0.40	1.40	7.47	4.42
LDPE/$W_{200/37/10}$	2.89	0.44	0.70	7.47	4.30

Thus, it is expected that the higher the wood content, the higher is the thickness swelling. In addition, thickness swelling depends on water absorption, with the composites having the highest moisture content, swelling the most.

Heat treatment temperatures also had a significant effect on the thickness swelling of the composites (Figure 4.52). A reduction in thickness swelling up to 18% and 31% were observed with composites made of wood flour heat-treated at 180°C and 200°C respectively, relative to the untreated WTC. Decrease in the hygroscopic character of the wood flour and the resultant improvement in interfacial adhesion [74] could be responsible for this trend.

The effect of MAPE content on the thickness swelling of the composites is presented in Figure 4.53. From the Figure, it can be seen that incorporation of MAPE decreased the thickness swelling of the composites, with the composites containing untreated wood flour and wood flour treated at 180°C showing higher influence of MAPE than those made from 200°C treated wood flour. It has been reported [179] that adding coupling agents to WTC has a positive effect on the dimensional stability of the composites arising from improved interfacial bonding between the hydrophilic wood particles and the hydrophobic polymer matrix. The thickness swelling of WTC made from 200°C treated wood flour was lowest even without the addition of MAPE. Incorporation of MAPE had no noticeable effect on the thickness swelling of this category of composite. These results demonstrated that treating wood flour at 200°C was more efficient in checking the thickness swelling of WTC than addition of coupling agents. This findings agree with the work of Kaboorani and Englund [171].

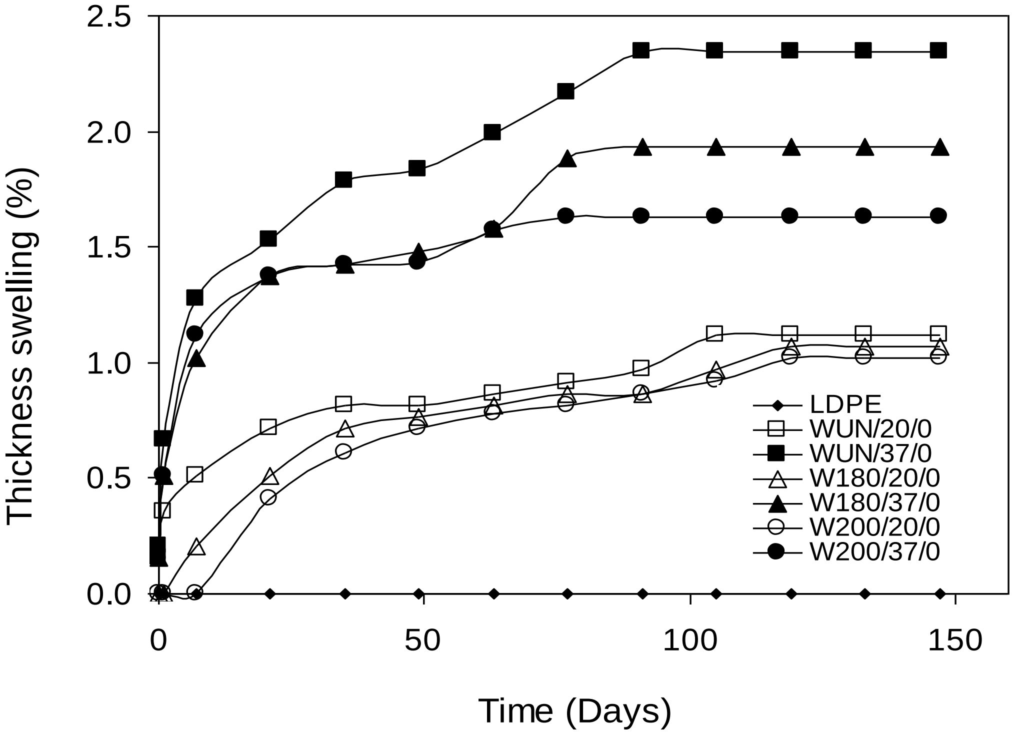


Figure 4.52: Variation of thickness swelling of neat LDPE and different filler loadings of untreated and heat-treated composites with time

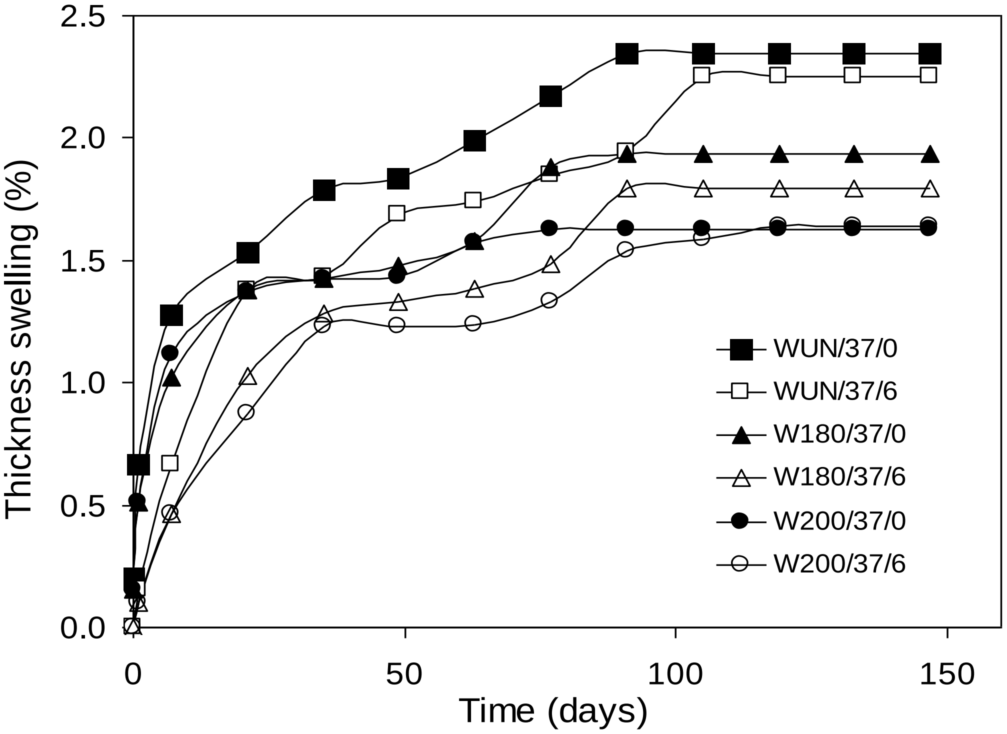


Figure 4.53: Thickness swelling of compatibilised and uncompatibilised composites made from 37 wt% untreated and heat-treated wood flour as a function time

4.3.1.5 Thermal properties

Thermogravimetric analysis, TGA

Thermograms showing the thermal stability of 37 wt% dry as-moulded and moisture saturated composites made from treated and untreated wood flour are presented in Figure 4.54. Data extracted from these thermograms are presented in Table 4.6. The neat LDPE exhibited no changes in thermal properties after long time immersion in water. T_p, T_{onset} and $T_{50\%}$ values remained relatively the same (compare Table 4.2, page 57 and Table 4.6). This is an indication that water absorption had no effect on the thermal stability of LDPE. Furthermore, composites made from untreated wood flour showed no appreciable change in thermal behaviour following long term immersion in water as the curves of wet and dry as-moulded samples overlapped (Figure 4.54). A peak at around 100°C indicated the amounts of water absorbed in the composites. Delta Y values of 4.97%, 3.34% and 3.17% were obtained for 37 wt% composites made from untreated, 180°C and 200°C treated wood flour respectively (Appendix A1). These values are similar to those presented in Table 4.6. Values of T_p, T_{onset} and $T_{50\%}$ of dry as-moulded and moisture saturated composites containing 37 wt% wood flour are similar (Tables 4.2, page 57 and 4.6). This indicated that moisture had no significant effect on the thermal stability of the composites. Generally, composites made from heat-treated wood flour showed a marginal increase in T_p values following moisture saturation, relative to the dry as-moulded samples. Incorporation of MAPE at 2% level showed the same trend displayed by the heat-treated WTC. However, no consistent trend could be established when higher levels of MAPE were used.

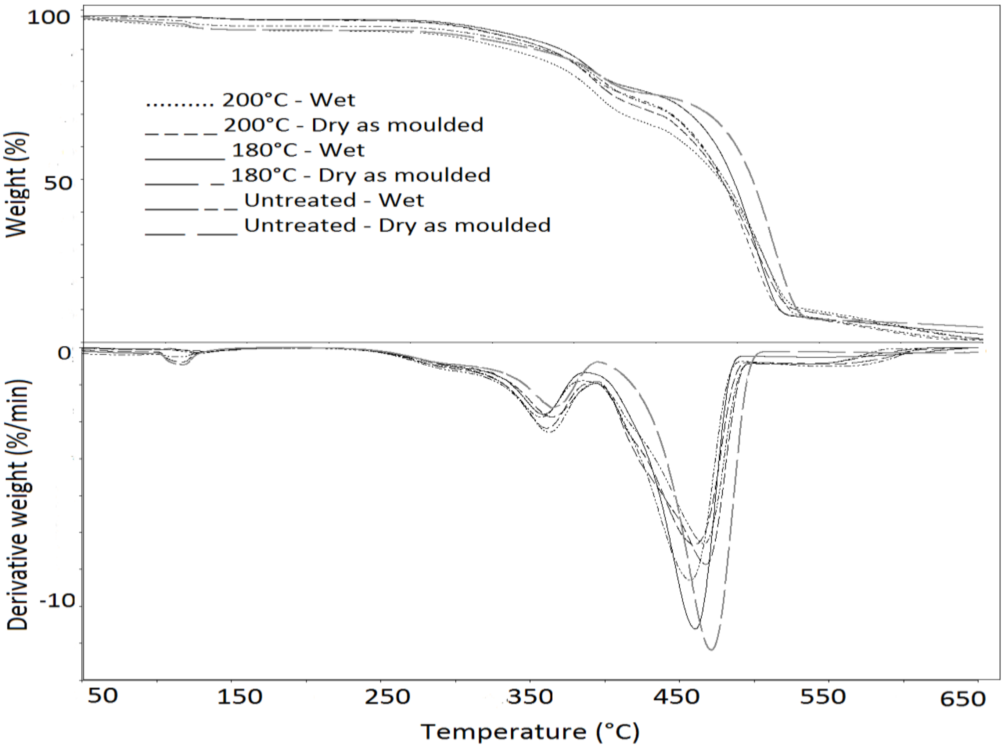


Figure 4.54: TGA thermograms of dry as-moulded and wet composites made from 37 wt% untreated and heat-treated wood flour

Table 4.6: TGA data of moisture saturated samples

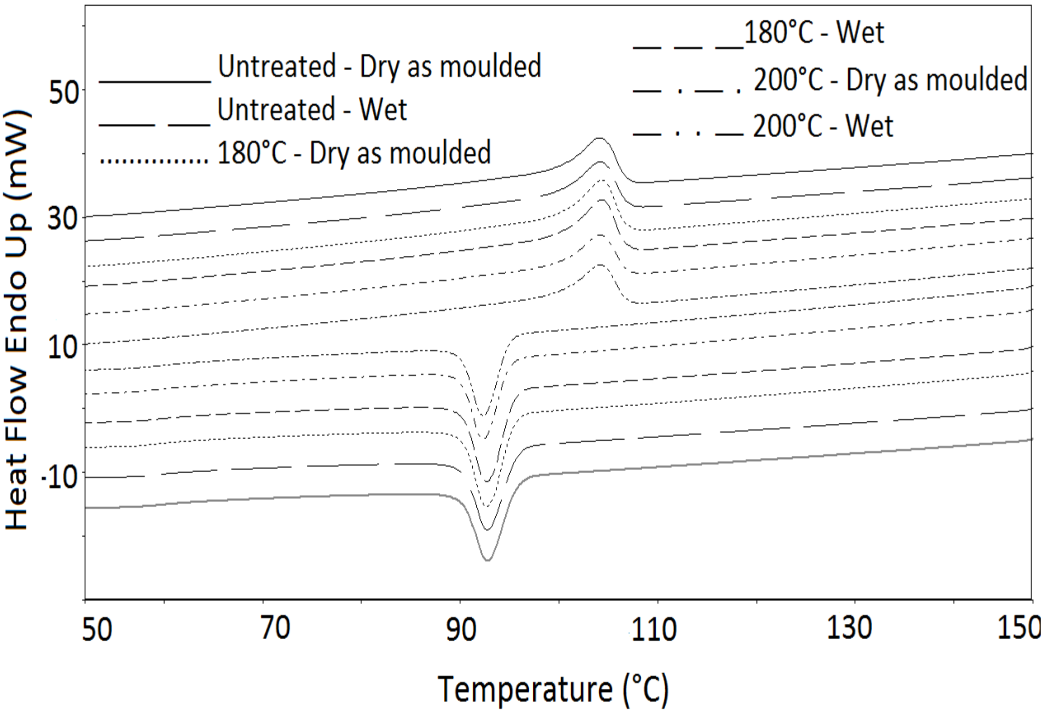
Sample	Wood treatment temperature (°C)	T_p (°C)	Onset temperature, T_{onset} (°C)	$T_{50\%}$ (°C)	Degradation temperature (°C)
LDPE	-	461.7	434.6	454.7	390.0-513.2
LDPE/$W_{UN/20/0}$	-	467.7	424.4	455.8	259.5-504.0
LDPE/$W_{180/20/0}$	180.0	459.6	399.8	438.2	225.2-493.7
LDPE/$W_{200/20/0}$	200.0	463.5	407.6	446.1	242.4-497.7
LDPE/$W_{UN/37/0}$	-	467.9	393.2	441.5	340.4-499.2
LDPE/$W_{180/37/0}$	180.0	471.9	428.9	458.6	236.1-507.5
LDPE/$W_{200/37/0}$	200.0	466.2	393.6	438.9	239.4-499.1
LDPE/$W_{UN/20/2}$	-	461.9	438.0	458.0	350.0-501.5
LDPE/$W_{180/20/2}$	180.0	455.7	398.9	441.0	226.1-497.8
LDPE/$W_{200/20/2}$	200.0	467.1	423.1	452.0	236.8-498.6
LDPE/$W_{UN/37/2}$	-	467.0	410.7	446.7	235.2-499.4
LDPE/$W_{180/37/2}$	180.0	465.7	373.0	427.6	216.8-496.1
LDPE/$W_{200/37/2}$	200.0	469.5	376.2	433.1	228.2-500.2
LDPE/$W_{UN/20/6}$	-	466.3	406.9	445.9	249.3-498.9
LDPE/$W_{180/20/6}$	180.0	465.7	429.9	454.9	245.4-499.4
LDPE/$W_{200/20/6}$	200.0	465.8	396.3	437.7	259.9-495.8
LDPE/$W_{UN/37/6}$	-	469.5	392.0	437.8	232.9-499.4
LDPE/$W_{180/37/6}$	180.0	463.4	395.9	439.8	233.7-498.4
LDPE/$W_{200/37/6}$	200.0	470.4	397.0	441.0	222.9-501.0
LDPE/$W_{UN/20/10}$	-	463.2	407.4	444.7	237.0-498.8
LDPE/$W_{180/20/10}$	180.0	462.5	419.0	444.1	347.3-498.2
LDPE/$W_{200/20/10}$	200.0	465.1	426.2	454.9	257.5-500.7
LDPE/$W_{UN/37/10}$	-	468.5	371.4	429.5	222.2-501.1
LDPE/$W_{180/37/10}$	180.0	465.3	386.8	434.8	229.3-499.5
LDPE/$W_{200/37/10}$	200.0	468.2	402.3	447.3	230.0-504.2

Differential Scanning Calorimetry

The effect of water immersion on the melting and crystallisation behaviours of uncoupled 37 wt% composites made from untreated and heat-treated wood flour and that with 6% MAPE content are shown in Figures 4.55. Data extracted from these and curves of 20 wt% composites are presented in Table 4.7. The T_m and T_c of neat LDPE remained relatively unchanged after long time immersion in water (Table 4.7). The fact that LDPE has very low affinity for water may be responsible for this trend. Also, moisture seemed to have had no observable effect on the T_m and T_c of the composites (compare Table 4.3, page 71 with Table 4.7). Values obtained were similar with those of the dry as-moulded samples. Furthermore, a trend in T_c, T_m and $-\Delta H_c$ could not be established with respect to filler loading and heat treatment. Comparing the effect of MAPE content on the dry as-moulded and moisture saturated samples, again, a clear behaviour could not be seen as coupled and uncoupled composites displayed quite similar trend.

Though the degree of crystallinity of LDPE remained the same before and after water immersion, a closer look at the values for the composites revealed a slight variation upon moisture saturation (Table 4.7). While X_c in wet composites containing 20 wt% untreated wood flour was relatively the same as its dry as-moulded counterparts, a decrement in X_c to the tune of 36% was observed in the 37 wt% untreated WTC. Moisture tended to have weakened the interfacial bond between the wood flour particles and the LDPE matrix, affecting the internal molecular arrangement of the composites. In addition, the interaction of water with the surface O-H groups of the untreated wood could inhibit the nucleating ability of wood, leading to reduced X_c. On the contrary, WTC made from heat-treated wood flour showed various levels of increase in X_c following moisture saturation, with composites containing 37 wt% wood flour treated at 200°C showing an increment in X_c of 6.6% in the dry as-moulded to 15.2% in the wet samples. Reduction in the surface O-H groups of heat-treated wood flour may mean reduced interaction with moisture, thereby resisting the deteriorative effect of moisture on the interface, with a positive influence on X_c. Table 4.7 reveals that with the addition of MAPE, X_c reduced generally in untreated WTC more than the heat-treated composites. Although the rate of decrement was higher at lower MAPE content, wet composites made from wood flour treated at 200°C maintained X_c at all MAPE levels.

a)



b)

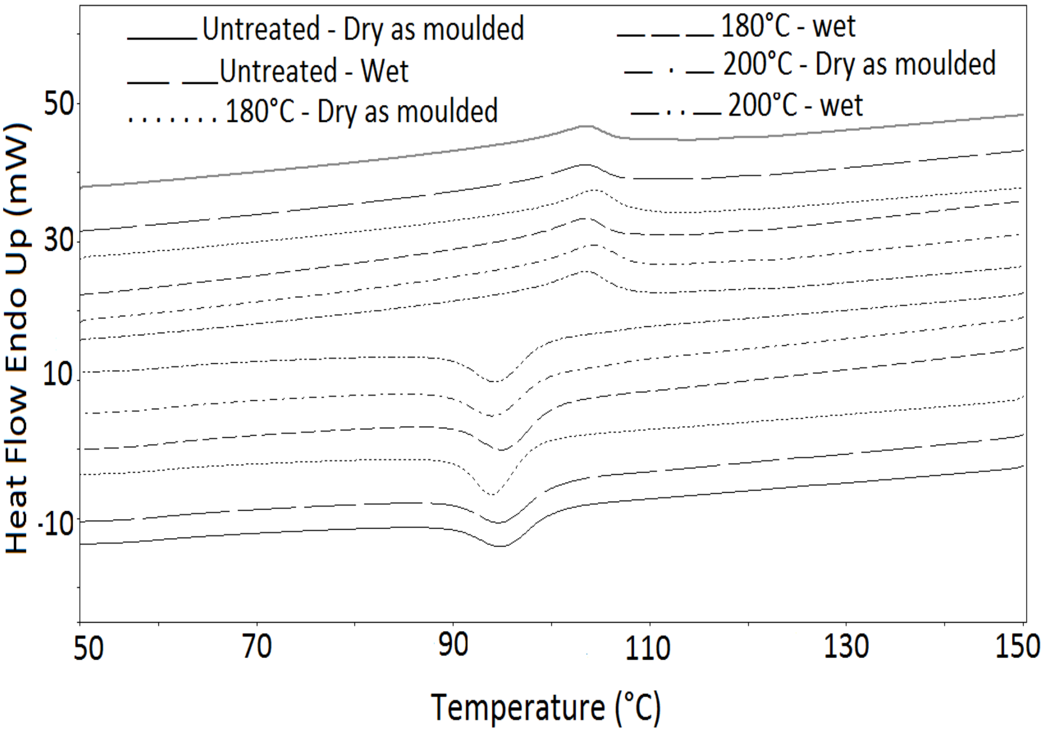


Figure 4.55: DSC thermograms of 37 wt% dry as-moulded and moisture saturated composites a): containing 0% and b): 6% MAPE

Table 4.7: DSC data of moisture saturated samples

Sample	Wood treatment temperature (°C)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	$-\Delta H_c$ (J/g)	X_c (%)
LDPE	-	104.1	90.9	43.5	59.0	14.8
LDPE/$W_{UN/20/0}$	-	104.4	92.0	52.2	55.6	22.3
LDPE/$W_{180/20/0}$	180.0	103.7	92.6	53.5	52.7	22.8
LDPE/$W_{200/20/0}$	200.0	103.9	91.8	49.8	42.6	21.2
LDPE/$W_{UN/37/0}$	-	104.0	92.6	41.7	34.4	22.6
LDPE/$W_{180/37/0}$	180.0	103.7	92.6	38.2	50.6	20.7
LDPE/$W_{200/37/0}$	200.0	103.7	92.0	28.1	46.3	15.2
LDPE/$W_{UN/20/2}$	-	103.9	94.0	32.5	41.1	13.9
LDPE/$W_{180/20/2}$	180.0	104.1	94.0	32.1	37.7	13.7
LDPE/$W_{200/20/2}$	200.0	104.9	93.6	29.9	36.6	12.8
LDPE/$W_{UN/37/2}$	-	103.6	94.0	28.7	30.5	15.5
LDPE/$W_{180/37/2}$	180.0	104.0	93.8	23.5	33.6	12.7
LDPE/$W_{200/37/2}$	200.0	104.3	93.6	26.9	33.4	14.6
LDPE/$W_{UN/20/6}$	-	101.4	95.0	21.9	37.6	9.3
LDPE/$W_{180/20/6}$	180.0	103.6	94.8	24.8	41.8	10.6
LDPE/$W_{200/20/6}$	200.0	103.2	95.4	20.3	36.6	8.7
LDPE/$W_{UN/37/6}$	-	103.3	94.8	17.3	31.8	9.4
LDPE/$W_{180/37/6}$	180.0	103.2	95.1	26.9	31.3	14.6
LDPE/$W_{200/37/6}$	200.0	103.4	94.4	21.7	28.0	11.8
LDPE/$W_{UN/20/10}$	-	103.1	94.5	21.0	34.6	9.0
LDPE/$W_{180/20/10}$	180.0	102.9	94.6	20.0	38.3	8.5
LDPE/$W_{200/20/10}$	200.0	102.6	94.4	25.9	34.3	11.0
LDPE/$W_{UN/37/10}$	-	102.6	94.6	14.1	30.7	7.6
LDPE/$W_{180/37/10}$	180.0	102.9	94.8	16.0	34.0	8.7
LDPE/$W_{200/37/10}$	200.0	102.8	94.7	18.0	33.0	9.8

4.3.1.6 Dynamic mechanical properties

Storage modulus

The E' curves of dry as-moulded and moisture saturated composites containing 37 wt% untreated and heat-treated wood flour without MAPE are presented in Figure 4.56a. Data extracted from these curves and those of 20 wt% samples are given in Table 4.8. The $E'_{-100°C}$ value of dry as-moulded LDPE was higher than the wet sample. It is expected that the magnitude of $E'_{-100°C}$ of the dry as-moulded and moisture saturated LDPE should be similar, since LDPE is not expected to absorb water, but this is not the case. No concrete reason could be given for this observation. However, the $E'_{25°C}$ values were similar. $E'_{-100°C}$ values of composites containing 20 wt% untreated and wood flour treated at 200°C did not show an appreciable decrement. Composites made from 180°C treated wood flour displayed a rather strange behaviour, with an increase in E' value upon water absorption (Table 4.8). This trend was also observed for the $E'_{25°C}$ values. This development could not be explained in light of the trend established for the untreated WTC and those made from 200°C treated wood flour. The $E'_{-100°C}$ values in the 37 wt% composites fell with moisture absorption (Table 4.8). A decrement to the tune of 15% and 16% were observed for composites made from untreated wood flour and wood flour treated at180°C. Weakening of the interfacial bond between the wood particles and the LDPE could be responsible for this tendency. This must have reduced the stress carrying capacity of the composites. In addition, water acts as a plasticiser, which softens the composites system, leading to reduced modulus [180]. However, $E'_{-100°C}$ values of composites containing 200°C treated wood flour showed a marginal 4% decrease. Reduced hydrophilicity of the 200°C treated wood flour must have lowered the effect of moisture on the interfacial degradation for this category of composite.

Incorporation of MAPE helped to retain the E' of the composites after water immersion (Table 4.8). From Figure 4.56b, although their coupled untreated WTC maintained a relatively higher E' values than the heat-treated counterparts, E' values were not appreciably changed with water immersion. This trend was observed in the $E'_{25°\mathrm{C}}$ and $E'_{-100°\mathrm{C}}$ in all the composites studied.

Loss modulus

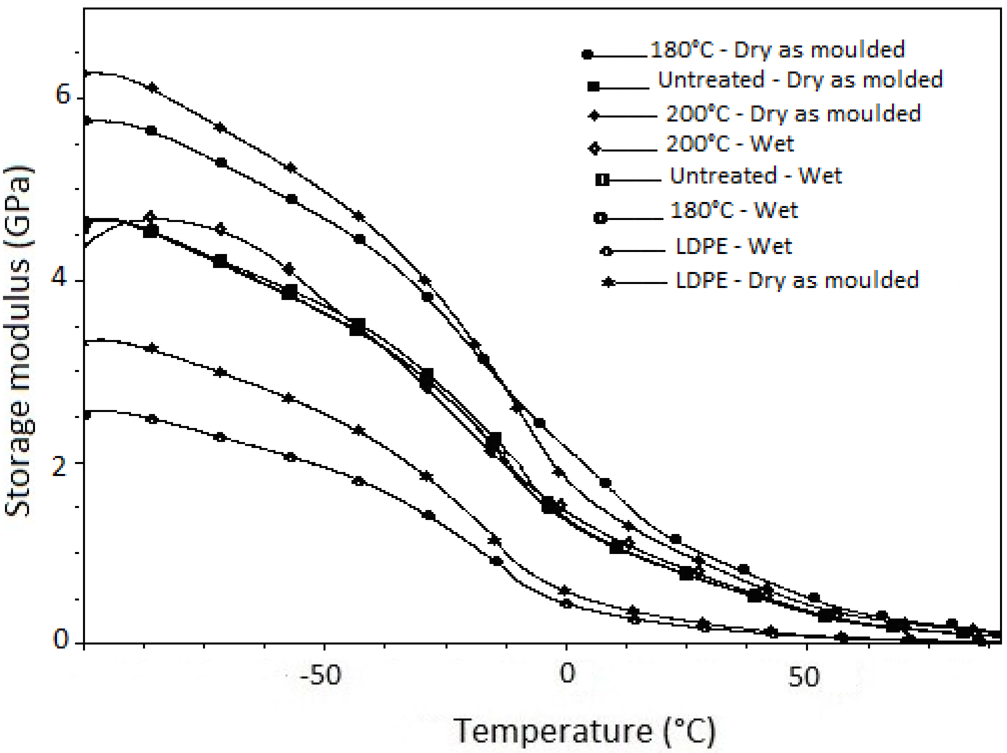
The E" of dry as-moulded and moisture saturated LDPE and 37 wt% composites without MAPE are presented in Figure 4.57a. A summary of extracted data from these curves are given in Table 4.8. For the neat LDPE, values of $T_{\beta}^{E'}$ shifted to higher temperatures upon moisture saturation, while E''_{max} and $E''_{25°\mathrm{C}}$ values were lower than the dry as-moulded samples (compare Table 4.4, page 80 with Table 4.8). Again, this is rather strange as neat LDPE did not show any sign of water absorption (Figure 4.50, page 138). However, $T_{\beta}^{E'}$ of the composites remained the same for 20 wt% and 37 wt% filler loadings in untreated and heat-treated WTC. In addition, E''_{max} values of the wet composites were lower than those of the dry as-moulded samples at all filler loadings and treatment temperatures. Once more, interfacial degradation due to moisture absorption could be responsible for this. Furthermore, reduction in E''_{max} values was more severe in untreated WTC than the heat-treated samples. 30% and 31% decrements in E''_{max} were observed in the 20 wt% and 37 wt% untreated WTC respectively, whereas, composites containing heat-treated wood flour showed a decreases to the tune of 5% and 6% for 20 wt% and 37 wt% WTC respectively. Better compatibility arising from reduced hydrophilicity of heat-treated WTC may be responsible for this observation. Generally, $E''_{25°C}$ values did not show any particular trend with wood content and treatment temperature. In general, $T_{\beta}^{E'}$ of coupled composites shifted to lower temperatures with water immersion. Values dropped in the range from -16°C in the dry as-moulded to -25°C in the wet WTC were observed for the untreated and heat-treated WTC (Figure 4.57b and Table 4.8). Apart from this, $E''_{25°C}$ and $E''_{\max}$ values presented no identifiable trend. It has been suggested that plasticisation can lower $T_{\beta}^{E'}$ by introducing free volume to the system. The explanation is that water acts to break intermolecular hydrogen bonds present in the material, thus allowing greater chain mobility and also more efficient packing, resulting in a decrease in $T_{\beta}^{E'}$ [181].

Tan delta

Tan delta curves of the dry as-moulded and wet LDPE and composites are given in Figure 4.58. Extracted data from these curves are also presented in Table 4.8. Although most of the curves overlap, a clearer view of the behaviour can be seen in the table. Values of $\tan\delta_{\max}$, $W_{\sqrt{2}}$ and $\tan\delta_{25°C}$ of the LDPE were more or less the same in the dry as-moulded and wet samples. However, a decrease was observed in the temperature at $\tan\delta_{\max}$ from 39°C in the dry sample to 29°C in the moisture saturated LDPE. Again, no explanation could be given for this trend because LDPE was not expected to absorb moisture. A closer look at the transitions in the composites revealed that $\tan\delta_{\max}$ values were basically the same in all the composites studied, indicating that moisture had no effect on the $\tan\delta$. Similarly, the temperature at $\tan\delta_{\max}$ was also essentially the same in most of the samples except in composites containing 37 wt% untreated wood flour without MAPE, where an increase was seen from 44°C in the dry as-moulded to 50°C in the wet composites (Compare Table 4.4, page 80 with Table

4.8). It is possible that interfacial degradation for this category of composites may be more severe than the rest, resulting in higher temperature at $\tan\delta_{\max}$. Furthermore, $\tan\delta_{25°\mathrm{C}}$ was also basically unaffected with water immersion in all the composites. However, there is a general increase in $W_{\sqrt{2}}$ upon moisture saturation. This may mean that the absorption of water by the composites at various levels have increased the damping characteristics of the system, thus leading to increased $W_{\sqrt{2}}$. Additionally, a clear trend in $W_{\sqrt{2}}$ with respect to the effect of heat treatment and MAPE content could not be established (Figure 4.58b).

a)



b)

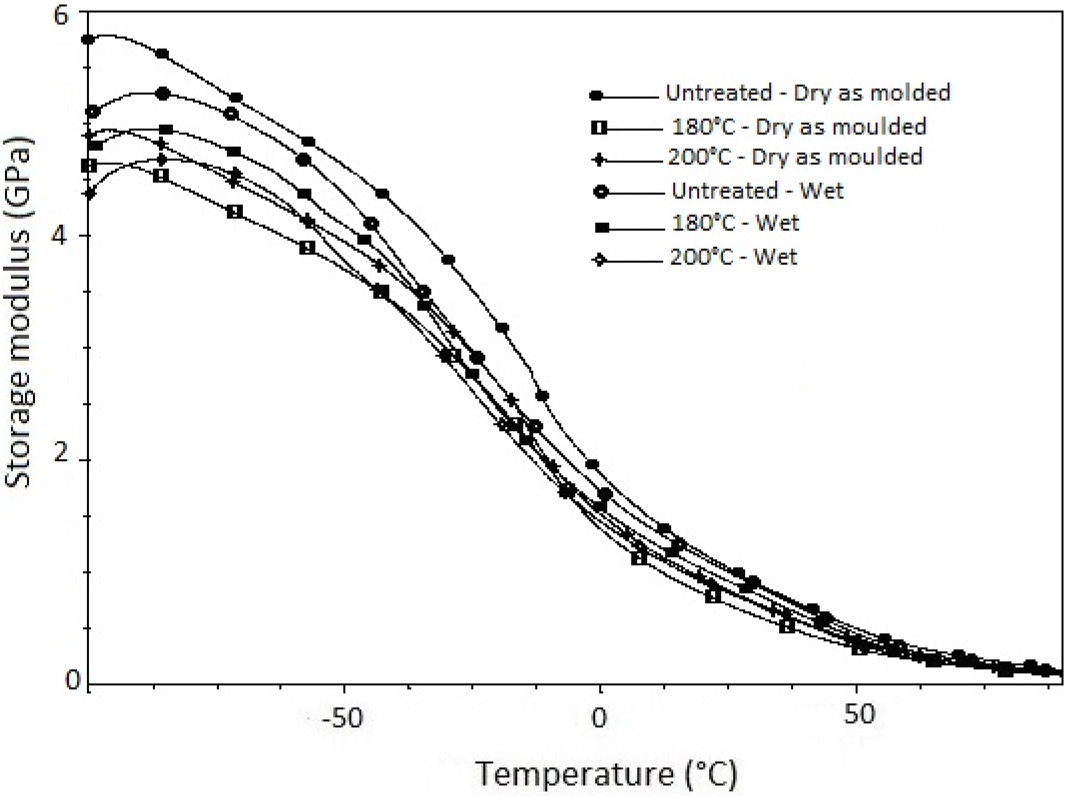
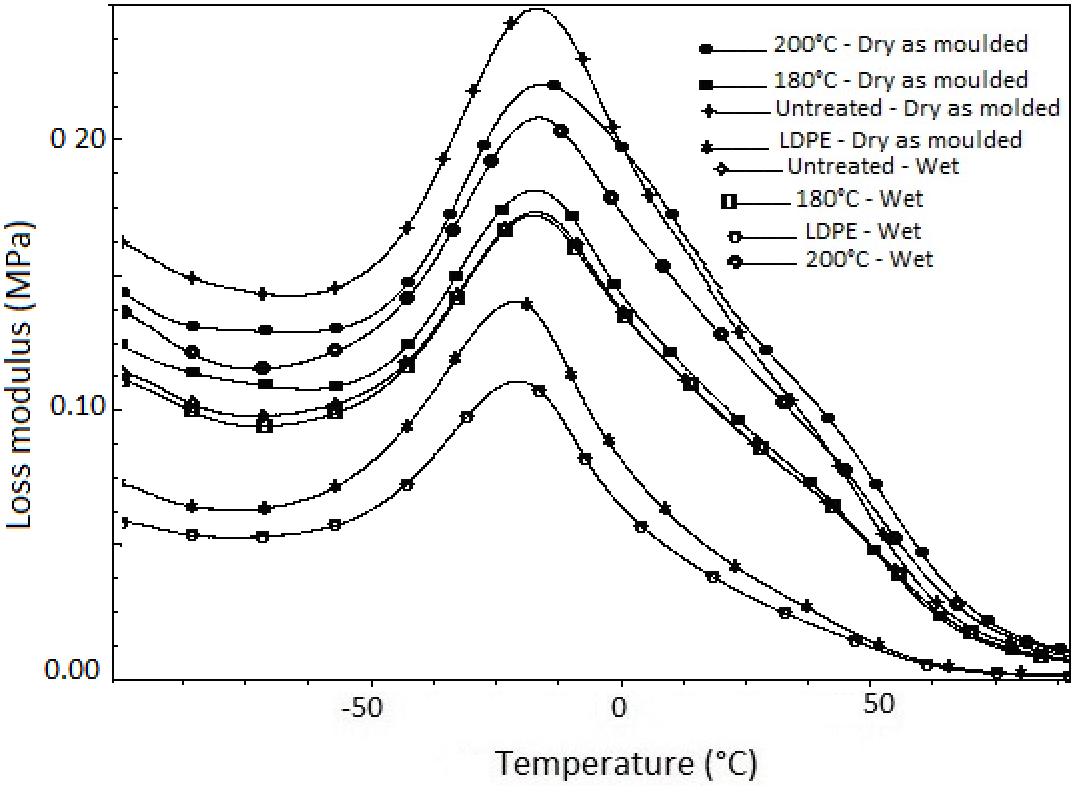


Figure 4.56: Storage modulus curves of LDPE and 37 wt% dry as-moulded and moisture saturated composites containing: a) 0% and b) 6% MAPE

a)



b)

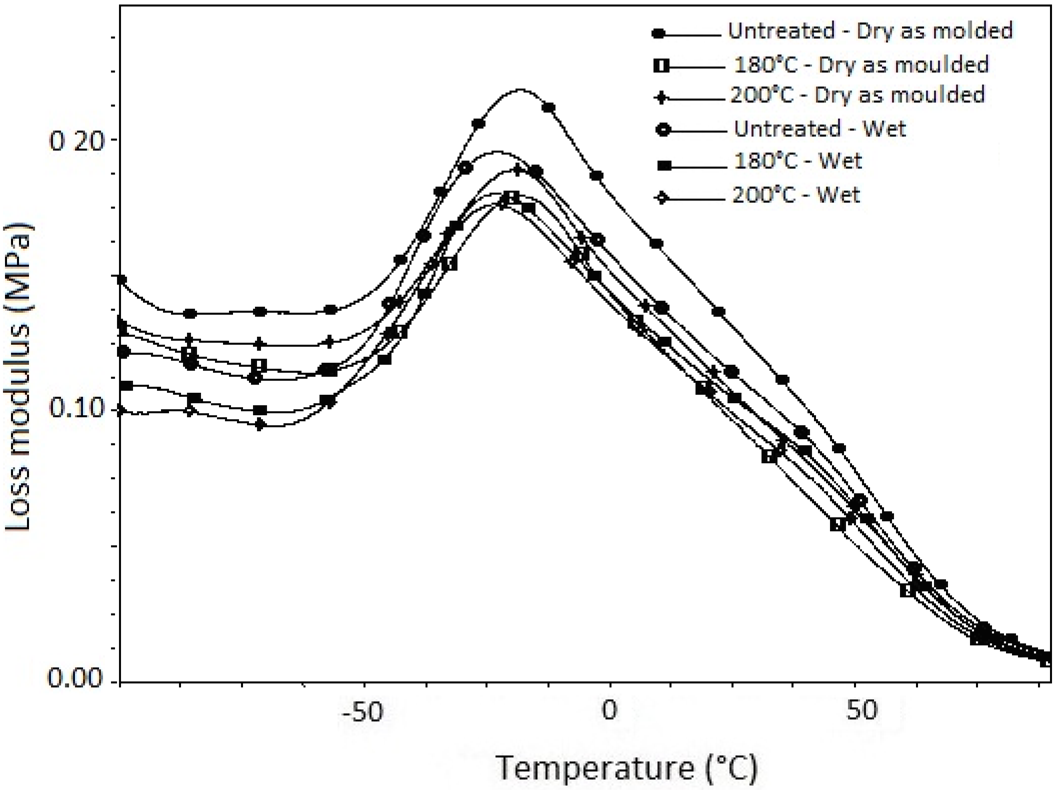
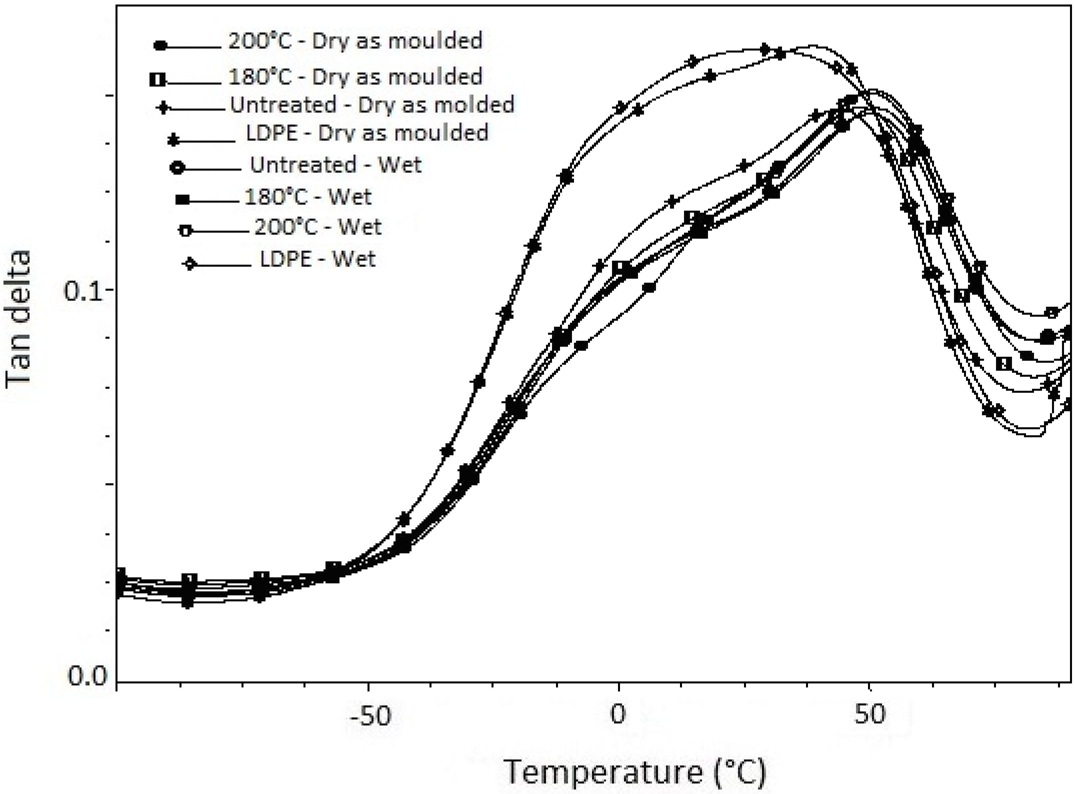


Figure 4.57: Loss modulus curves of LDPE and 37 wt% dry as-moulded and moisture saturated composites containing: a) 0% and b) 6% MAPE

a)



b)

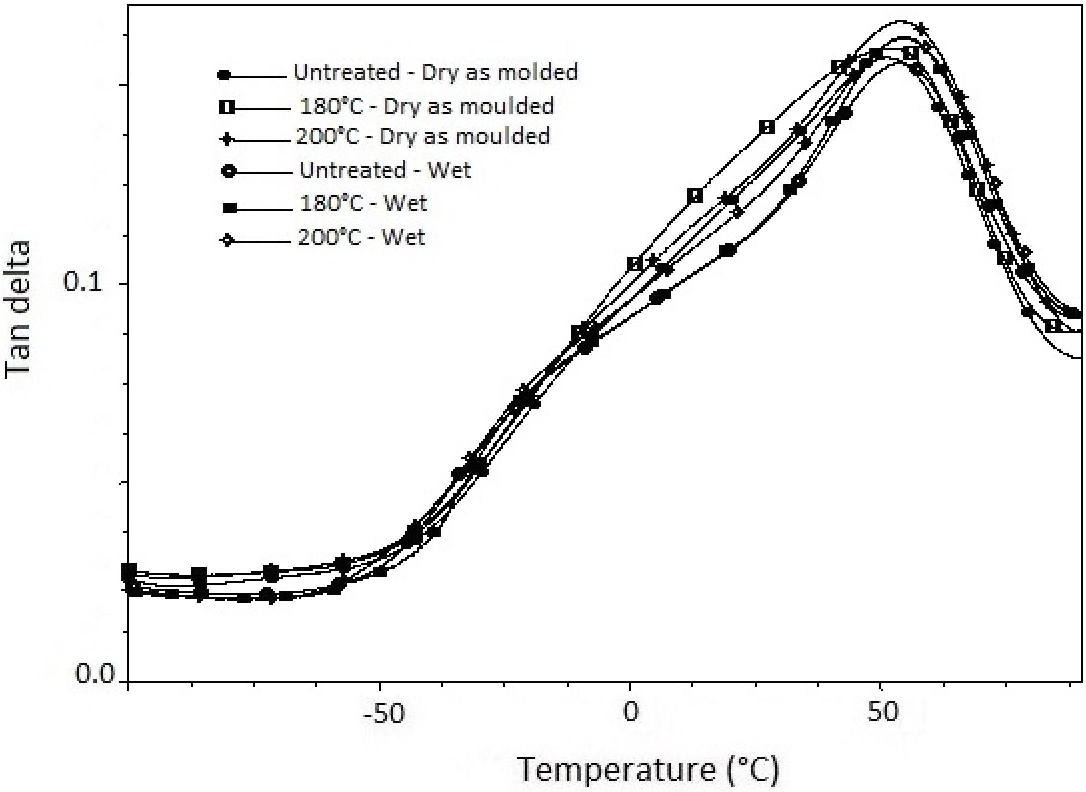


Figure 4.58: Tan delta curves of dry as-moulded and moisture saturated LDPE and 37 wt% composites containing: a) 0% and b) 6% MAPE

Table 4.8: DMA data of moisture saturated samples

Sample	Wood treatment temperature (°C)	$Tan\delta$				Storage modulus E'		Loss modulus E"		
		$Tan\delta_{max}$	Temperature at $tan\ \delta$ (℃)	$W_{\sqrt{2}}$	$Tan\delta_{25°C}$	$E'_{25°C}$ (GPa)	$E'_{-100°C}$ (GPa)	$E''_{25°C}$ (MPa)	$T_{\beta}^{E''}$ (℃)	E''_{max} (MPa)
LDPE	-	0.16	29.2	76.9	0.16	0.20	2.6	31.0	-20.1	110.0
LDPE/$W_{UN/20/0}$	-	0.15	47.8	76.9	0.13	0.44	3.6	59.0	-19.1	140.0
LDPE/$W_{180/20/0}$	180.0	0.15	48.7	70.8	0.13	0.64	4.5	85.0	-18.7	170.0
LDPE/$W_{200/20/0}$	200.0	0.15	48.3	70.4	0.13	0.52	3.9	68.0	-18.1	150.0
LDPE/$W_{UN/37/0}$	-	0.14	50.3	72.2	0.12	0.75	4.5	90.0	-17.1	170.0
LDPE/$W_{180/37/0}$	180.0	0.14	51.6	68.0	0.12	0.77	4.7	90.0	-18.0	170.0
LDPE/$W_{200/37/0}$	200.0	0.15	50.3	66.2	0.12	0.96	5.5	117.0	-16.4	210.0
LDPE/$W_{UN/20/2}$	-	0.15	47.0	70.9	0.13	0.46	3.2	62.0	-24.5	140.0
LDPE/$W_{180/20/2}$	180.0	0.16	50.3	62.6	0.13	0.60	4.2	80.0	-18.8	161.0
LDPE/$W_{200/20/2}$	200.0	0.16	50.5	68.0	0.13	0.52	3.7	69.0	-22.4	160.0
LDPE/$W_{UN/37/2}$	-	0.15	51.8	63.2	0.12	0.80	4.4	94.0	-23.9	180.0
LDPE/$W_{180/37/2}$	180.0	0.15	51.2	64.2	0.13	0.95	5.1	119.0	-22.3	200.0
LDPE/$W_{200/37/2}$	200.0	0.15	51.3	59.8	0.12	1.00	5.0	123.0	-21.0	210.0
LDPE/$W_{UN/37/6}$	-	0.16	53.8	53.7	0.11	1.00	5.0	114.0	-22.5	200.0
LDPE/$W_{180/37/6}$	180.0	0.16	54.6	50.4	0.11	0.91	4.8	105.0	-23.0	180.0
LDPE/$W_{200/37/6}$	200.0	0.16	54.3	57.3	0.12	0.81	4.4	99.0	-23.6	180.0
LDPE/$W_{UN/37/10}$	-	0.16	56.4	58.1	0.12	1.03	5.2	124.0	-24.1	200.0
LDPE/$W_{180/37/10}$	180.0	0.17	57.4	53.5	0.12	0.81	4.2	95.0	-24.5	170.0
LDPE/$W_{200/37/10}$	200.0	0.17	56.6	63.0	0.13	0.74	4.2	95.0	-24.5	170.0

4.3.1.7 Mechanical properties

Apart from their susceptibility to moisture, another very important concern in the use of natural filler as reinforcement in WTC is the negative effects that moisture has on the physical and mechanical properties. Reports [157, 182] have shown that mechanical properties of WTC deteriorated with water absorption. It is, therefore, necessary that this problem is tackled so that natural fillers can be seen as a viable reinforcement material in WTC. In this section, the mechanical properties of moisture-saturated specimens were evaluated in order to determine the effects of heat treatment of wood flour and MAPE content on the mechanical properties of water soaked WTC.

Tensile properties

Tensile modulus

There is no appreciable decrease in the tensile modulus of the neat LDPE upon immersion in water. Tensile modulus values of 0.231 GPa and 0.228 GPa are obtained for the dry as-moulded and wet LDPE, respectively. This is expected because neat LDPE did not absorb moisture (Figure 4.50, page 138). Therefore, retention of tensile modulus after immersion in water is in order. Figure 4.59 shows the tensile modulus of dry and wet specimens at equilibrium moisture content. Tensile modulus of the composites decreased generally with water immersion. The relative extent of decrease is greater in untreated wood composites when compared to the heat-treated composites. 38% and 19% decreases were observed in wet untreated WTC containing 20 wt% and 37 wt% fillers respectively when compared to the dry as-moulded WTC. The effects of water molecules interacting with the wood at the composites interface due to the inherent incompatibility between the polar wood and the non polar matrix (Figure 4.19, page 94) may be responsible for this observation. As a result of the hydrophilic nature of wood, when WTC is exposed to water, the wood particles take up water, resulting in the swelling of the wood cell wall, leading to changes in the dimensional stability of the composites and consequently, reduced mechanical properties. Also, water molecules present at the interface reduce the interaction between the filler and the matrix which can lead to poor mechanical properties [174]. Tensile modulus of WTC made from 180°C treated wood flour reduced slightly with water absorption. 27% and 20% reductions are observed in 20 wt% and 37 wt% wet composites, relative to the dry composites. This may be due to the reduced hydrophilicity in heat-treated wood which enhanced better compatibility between the filler and the matrix. It has been reported [183] that water molecules can act as plasticizers to soften the wood cell wall. Also, the tensile modulus of a composite is determined by the stiffness of the filler and the matrix. In addition, it is a filler-sensitive property in composites that is affected by moisture absorption [184]. Therefore, the lower the water uptake (Table 4.5 page 147, Figure 4.50, page 138), the lower is the amount of water molecules available to act as plasticizer to affect the tensile modulus [182]. However, composites from heat-treated wood at 200°C exhibited no observable decrease in tensile modulus with water immersion (Figure 4.59). This may be due to the better wetting (Figure 4.20, page 96) shown by these composites and hence indicating that the amount of water absorbed at equilibrium moisture content has minimal effects on the stress transfer capability. Incorporation of MAPE helps to retain the tensile modulus of the composites (Figure 4.60). Better interfacial adhesion resulting from the effect of MAPE could be responsible for this.

Tensile strength

The tensile strength of the neat LDPE (9.11 MPa) did not change much with moisture exposure (9.14 MPa). However, a decrement in tensile strength of the untreated wood composites is seen after immersion in water (Figure 4.61). Again, this may be a result of the plasticization effects of water on WTC. This is in agreement with reports [14, 78, 185]. More so, in the presence of moisture, cellulose at the filler-matrix interface tends to swell. This results in a shear stress at the interface which favours ultimate debonding of the fillers, leading to a reduction in the tensile strength [157]. However, tensile strength for heat-treated WTC did not show a significant decrease. This could mean that the high interfacial adhesion in these composites, due to heat treatment, became predominant relative to the induced shear stress. Again, incorporation of MAPE helped to maintain the tensile strength in water saturated composites (Figure 4.62).

Tensile strain

The tensile strain of the wet LDPE (91.15%) is relatively the same as the dry as-moulded sample (91.14 %). The values of the tensile strain of the composites decreased generally for all the composites studied, relative to the dry composites. It is expected that with moisture saturation, the tensile strain should increase as the system should soften due to plasticisation, but this is not the case in this investigation (Figure 4.63). Absorption of water must have weakened the wood particles, leading to low strain. With the addition of MAPE (Figure 4.64), the trend did not changed, although the rate of increase was significantly altered.

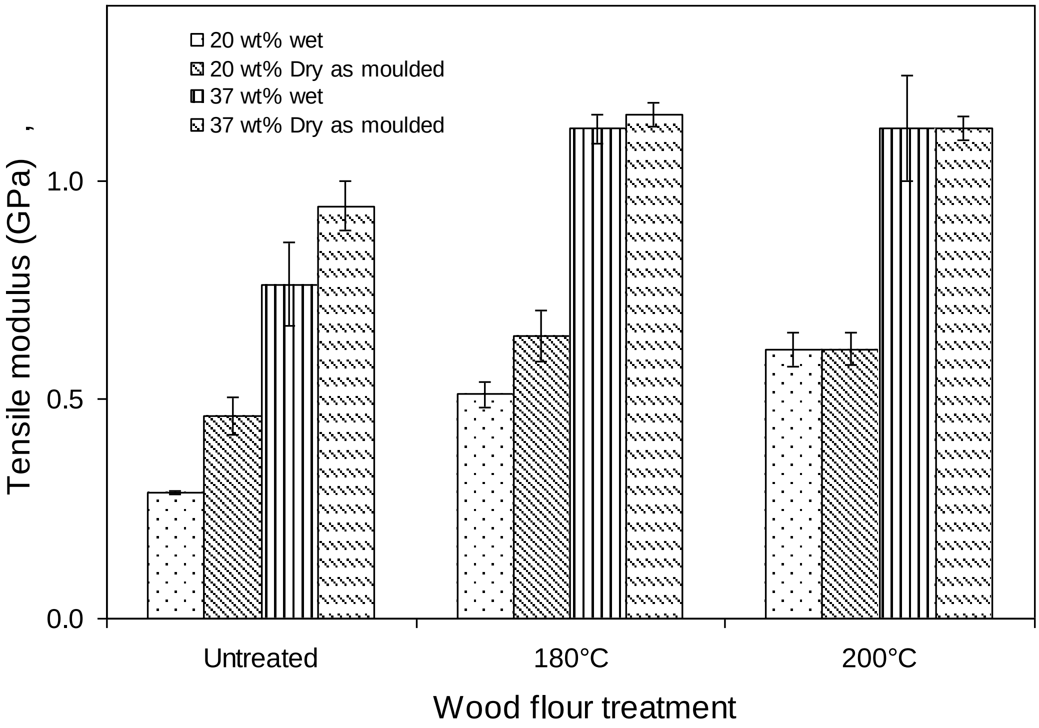


Figure 4.59: Tensile modulus of wet and dry composites as a function of wood content heat treatment

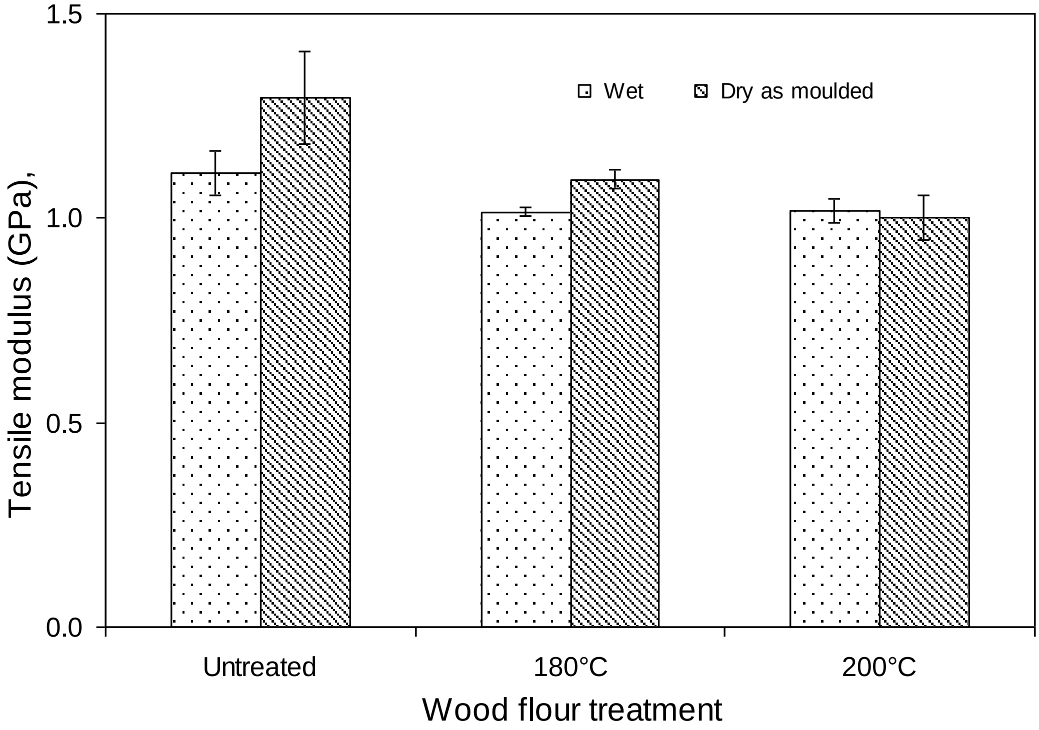


Figure 4.60: Tensile modulus of 37 wt% wet and dry composites containing 6% MAPE

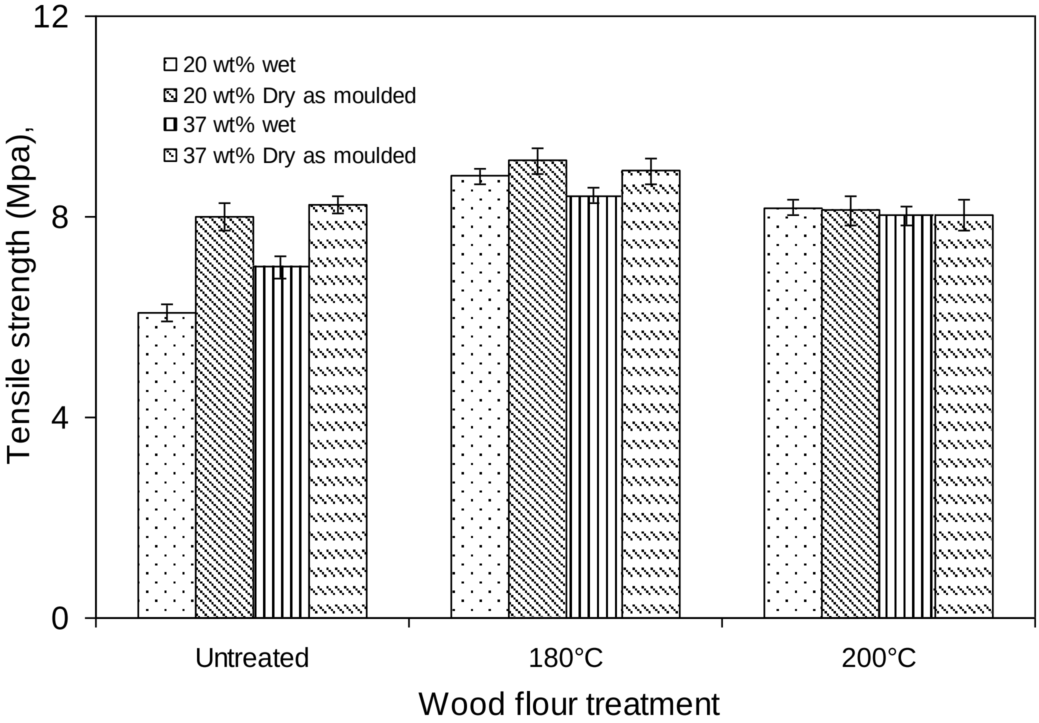


Figure 4.61: Tensile strength of wet and dry as-moulded composites as a function of wood content and heat treatment

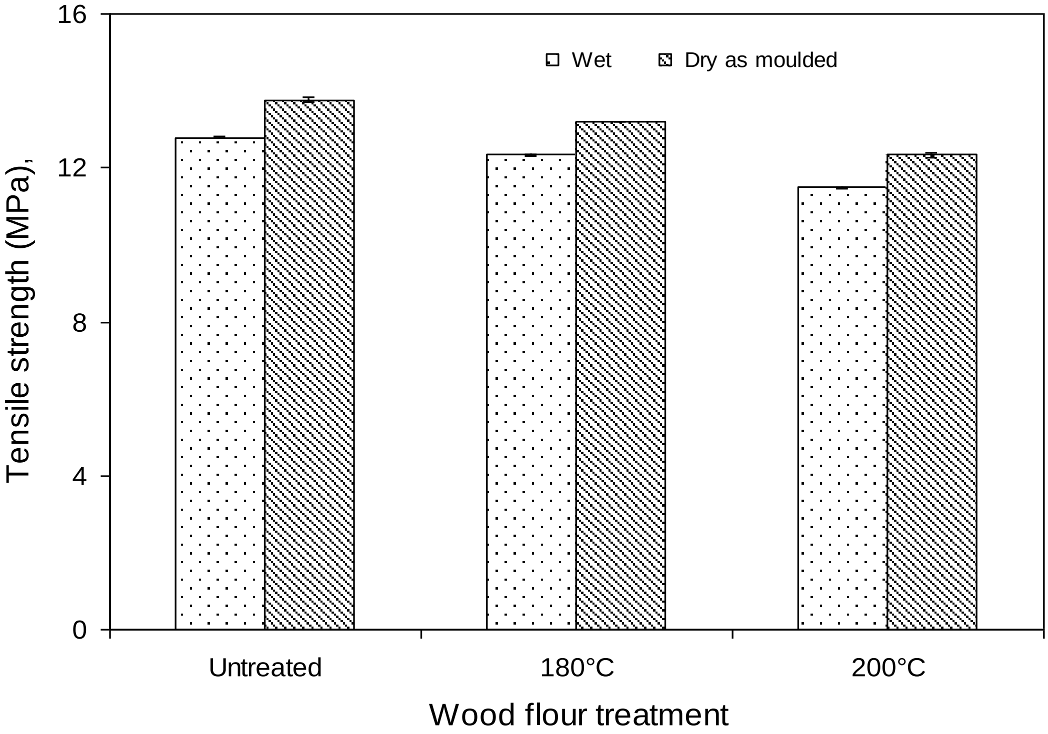


Figure 4.62: Tensile strength of 37 wt% wet and dry as-moulded composites containing 6% MAPE

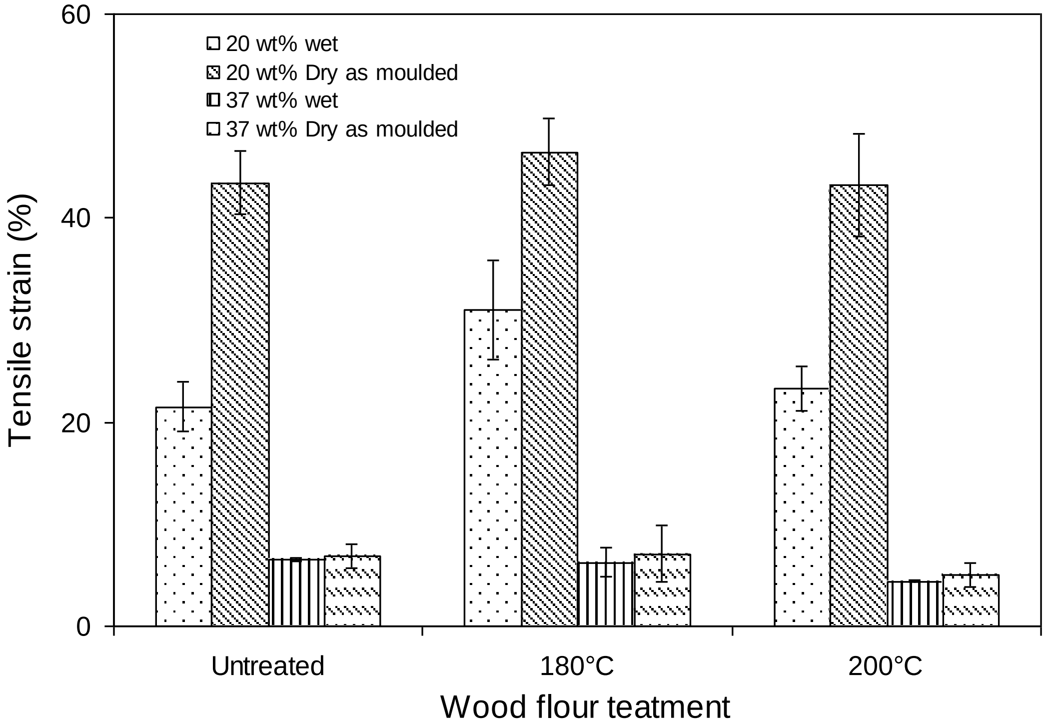


Figure 4.63: Tensile strain of wet and dry composites as function of wood content and heat treatment

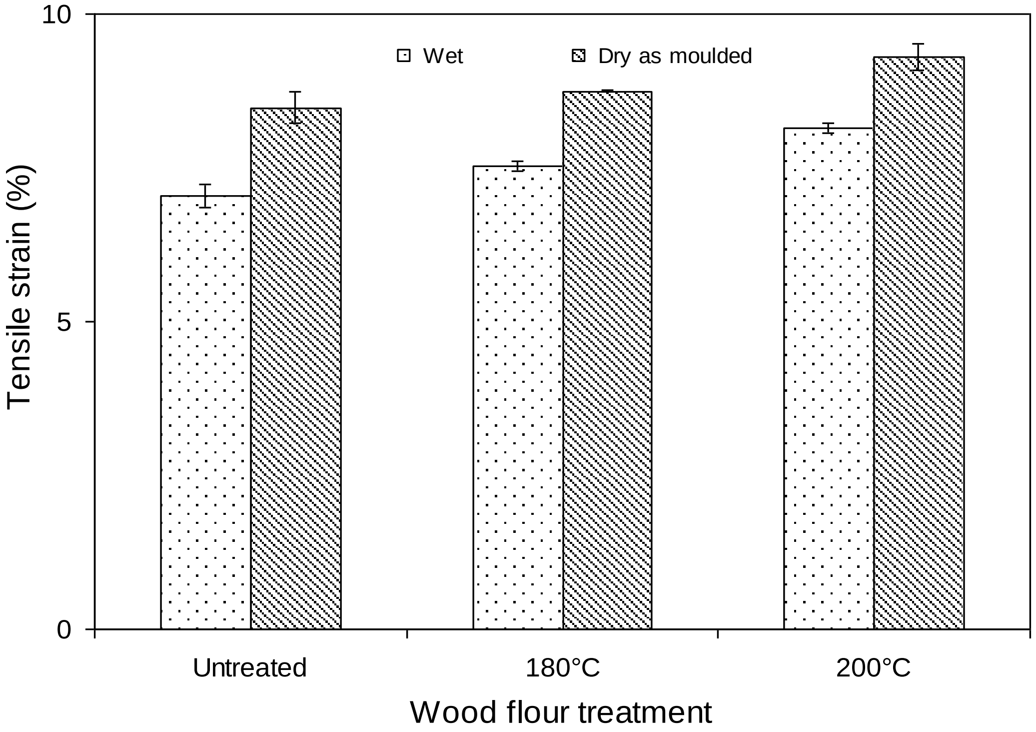


Figure 4.64: Tensile strain of 37 wt% wet and dry composites containing 6% MAPE

Flexural properties

Flexural modulus

The neat LDPE did not show any change in flexural modulus with water absorption. Values of 0.121 GPa and 0.123 GPa were obtained for the dry as-moulded and wet LDPE respectively. Figure 4.65 presents the flexural modulus of water-soaked and dry as-moulded composites. Generally, there is a decrease in flexural modulus values with moisture absorption. A higher reduction is observed for composites made from untreated wood, showing a 22% decrease, relative to the dry as-moulded samples. This reduction is also higher with higher wood content. Interfacial degradation resulting from moisture infiltration into the composites could be responsible for this trend. The flexural modulus of the heat-treated WTC was not altered appreciably, with water immersion. It is possible that the better compatibility in heat-treated wood composites has alleviated the interfacial degradation of the filler-matrix interface by water, resulting in better stress transfer. This result agrees with the work of Dhakal *el al* [184]. Despite the reduction in the amount of water absorbed with the addition of MAPE at equilibrium moisture content (Figure 4.50, page 138), the flexural modulus remained almost the same as the uncoupled WTC except in 37 wt% untreated WTC where a 20% decrement in flexural modulus was recorded when 6% MAPE is added (Figure 4.66). However, the heat-treated WTC containing MAPE showed only a marginal decrease in flexural modulus, the same trend exhibited by the uncoupled counterparts.

Flexural strength

The flexural strength of the LDPE exhibited an insignificant change with water absorption. The dry as-moulded LDPE presented flexural strength values of 7.13 MPa, while the moisture saturated had a value of 7.15 MPa. On the other hand, there was a marginal decrease in the flexural strength with water absorption in all the categories of composites studied (Figure 4.67), with the coupled composites presenting the same trend as the uncoupled WTC at the various treatment temperatures (Figure 4.68).

Flexural displacement

Also, the flexural displacement of the dry as-moulded LDPE (0.098 mm/mm) did not change appreciably with moisture absorption (0.095 mm/mm). However, no particular trend was recorded in the flexural displacement of the uncoupled composites with water absorption (Figure 4.69). Conversely, a decreasing trend in flexural displacement was observed in the wet composites containing 6% MAPE, relative to the dry as-moulded composites upon moisture saturation (Figure 4.70). This trend is inconsistent with that established with the flexural modulus and strength. Again, this may mean that excessive moisture softens the composites system, resulting in low displacement at yield.

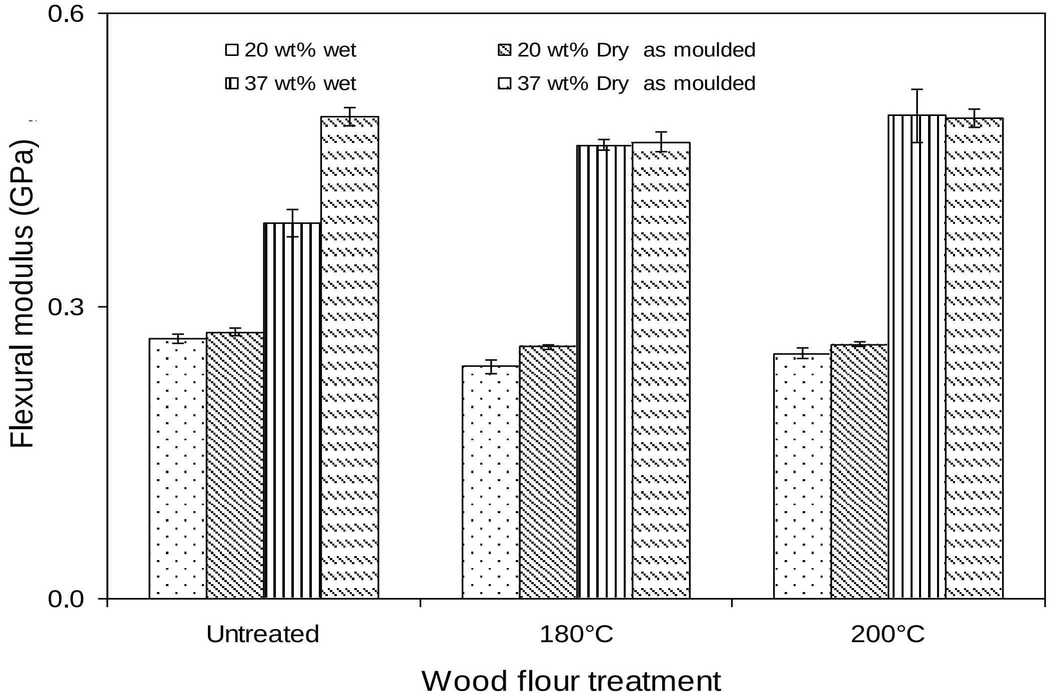


Figure 4.65: Flexural modulus of wet and dry composites as a function of wood content and heat treatment

Figure 4.66: Flexural modulus of 37 wt% wet and dry composites containing 6% MAPE

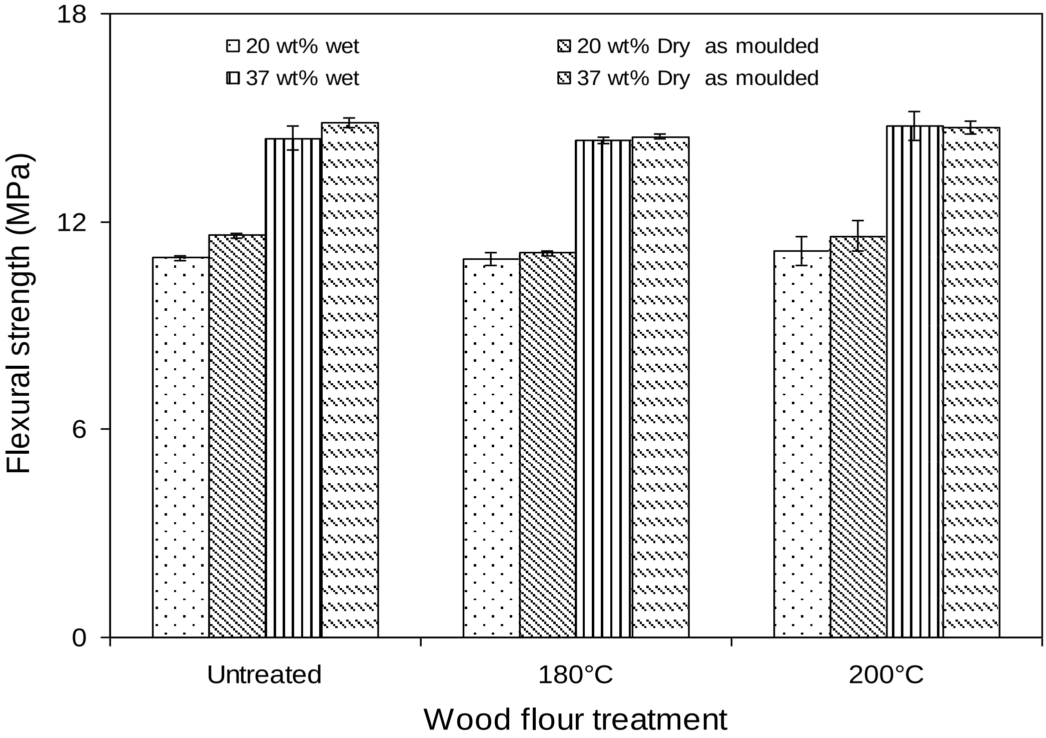


Figure 4.67: Flexural strength of wet and dry composites as a function of wood content and heat treatment

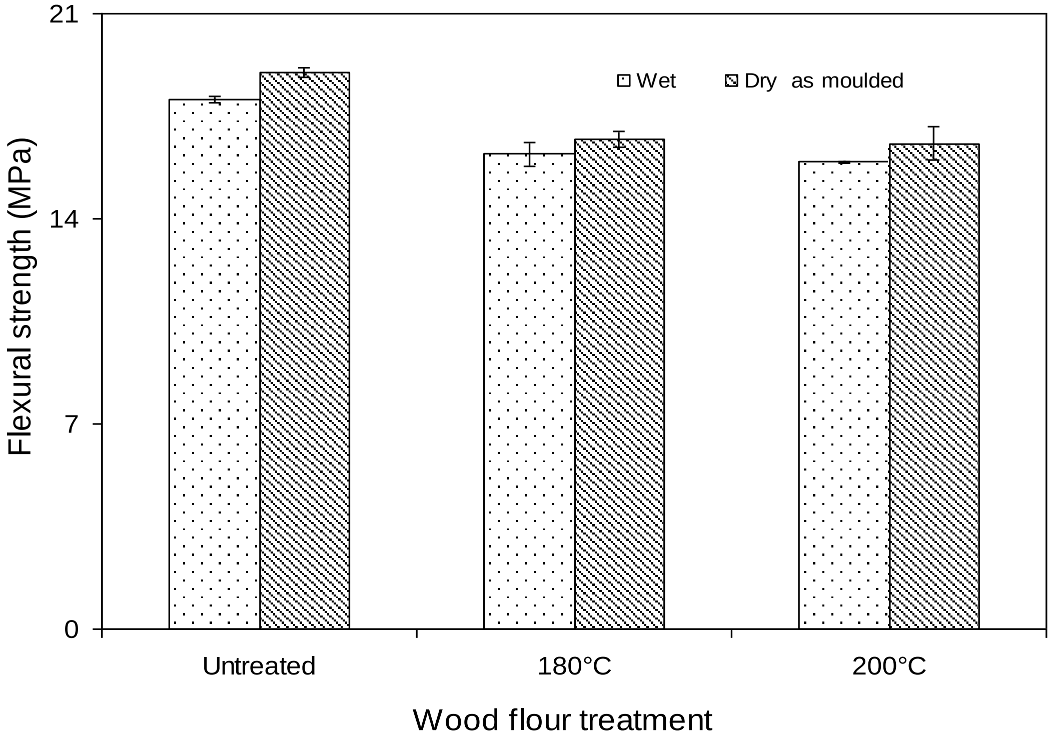


Figure 4.68: Flexural strength of 37 wt% wet and dry composites containing 6% MAPE

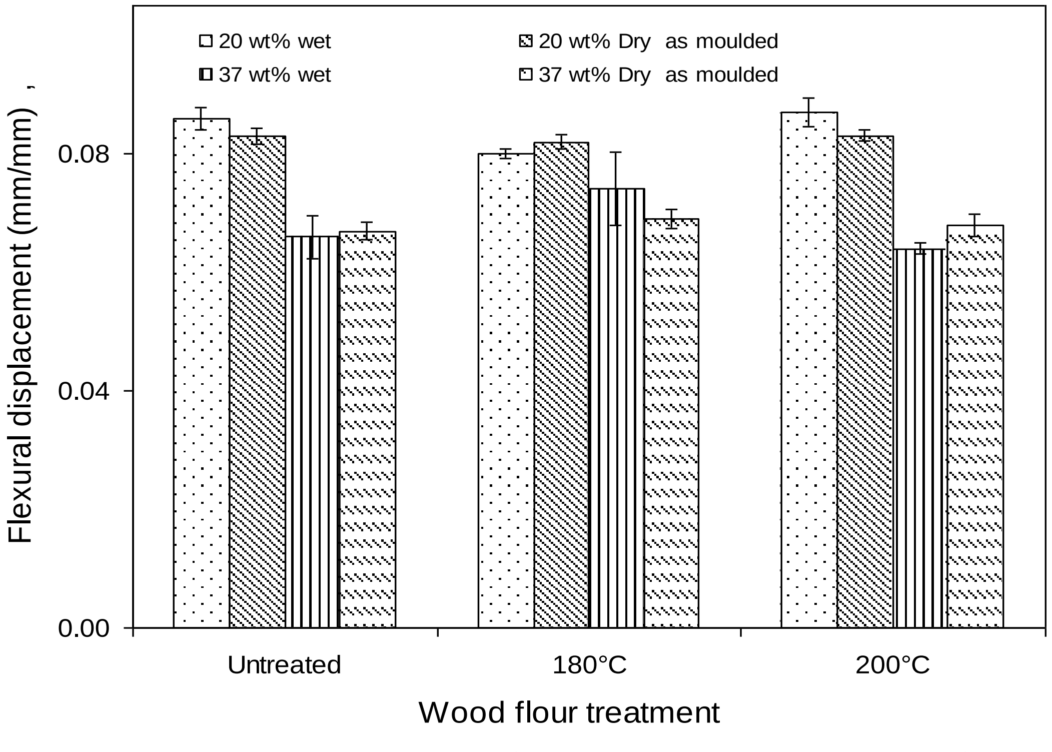


Figure 4.69: Flexural displacement of wet and dry composites as a function of wood content and heat treatment

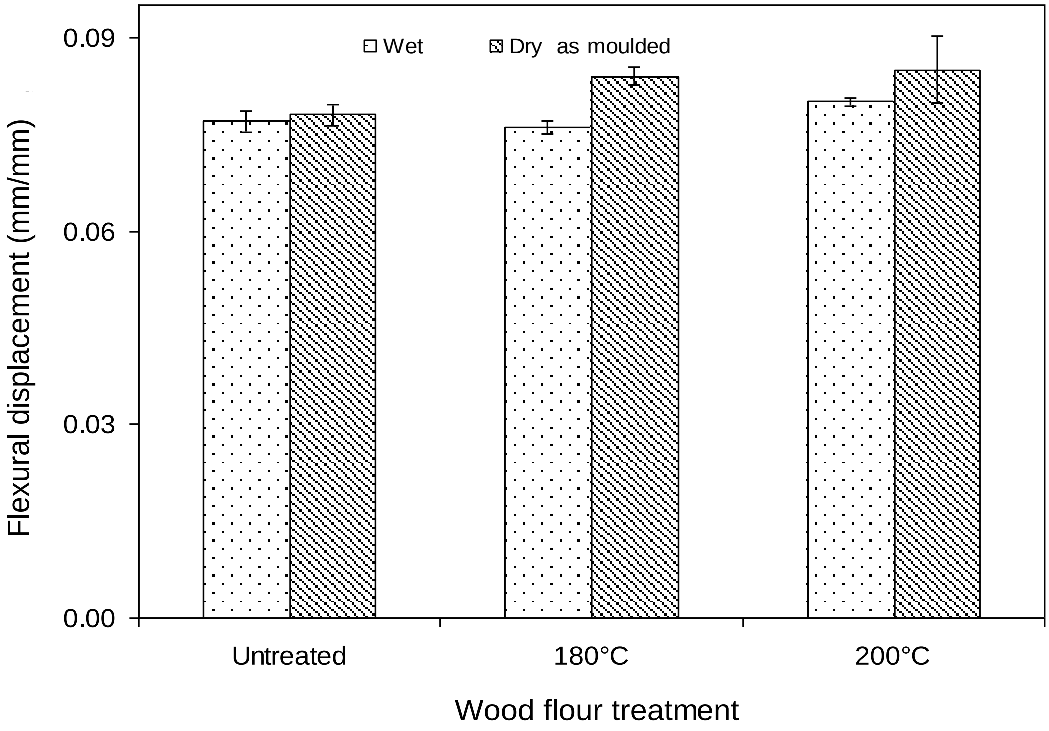


Figure 4.70: Flexural displacement of 37 wt% wet and dry composites containing 6% MAPE

Impact properties

Peak load

The peak load increased with water absorption (Figure 4.71). The peak load of the neat LDPE remained relatively the same because it did not absorb water. Values of 273.3 N, 235.9 N, 188.9 N and 139.1 N were obtained in the wet LDPE for a/D ratios 0.1, 0.2, 0.3 and 0.4 respectively. While 266.9 N, 225.3 N, 184.5 N and 137.4 N were recorded in the dry as-moulded LDPE for a/D ratios 0.1, 0.2, 0.3 and 0.4 respectively. However, the composites displayed an increase in *P* values with water absorption, with composites containing 37 wt% wood flour showing the highest increment, even above the values of the dry as-moulded and wet neat LDPE. It is possible that plasticisation of the composite system by water absorption may have rendered the composites more ductile than its dry as-moulded counterparts, thereby increasing the maximum load required to break the material. Composites loaded with 37 wt% wood flour exhibited the highest values of *P*. Since this category of composites showed the highest water absorption rate, it is pertinent to think that it should also be plasticised the most. Composites made from heat-treated wood flour have lower *P* values when compared with their untreated counterparts (Figure 4.71). Again, reduced attraction to water by heat treatment could be responsible for this behaviour. Increase in *P* with moisture absorption agrees with earlier findings [186]. Incorporation of MAPE reduced the *P* values of wet composites, relative to the dry as-moulded composites (Figure 4.72). This is expected because improved interfacial bonding was enhanced by the presence of MAPE and consequently, reduced water absorption which in turn led to reduced plasticisation.

Critical stress intensity factor, K_c

Figure 4.73 presents the K_c plot of the dry as-moulded and moisture saturated composites as a function of wood content and heat treatment. The K_c values of the dry as-moulded and wet LDPE are 1.70 MPa.m$^{0.5}$ and 1.63 MPa.m$^{0.5}$, respectively. These values showed no appreciable change in K_c of the neat LDPE upon moisture absorption. The hydrophobic character of LPDE could be responsible for this. As observed in the peak load, the K_c values of the composites increased in the wet samples, relative to the dry as-moulded samples. This increment is proportional to the wood content, with composites loaded with 37 wt% wood flour showing the highest values of 1.78 MPa.m$^{0.5}$, 1.82 MPa.m$^{0.5}$ and 1.77 MPa.m$^{0.5}$ for moisture saturated untreated, 180°C and 200°C treated WTC, respectively. The dry as-moulded samples exhibited values of 1.40 MPa.m$^{0.5}$, 1.41 MPa.m$^{0.5}$ and 1.60 MPa.m$^{0.5}$ for untreated, 180°C and 200°C treated WTC, in that order. This is rather strange as the plasticisation effect of water should lower the stiffness of the material. On the other hand, what appears to be obvious here is the fact that the material becomes pliable with water absorption, thereby increasing its resistance to brittle failure and raising its K_c value. Furthermore, it has been reported [187] that the impact behaviour of WTC is a complex phenomenon involving the nature of the fillers and matrix, the filler-matrix bond, filler distribution and orientation. In addition, possible damage modes, which is also an important factor to consider, have been identified as matrix cracking, interfacial bond failure, filler breakage, void growth and delamination. Besides, the fact that one or more of these factors act in synergy to cause the failure of WTC could further complicate the understanding of the fracture behaviour of WTC. Addition of MAPE reduced the K_c value of the composites (Figure 4.74). It is expected that coupling agent should improve the interfacial adhesion, thereby reducing the water absorption capacity and consequently, the softening effect of water.

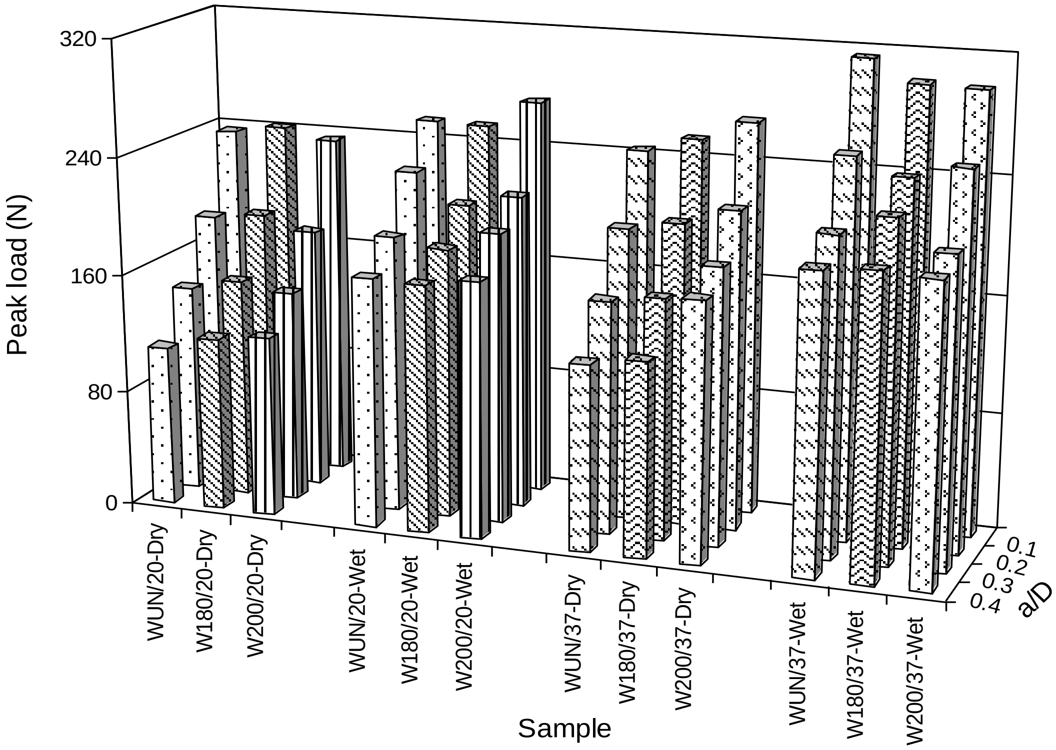


Figure 4.71: Peak load of dry as-moulded and wet samples as a function of wood content and heat treatment

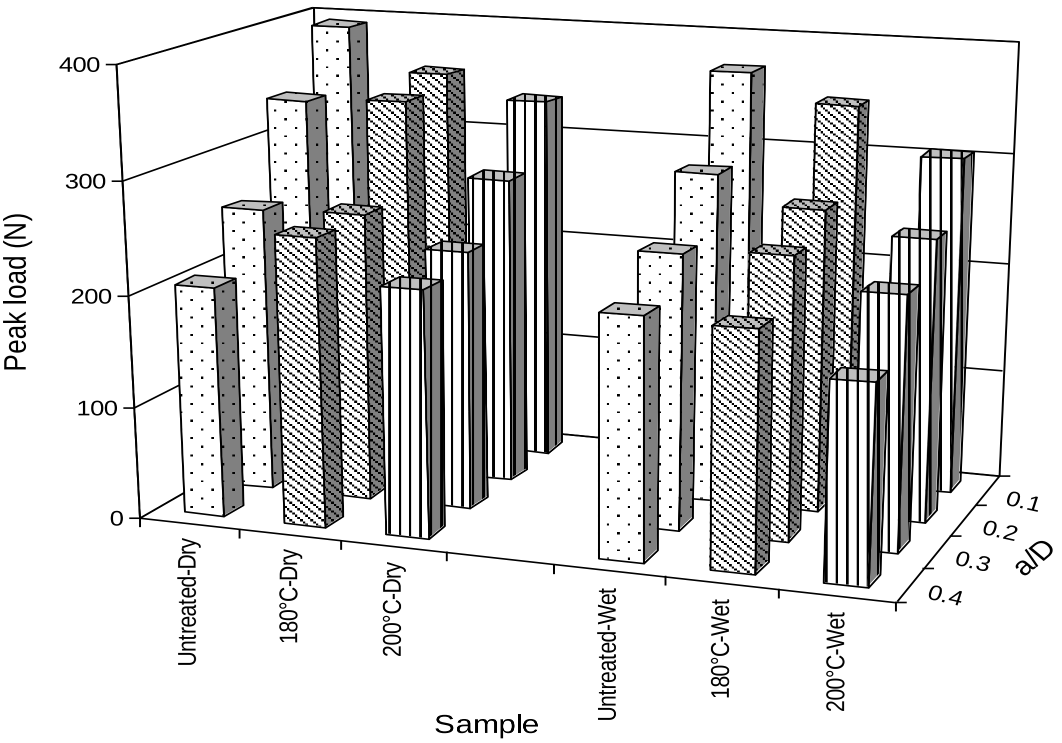


Figure 4.72: Peak load of 37 wt% dry as-moulded and wet samples containing 6% MAPE

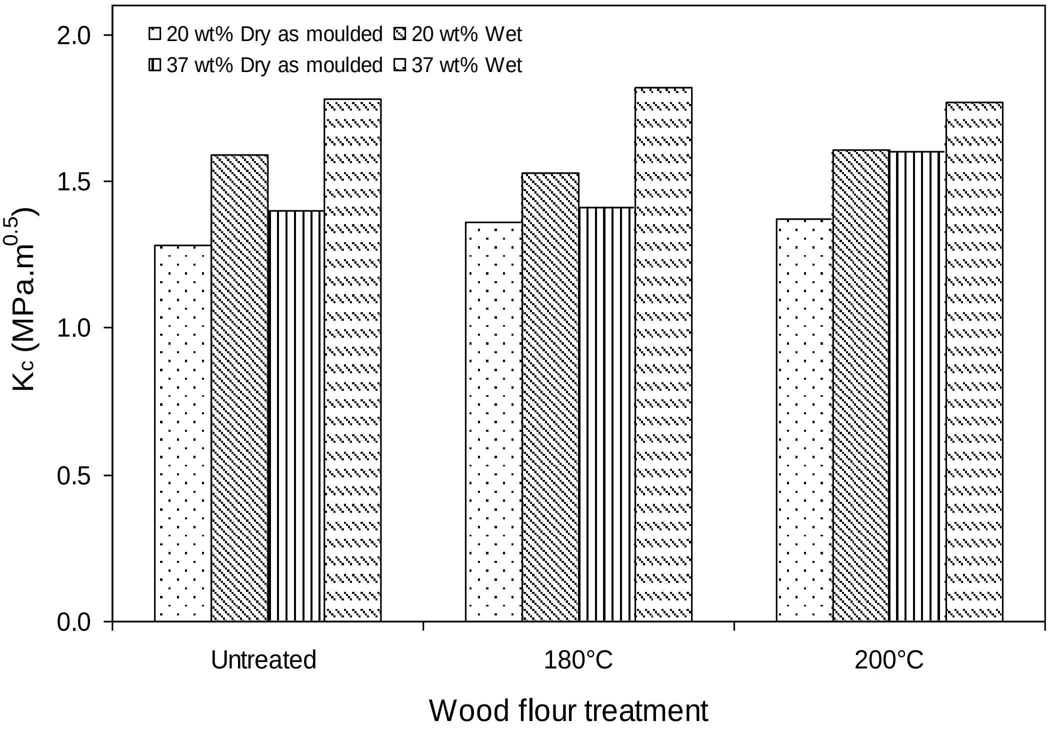


Figure 4.73: K_c plot of dry as-moulded and wet samples as a function of wood content and heat treatment

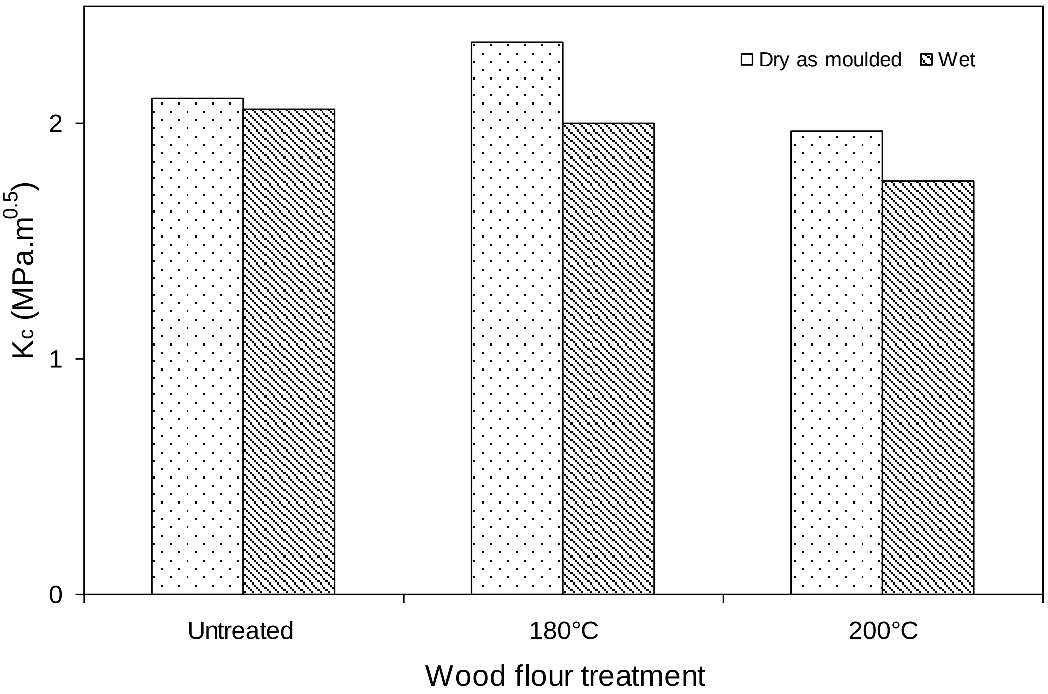


Figure 4.74: K_c of 37 wt% dry as-moulded and wet samples with 6% MAPE

Energy to failure, W

The *W* of the dry as-moulded and wet LDPE is relatively the same. Values of 4.62 J, 3.48 J, 3.17 J and 2.12 J were recorded for a/D ratios 0.1, 0.2, 0.3, 0.4 respectively in the dry as-moulded samples, while 4.59 J, 3.51 J , 3.12 J and 2.11 J were obtained for a/D ratios of 0.1, 0.2, 0.3 and 0.4 correspondingly. This is because LDPE did not absorb water and as such, the energy required to fracture the dry and wet specimens remained almost the same. Figure 4.75 presents the energy to failure of the dry as-moulded and wet composites. *W* values of the moisture saturated composites were generally lower than those of the dry as-moulded composites. This decrement is higher in composites with high wood content, with the untreated WTC showing slightly higher values than their heat-treated counterparts. Again, the possibility of interfacial degradation by water might have lowered the energy to break the moisture saturated specimens relative to the dry as-moulded specimens, resulting in the trend observed. Addition of MAPE did not show any appreciable difference in *W* values between the wet and dry samples (Figure 4.76).

Critical strain energy release rate, G_c

The G_c values of the dry as-moulded and wet LDPE (96.6 kJ.m^{-2} and 97.2 kJ.m^{-2} respectively) were very much alike, an indication that moisture has no effect on the impact strength of LDPE. However, the G_c values of the composites shown in Figure 4.77, decreased generally with water absorption. The difference in G_c values between the dry as-moulded and wet samples was higher in composites made from wood flour treated at 200°C. It could be that since the composite exhibited good interfacial bonding in the dry as-moulded sample (Figure 4.42b, page 124), upon moisture absorption and the consequent degradation of the interface, crack propagation along the interfacial area was enhanced (Figure 4.78), thereby preventing dissipation of energy and thus, reducing G_c.

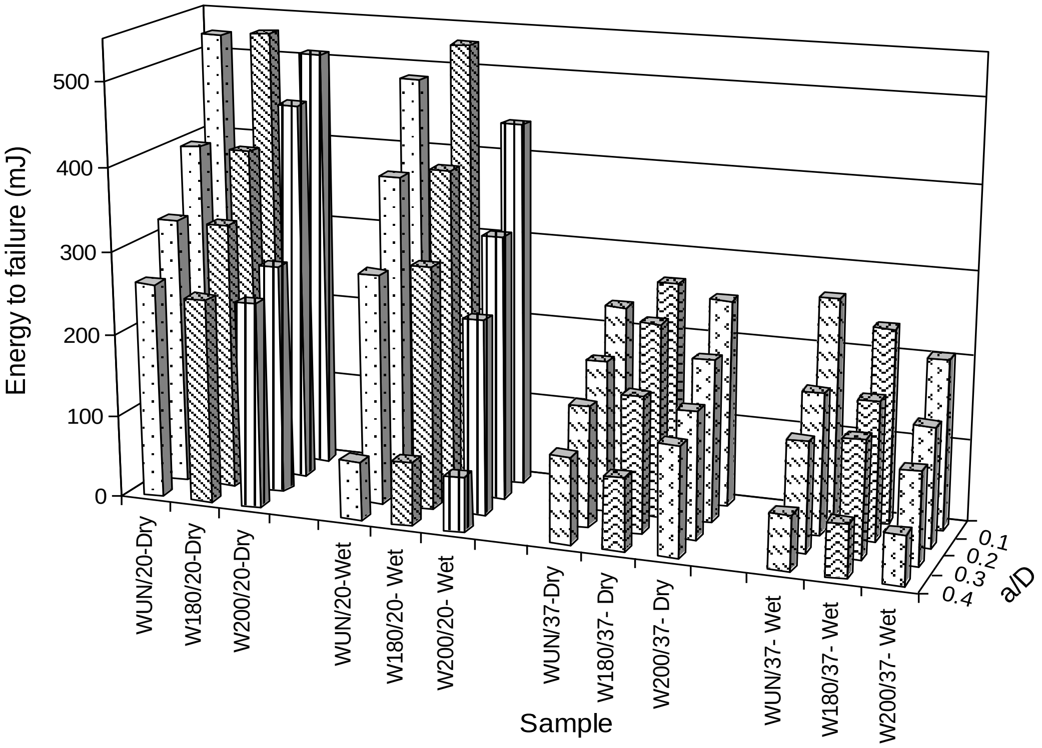


Figure 4.75: Energy to failure of dry as-moulded and wet samples as a function of wood content and heat treatment

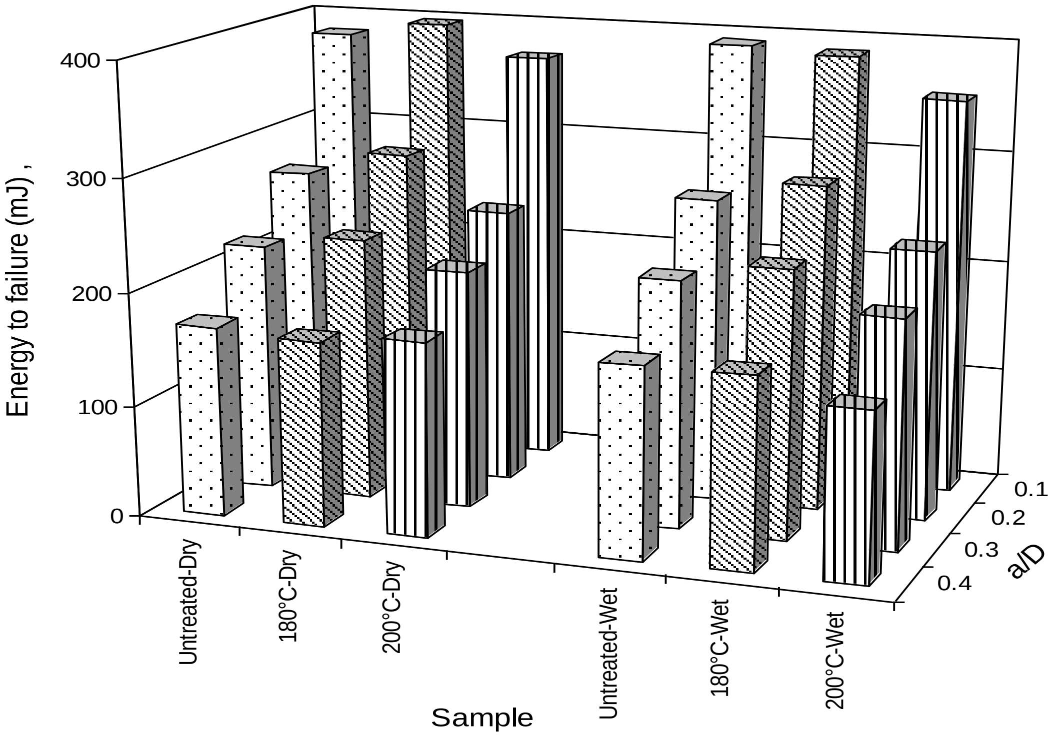


Figure 4.76: Energy to failure of 37 wt% dry as-moulded and wet samples with 6% MAPE

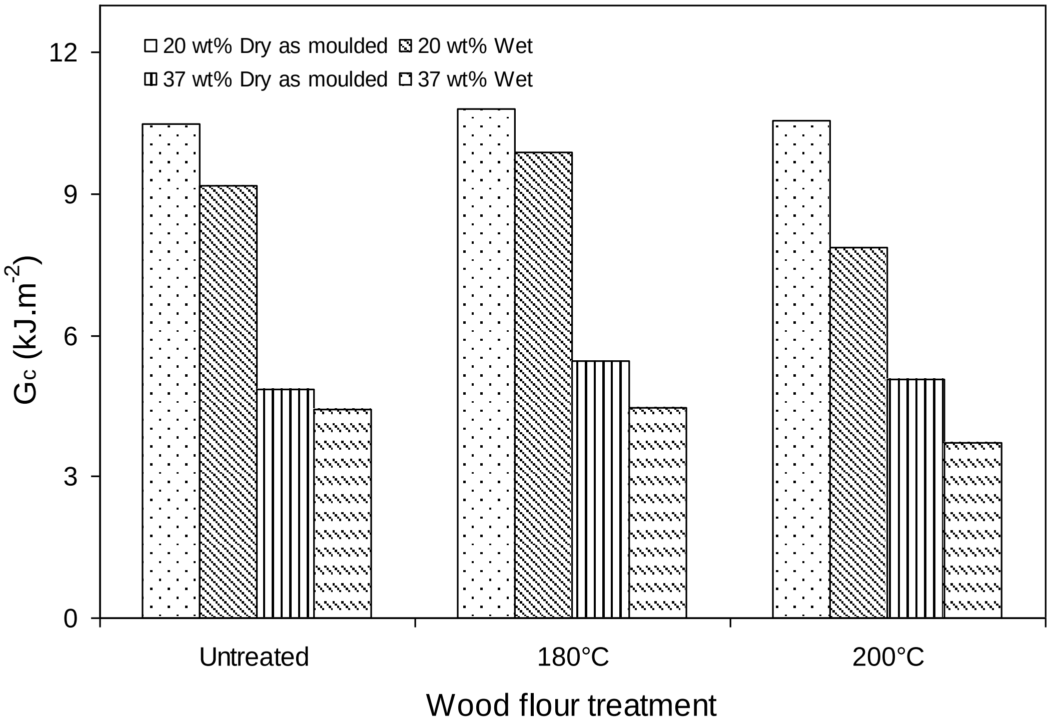


Figure 4.77: G_c of dry as-moulded and wet samples as a function of wood content and heat treatment

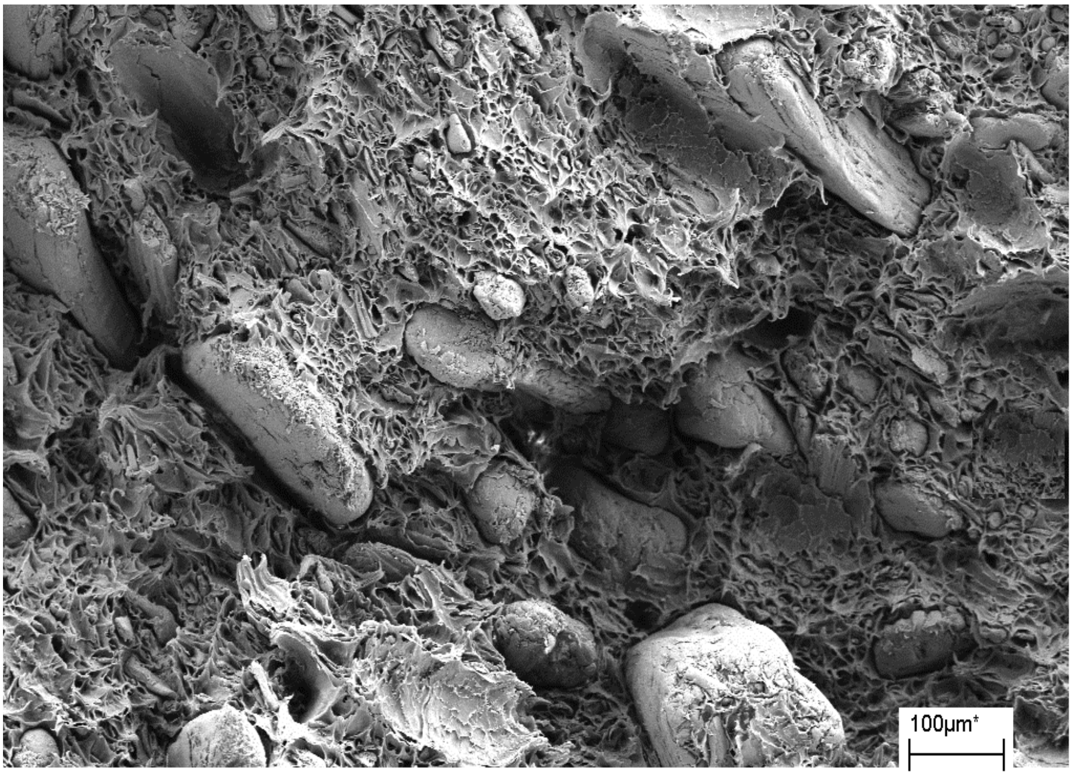


Figure 4.78: Impact fractured surface of 37 wt% 200°C treated wood flour

Figure 4.79: Impact fractured surface of 37 wt% untreated wood flour

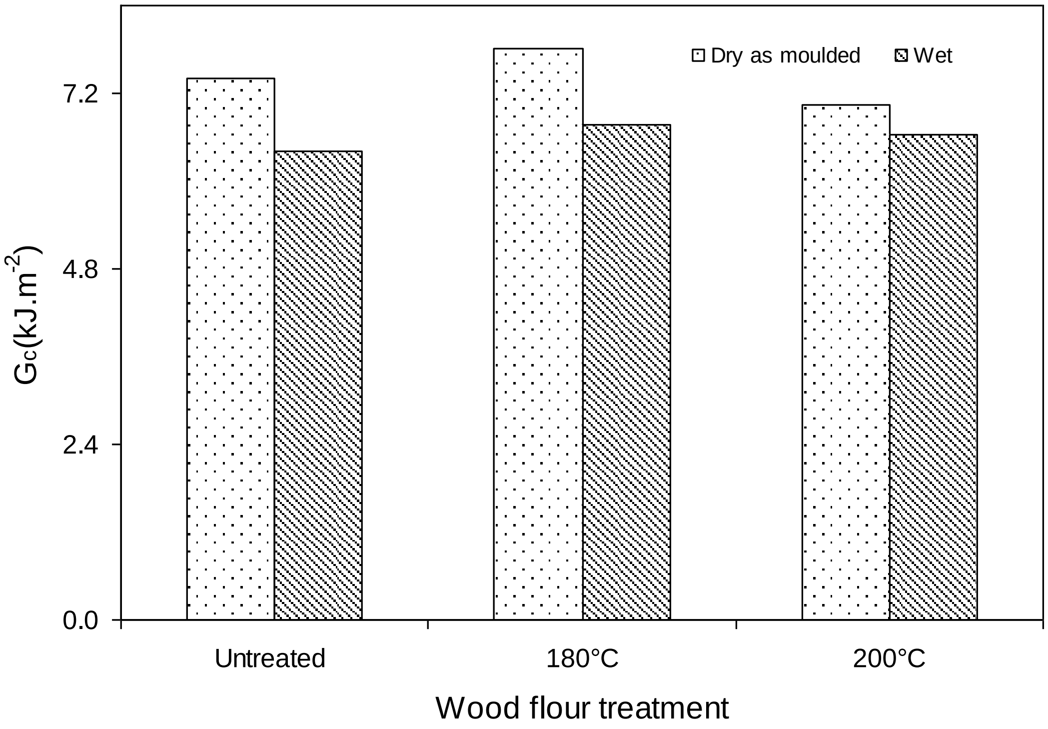


Figure 4.80: *G_c* of 37 wt% dry as-moulded and wet samples with 6% MAPE

In the wet composites containing untreated and 180°C treated wood flour, the poor interfacial adhesion already existing in the dry as-moulded specimen (Figure 4.42a, page 124) meant further degradation of its interface with moisture absorption, leading to fibre pull-out (Figure 4.79), meaning higher energy dissipation and higher G_c. However, on addition of MAPE, the trend was reversed (Figure 4.80), indicating that MAPE is more efficient in coupling untreated and 180°C treated WTC, probably due to the reduced O-H groups on the surface of 200°C treated wood flour.

4.3.2 Effect of outdoor soil burial

Soil has been identified as one of the environments suitable for biodegradation. In soil, fungi are mostly responsible for biodegradation of organic matter as well as polymeric materials [188]. Natural polymers such as cellulose are able to undergo degradation through microbiological processes. However, synthetic polymers which are relatively less wettable by water should inhibit attack by aqueous enzyme systems of micro organisms [189]. Addition of natural fillers generally enhances the degradation of WTC and depends on a number of factors including the filler content, biodegradability of each of the components and the quality of the interface. Since moisture is required by fungi in the degradation of wood and its components, it is clear that the hydrophilic nature of wood, will obviously favour its degradation [190, 191] and the tropical weather in Malaysia should provide the necessary moisture required for fungal degradation. Furthermore, once wood is incorporated into a hydrophobic polymeric matrix like LDPE, exposure to moisture is, in principle, limited. On the other hand, addition of hydrophilic natural filler into LDPE ought to lower its hydrophobic character. By implication, WTC should be more liable to fungal attack than the neat LDPE. Therefore, bio-deterioration of LDPE could be initiated due to the decay of the additives (fillers) included in the plastic. Biological deterioration of WTC may include attack by decay fungi, moulds, algae and termites [192].

Alhough this research is not intended to study the biodegradability of WTC, the effect of soil burial on the properties of composites made from different filler loadings of untreated and heat-treated wood flour was investigated in order to ascertain the resistance of the composites when buried under the soil for a period of time.

4.3.2.1 Physical appearance

There was no observable fungal growth on the surface of neat LDPE after soil burial (Figure 4.81). This is as a result of the hydrophobic character and the absence of organic matter in neat LDPE. However, the composites exhibited various degree of fungal plague (Figures 4.82). The untreated WTC showed the highest visible fungal growth (Figure 4.82a). This is closely connected with the water absorbing capacity of untreated wood flour which provided a favourable moisture environment for fungal infestation. In addition, it is expected that the presence of organic matter in untreated wood flour should present an adequate atmosphere for fungal activity [193]. Furthermore, a reduction in fungal growth is observed in composites made from 200°C treated wood flour (Figure 4.82b). Reduced hydrophilicity with heat treatment and possible degradation of the organic matter in heat-treated wood flour could be responsible for this trend.

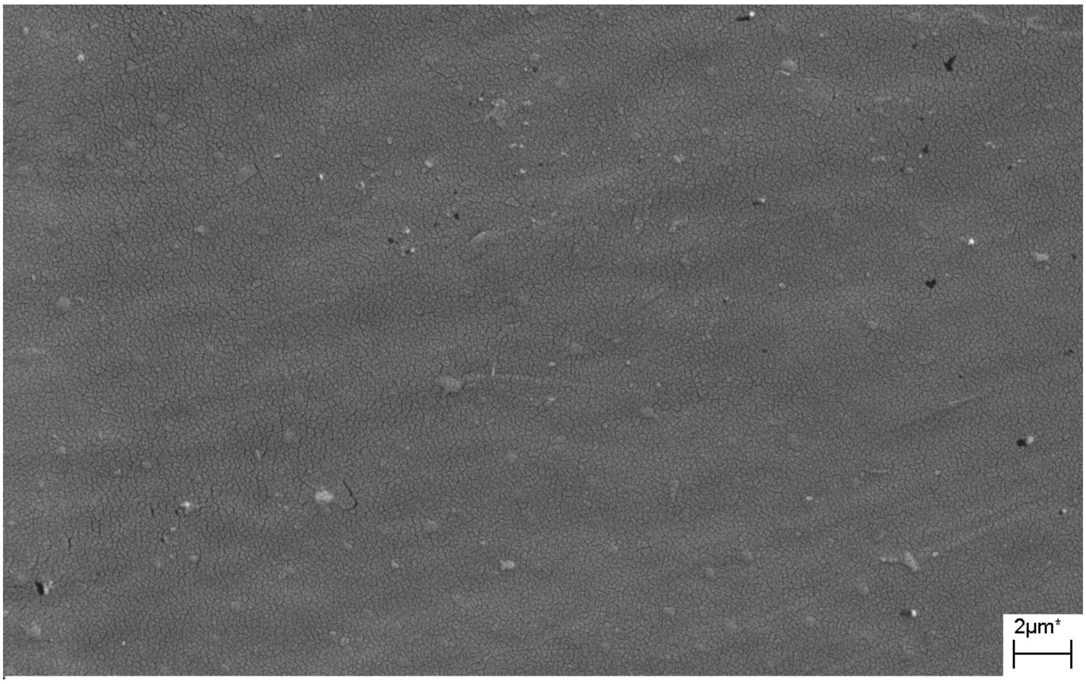
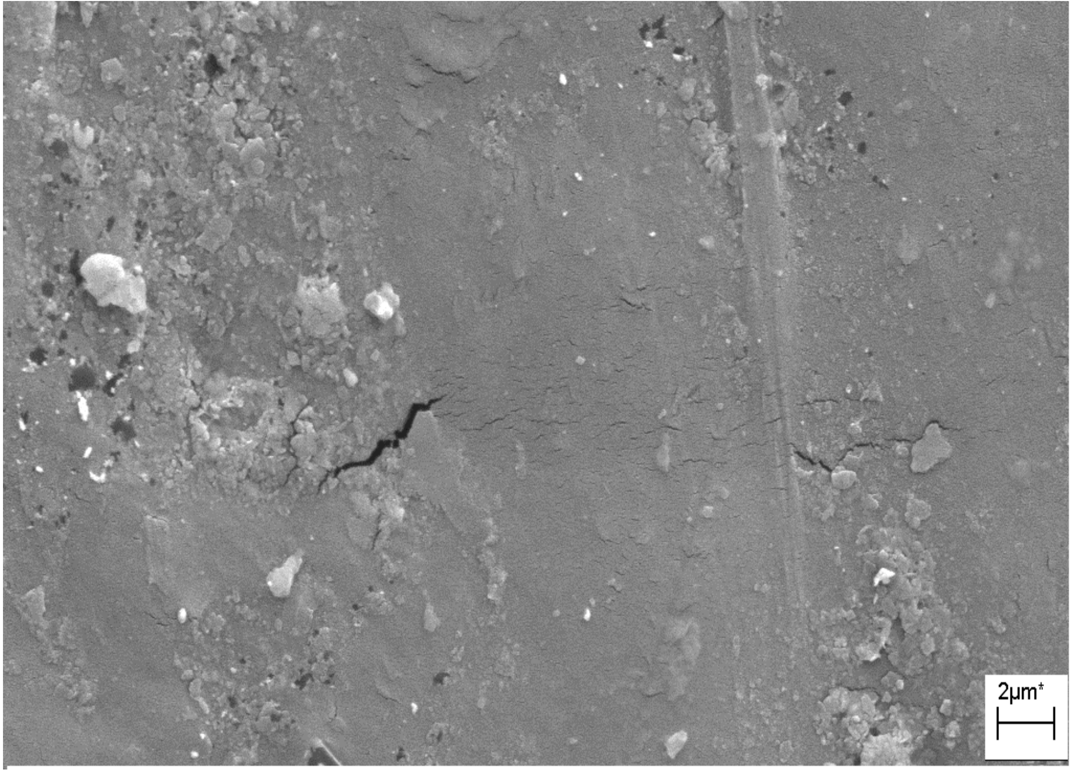


Figure 4.81: SEM micrograph of the moulded surface of buried neat LDPE showing no fungal growth

a)



b)

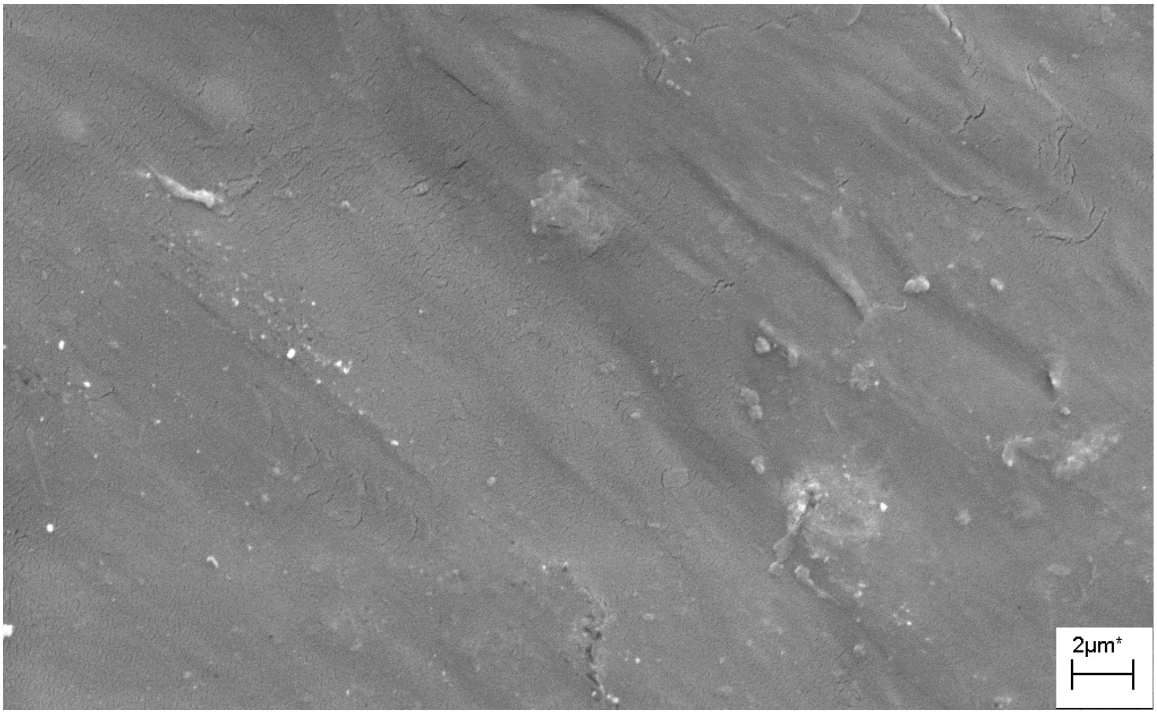


Figure 4.82: SEM micrograph of the surfaces of buried 37 wt% WTC containing a): untreated and b): 200°C treated wood flour

While the colour changes in the composites upon outdoor burial was not captured quantitatively, visual inspection of the samples revealed that the composites changed colour from dark brown to a lighter shade of brown, with a rough feeling on the surface. This may be the result from the leaching effect of water in the soil as a result of the tropical nature of Malaysia with heavy rainfall (Table 3.3, page 46).

4.3.2.2 Thermal properties

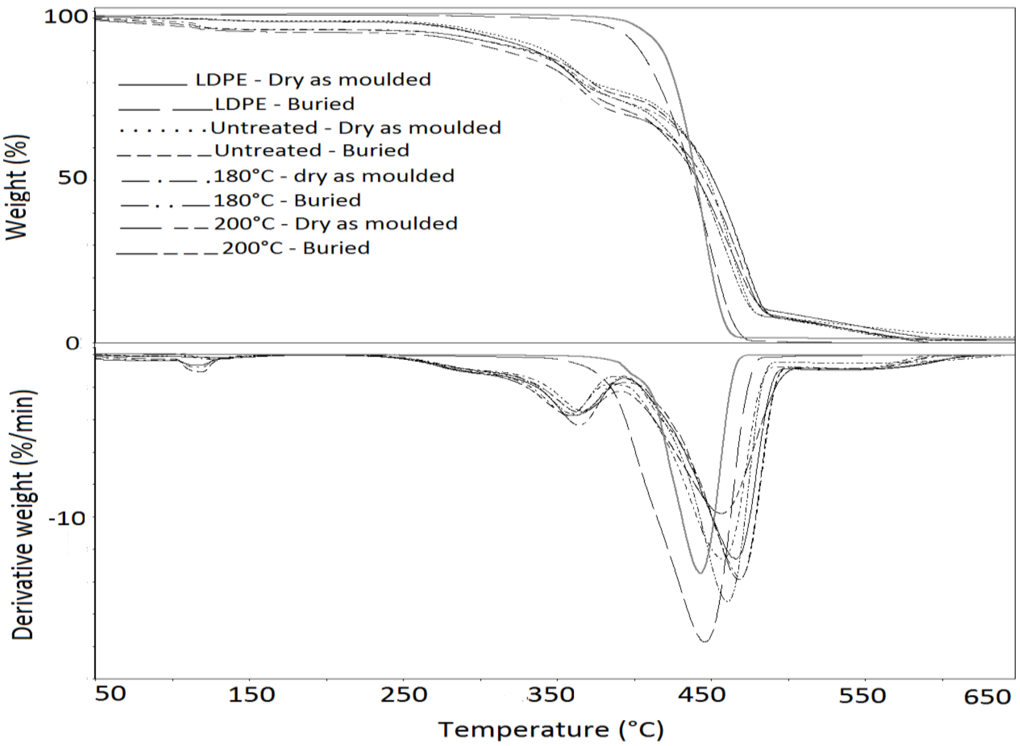
Thermogravimetric analysis

Thermograms of dry as-moulded and buried composites are presented in Figure 4.83. Data extracted from these thermograms are presented in Table 4.9. The T_p, T_{onset} and $T_{50\%}$ values of dry as-moulded LDPE were lower than the buried LDPE. This result was rather strange because the neat LDPE was not expected to undergo appreciable degradation during the period of burial because of its hydrophobic nature (Figure 4.81). A peak at about 100°C showed the amount of water contained in the buried composites. In the 37 wt% composites, 3.96%, 3.07% and 2.98% water evaporated in the buried samples containing untreated, 180°C and 200°C treated wood flour, respectively. While these values were slightly lower than those observed in the moisture saturated samples, it is an indication that the tropical environment provides substantial moisture for the buried samples. Although most of the curves of the buried composites overlapped, from Table 4.9, the T_p, T_{onset} and $T_{50\%}$ of composites loaded with 20 wt% showed no definite trend when compared with the dry as-moulded samples (Table 4.2, page 57). However, buried composites containing 37 wt% wood flour showed an increase in thermal stability, relative to the dry as-moulded samples. While the improvement in T_p and $T_{50\%}$

is quite marginal with a difference of about 5°C to 8°C, the T_{onset} showed appreciable increment of 14°C in untreated WTC to 47°C in 180°C treated WTC. Buried composites containing wood flour treated at 200°C showed a 24°C difference in T_{onset} values. Although no scientific evidence could be given for this observation, the presence of fungal growth on the surface of the composites (Figure 4.82) could be responsible. It has been suggested [190] that addition of fillers attracts fungi to the composites. In addition, higher filler loading should draw more fungi to the composite, which might probably account for the behaviour of the 20 wt% composites when compared to those containing 37 wt% filler.

Though heat treatment seemed to have influenced the thermal stability of the buried composites, a clear trend could not be established with respect to treatment temperature. T_p, T_{onset} and $T_{50\%}$ values of dry as-moulded samples containing MAPE were generally similar to those of the buried samples (Figure 4.83b and Table 4.9). It is expected that better compatibility with incorporation of MAPE should lower moisture infiltration which ought to reduced the infestation of fungi and consequently, the thermal stability.

a)



b)

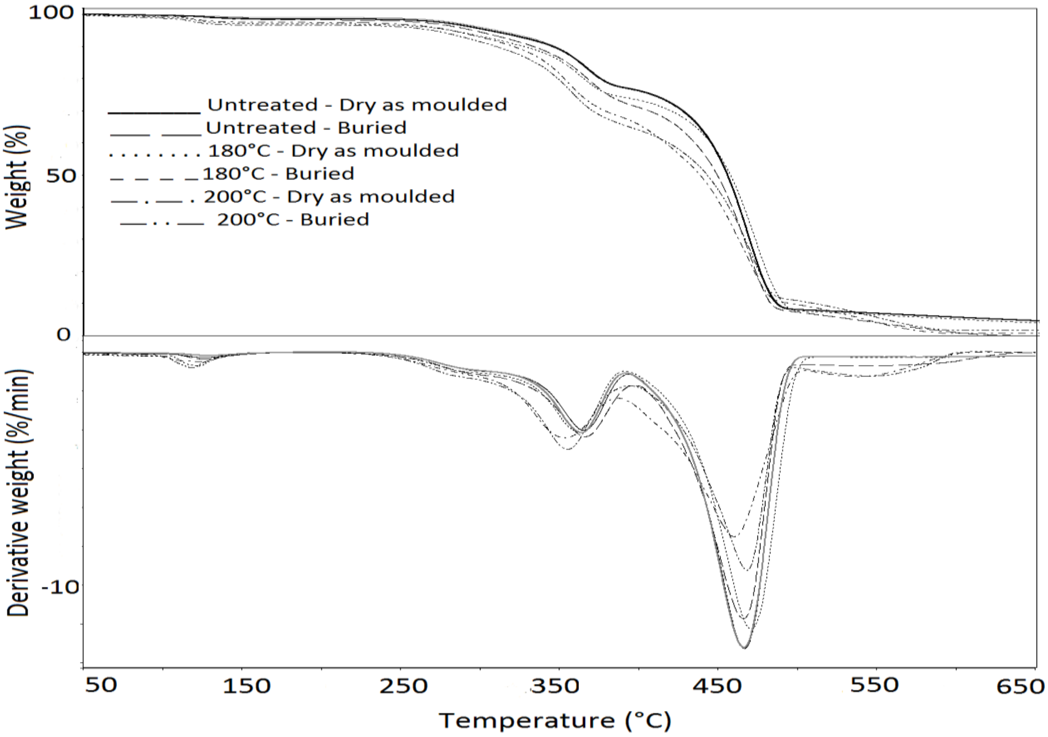


Figure 4.83: TG/DTG curves of dry as-moulded and buried LDPE and 37 wt% composites containing a): 0% and b): 6% MAPE

Table 4.9: TGA/DTG data of buried samples

Sample	Treatment temperature (°C)	T_p (°C)	Onset temperature, T_{onset} (°C)	$T_{50\%}$ (°C)	Degradation temperature (°C)
LDPE	-	461.6	428.0	453.3	328.0-517.3
LDPE/$W_{UN/20/0}$	-	464.8	424.7	456.6	269.7-517.3
LDPE/$W_{180/20/0}$	180.0	465.5	420.3	452.5	228.9-500.7
LDPE/$W_{200/20/0}$	200.0	461.2	418.9	450.4	224.4-500.7
LDPE/$W_{UN/37/0}$	-	469.2	412.5	450.3	227.5-499.4
LDPE/$W_{180/37/0}$	180.0	468.6	414.1	449.8	230.0-500.6
LDPE/$W_{200/37/0}$	200.0	466.2	408.7	443.9	226.7-498.2
LDPE/$W_{UN/20/2}$	-	466.4	404.4	442.3	244.4-497.2
LDPE/$W_{180/20/2}$	180.0	460.9	414.0	446.9	226.6-498.5
LDPE/$W_{200/20/2}$	200.0	459.3	401.2	440.9	236.5-500.1
LDPE/$W_{UN/37/2}$	-	455.7	381.6	434.1	219.7-507.3
LDPE/$W_{180/37/2}$	180.0	460.2	381.6	436.1	221.0-502.1
LDPE/$W_{200/37/2}$	200.0	467.0	362.1	426.3	230.8-508.2
LDPE/$W_{UN/20/6}$	-	475.2	392.6	441.6	223.8-505.1
LDPE/$W_{180/20/6}$	180.0	458.7	407.5	446.0	237.8-505.7
LDPE/$W_{200/20/6}$	200.0	462.5	435.9	458.7	240.9-502.6
LDPE/$W_{UN/37/6}$	-	469.1	401.0	441.0	215.2-497.9
LDPE/$W_{180/37/6}$	180.0	469.4	391.8	437.8	219.3-505.0
LDPE/$W_{200/37/6}$	200.0	464.9	386.9	436.4	230.9-499.0
LDPE/$W_{UN/20/10}$	-	461.2	417.0	449.1	224.4-502.0
LDPE/$W_{180/20/10}$	180.0	458.1	405.3	444.7	238.4-503.7
LDPE/$W_{200/20/10}$	200.0	462.7	402.3	443.0	242.6-497.7
LDPE/$W_{UN/37/10}$	-	467.2	367.2	435.4	219.7-508.0
LDPE/$W_{180/37/10}$	180.0	466.6	412.1	448.7	224.2-502.3
LDPE/$W_{200/37/10}$	200.0	465.1	383.9	440.9	219.3-509.5

Differential scanning calorimetry

The cooling and second heating DSC thermograms of the 37 wt% dry as-moulded and buried composites are presented in Figure 4.84. Data taken from these curves and those of 20 wt% are presented in Table 4.10. The melting and crystallisation behaviour of buried and dry as-moulded LDPE are similar. T_m, T_c and X_c showed no significant difference, implying that soil burial had no observable influence on the melting, crystallisation and the degree of crystallinity of LDPE. However, ΔH_m and $-\Delta H_c$ increased only slightly. On the other hand, values of T_c and T_m in the composites were also not significantly altered, but ΔH_m showed no identifiable trend in the buried samples relative to the dry as-moulded samples, irrespective of the MAPE level. This is in agreement with earlier findings where polypropylene blended with biodegradable additives and buried in an outdoor soil for one year period was found to exhibit no change in T_m [194]. In addition, a general increase in $-\Delta H_c$ was recorded in 37 wt% composites with 0% and 2% MAPE, indicating that higher energy was released during crystallisation. At higher MAPE content, these values remained constant or were slightly increased. Except in composites made from untreated wood containing lower MAPE levels where a decrease in X_c was observed after soil burial, no significant change in X_c was recorded in the buried composites, relative to the dry as-moulded composites. This is contrary to literature reports [195] where an increase in X_c was reported in outdoor buried HDPE/PP blends and is attributed to the degradation by soil burial of the amorphous rather than the crystalline region of the blends. Above all, heat treatment presented no observable trend apart from that which is established in DSC properties of the dry as-moulded composites.

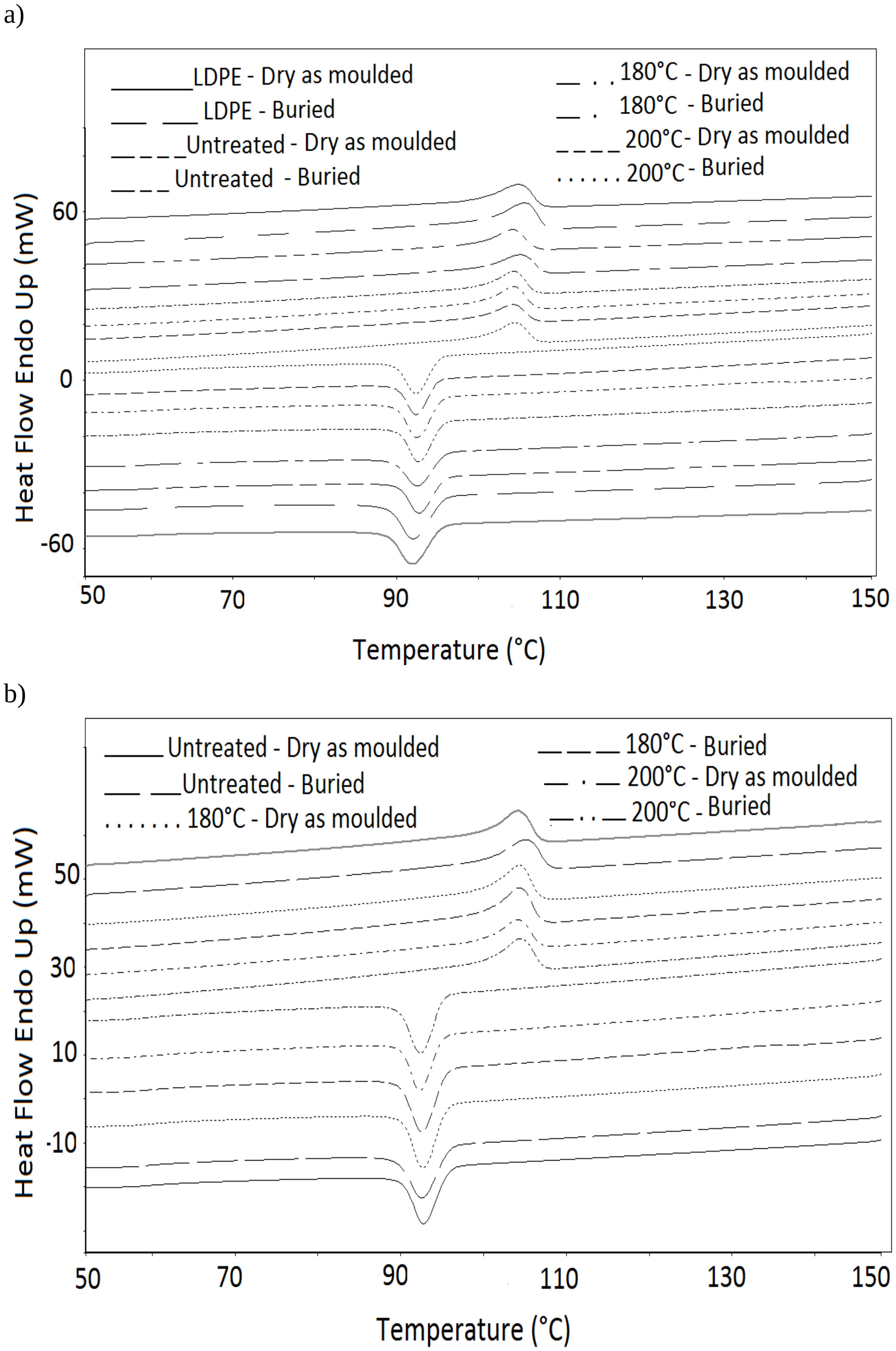


Figure 4.84: DSC curves of dry as-moulded and buried LDPE and composites containing 37 wt% untreated and heat-treated wood flour containing: a) 0% and b) 6% MAPE

Table 4.10: DSC data of buried samples

Sample	Treatment temperature (°C)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	$-\Delta H_c$ (J/g)	X_c (%)
LDPE	-	105.6	92.1	51.3	62.7	17.5
LDPE/W$_{\mathrm{UN/20/0}}$	-	104.6	92.7	44.1	48.2	18.8
LDPE/W$_{\mathrm{180/20/0}}$	180.0	104.2	92.6	41.6	52.5	17.7
LDPE/W$_{\mathrm{200/20/0}}$	200.0	104.9	92.8	42.0	48.5	17.9
LDPE/W$_{\mathrm{UN/37/0}}$	-	105.1	92.6	37.0	37.6	20.0
LDPE/W$_{\mathrm{180/37/0}}$	180.0	104.4	92.5	33.5	14.2	18.1
LDPE/W$_{\mathrm{200/37/0}}$	200.0	104.5	92.5	29.3	35.4	15.9
LDPE/W$_{\mathrm{UN/20/2}}$	-	104.1	93.8	33.2	44.1	14.2
LDPE/W$_{\mathrm{180/20/2}}$	180.0	104.1	93.7	32.5	42.9	13.9
LDPE/W$_{\mathrm{200/20/2}}$	200.0	104.1	93.8	33.5	39.7	14.3
LDPE/W$_{\mathrm{UN/37/2}}$	-	103.9	93.7	30.1	36.0	16.3
LDPE/W$_{\mathrm{180/37/2}}$	180.0	104.1	94.0	26.0	30.0	14.1
LDPE/W$_{\mathrm{200/37/2}}$	200.0	103.9	94.0	26.2	32.8	14.2
LDPE/W$_{\mathrm{UN/20/6}}$	-	103.5	94.8	28.0	41.9	11.9
LDPE/W$_{\mathrm{180/20/6}}$	180.0	103.6	94.8	29.7	40.8	12.7
LDPE/W$_{\mathrm{200/20/6}}$	200.0	103.1	95.3	26.9	39.2	11.5
LDPE/W$_{\mathrm{UN/37/6}}$	-	103.2	95.0	21.2	32.0	11.5
LDPE/W$_{\mathrm{180/37/6}}$	180.0	103.5	95.2	23.5	34.1	12.7
LDPE/W$_{\mathrm{200/37/6}}$	200.0	103.6	94.3	21.6	31.0	11.7
LDPE/W$_{\mathrm{UN/20/10}}$	-	102.9	94.7	20.9	38.1	8.9
LDPE/W$_{\mathrm{180/20/10}}$	180.0	103.1	94.5	21.8	39.6	9.3
LDPE/W$_{\mathrm{200/20/10}}$	200.0	103.1	94.5	23.6	32.6	10.1
LDPE/W$_{\mathrm{UN/37/10}}$	-	103.2	94.6	16.4	34.3	8.9
LDPE/W$_{\mathrm{180/37/10}}$	180.0	102.8	94.9	17.9	34.3	9.7
LDPE/W$_{\mathrm{200/37/10}}$	200.0	102.9	94.6	17.6	31.7	9.5

4.3.2.3 Dynamic mechanical analysis, DMA

Storage modulus

Figure 4.85 presents the storage modulus of dry as-moulded and buried samples. Data extracted from these curves are presented in Table 4.11. From the figure, the E′ of the buried LDPE is lower than the dry as-moulded sample. This is rather odd because the hydrophobic character of LDPE should inhibit fungal growth and the resultant effect on the E′. Comparing Table 4.11 with Table 4.4 (page 80), E′ values decreased generally in buried composites, relative to the dry as-moulded samples. Despite the general decrease in E′ of buried composites, heat treatment of wood flour seemed to have enhanced the E′ of buried samples more than the untreated wood flour, with composites made from wood flour treated at 200°C showing the highest resistance to the elements of soil burial. This is shown in the values of $E'_{25^\circ C}$ and $E'_{-100^\circ C}$. Interfacial degradation, possibly due to microbial attack on the samples might have lowered the E′ values. In addition, better wetting of composites made from heat-treated wood flour, resulting in improved interfacial adhesion might have reduced the moisture requirement for microbial growth, thereby lowering the possible effect of fungal colonisation. However, no identifiable trend (in E′) could be established with the incorporation of MAPE (Figure 4.85b).

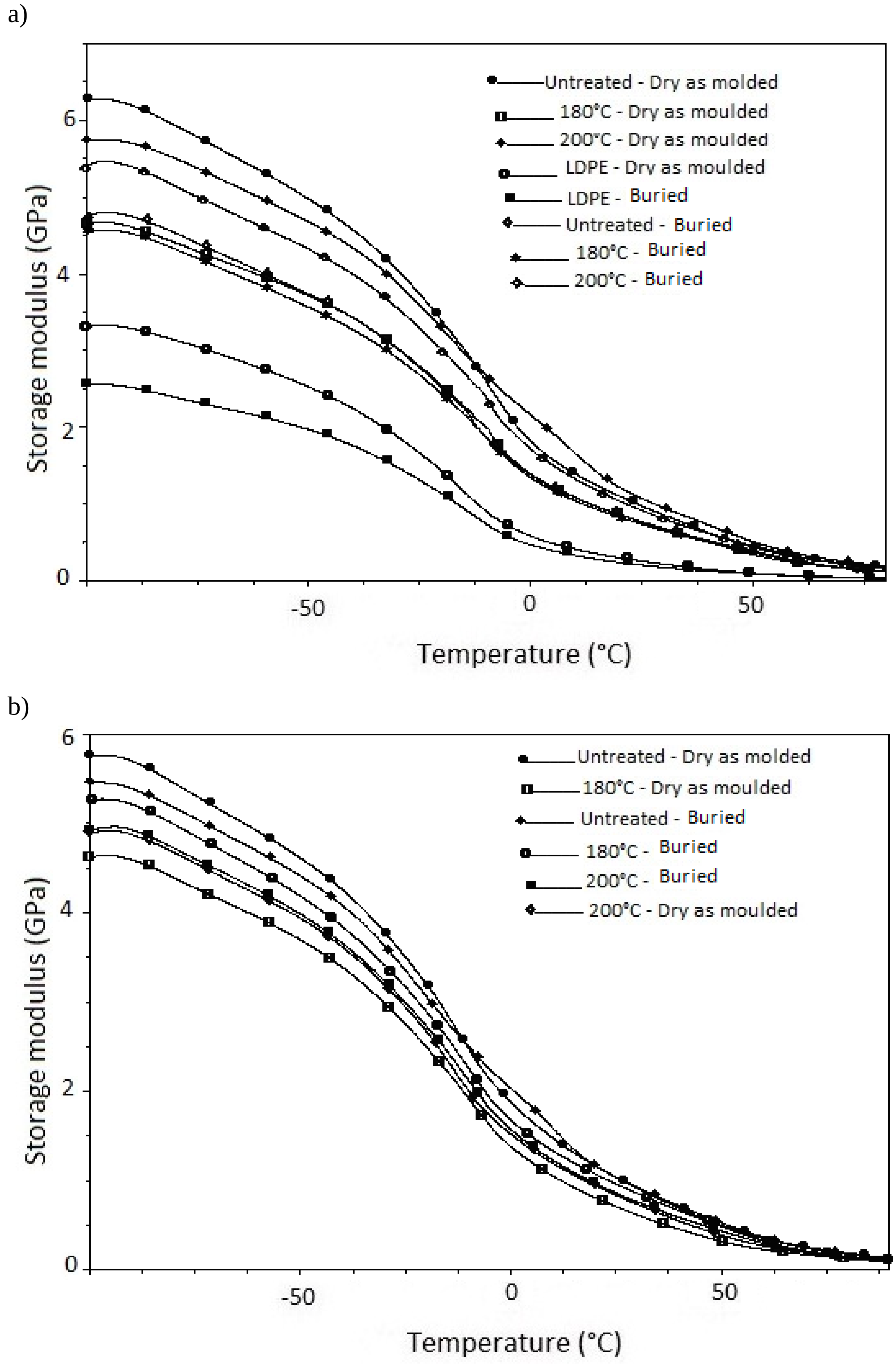


Figure 4.85: Storage modulus curves of dry as-moulded and buried 37 wt% untreated and heat-treated composites containing: a) 0% and b) 6% MAPE

Loss modulus

The variation of loss modulus with temperature in buried heat-treated and untreated WTC with varying wood flour contents and treatment temperatures are presented in Figure 4.86. Data extracted from these curves are also presented in Table 4.11. The values of $T_{\beta}^{E''}$ remain relatively constant in buried samples when compared with the dry as-moulded samples. This may indicate that outdoor soil burial had no observable effect on the segmental mobility of the neat LDPE and the composites. Nevertheless, $E''_{\max}$ values reduced in the buried samples relative to the dry as-moulded samples. The neat LDPE exhibited a decrement, to the tune of 21%, after soil burial. Once again, cogent explanation could not be given for this trend because LDPE is hydrophobic and no signs of severe fungal infestation was observed (Figure 4.81, page 185). In the same manner, the composites show varying levels of reduction in $E''_{\max}$ with soil burial, where composites made from untreated wood flour showing the highest decrement. $E''_{\max}$ values decreased from 200 MPa in dry as-moulded composites loaded with 20 wt% untreated wood flour to 140 MPa when subjected to soil burial, while in the composites containing 37 wt% untreated wood flour, $E''_{\max}$ reduce from 237 MPa to 180 MPa upon soil burial. However, in the heat-treated WTC, $E''_{\max}$ values are only marginally reduced except in composites loaded with 20 wt% wood flour treated at 180°C which displayed a decrement to the tune of 18%. The other heat-treated WTC only showed about 6% reduction in $E''_{\max}$ after soil burial. This trend is also repeated in the values of $E''_{25^{\circ}\mathrm{C}}$. Reduction in E'' values of the buried composites relative to the dry as-moulded samples may indicate increased flexibility of the composites with soil burial, as a result of fungal attack that may have led to increased segmental mobility of the polymer chains.

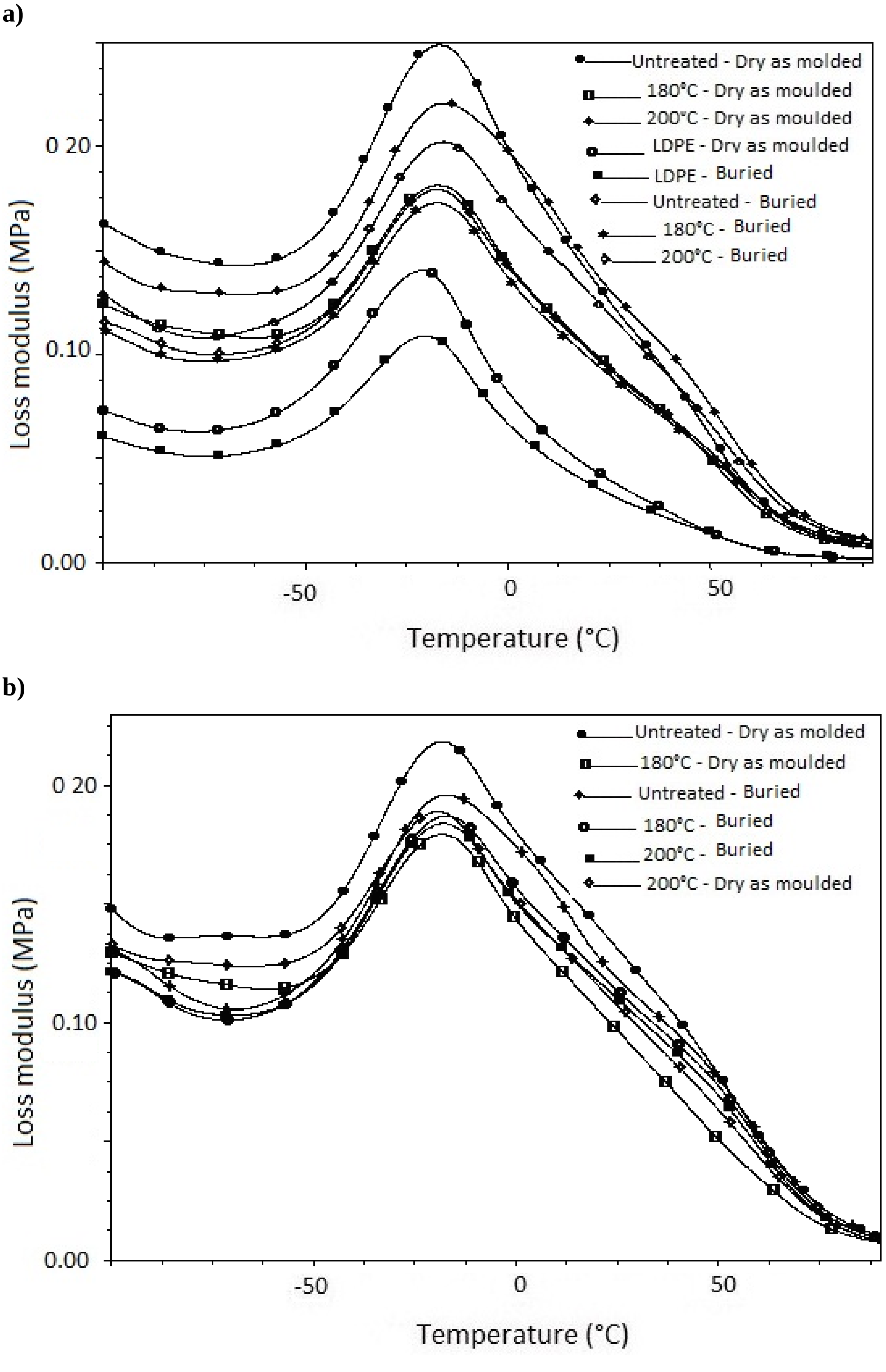


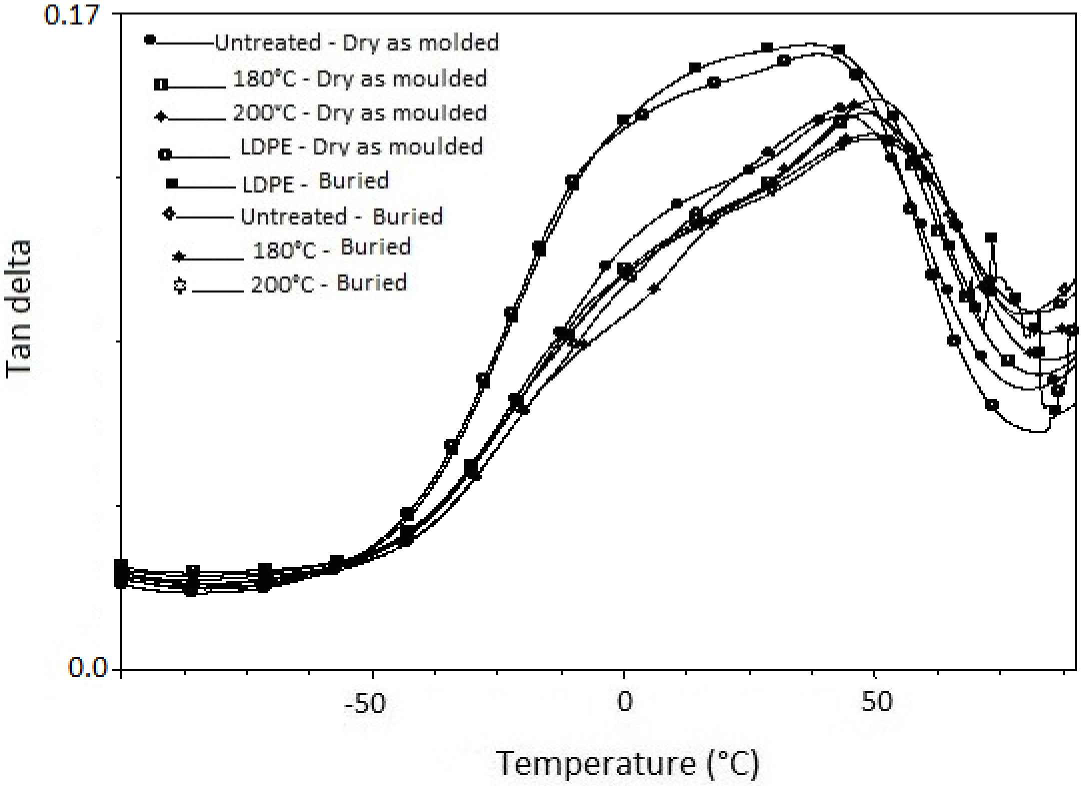
Figure 4.86: Loss modulus of dry as-moulded and buried LDPE and 37 wt% composites with: a) 0% and b) 6% MAPE

Although it has been suggested [143] that reduction of E'' values may mean the presence of genuine interface, it is not clear if this trend is due to the result of improved interface as a degree of interfacial degradation is expected with soil burial. Furthermore, addition of MAPE presents no identifiable trend (Figure 4.86b) in E'' values of the dry as-moulded samples following soil burial.

Tan delta

Tan delta curves of treated and untreated WTC containing 37 wt% wood content is presented in Figure 4.87. Although most of the curves (apart from the LDPE) overlapped, Table 4.11 presents the $tan\ \delta$ values. Soil burial has no observable effect on $tan\ \delta_{max}$, $tan\ \delta_{25°C}$ and temperature at $tan\ \delta_{max}$ as the values of the neat LDPE and composites show no appreciable change with soil burial. However, $W_{\sqrt{2}}$ values present an increasing trend in the composites with burial, especially at high wood content and this may indicate increased damping characteristics of the composites upon burial in soil. The increment in $W_{\sqrt{2}}$ seems somehow consistent (approximately 17%) in the treated and untreated WTC without compatibiliser. Increased damping might again be attributed to interfacial degradation by elements of the soil environment. Addition of 2% MAPE exhibited the same behaviour as the uncompatibilised composites. However, as the MAPE content increases, no identifiable trend could be established (Figure 4.87b).

a)



b)

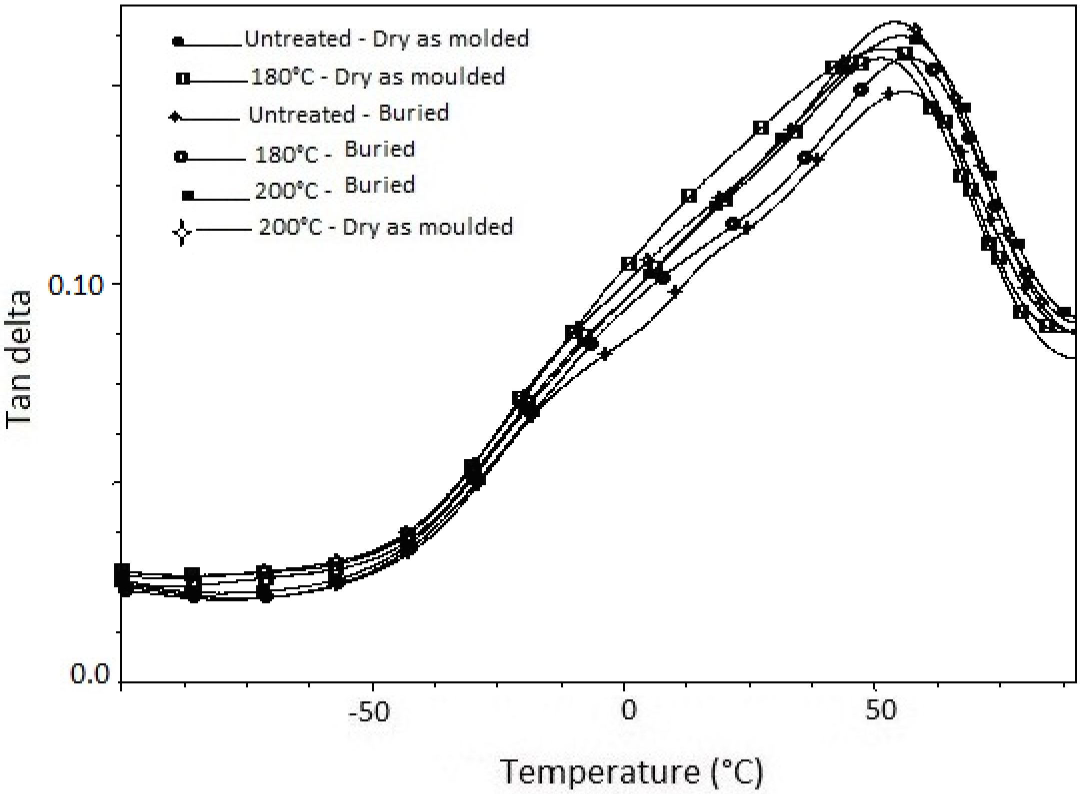


Figure 4.87: Tan delta of dry as-moulded and buried LDPE and 37 wt% composites containing: a) 0% and b) 6% MAPE

Table 4.11: DMA data of buried samples

Sample	Wood treatment temperature (°C)	$Tan\ \delta$				Storage modulus, E'		Loss modulus, E"		
		$Tan\ \delta_{max}$	Temperature at $Tan\ \delta_{max}$ (℃)	$W_{\sqrt{2}}$	$Tan\ \delta_{25°C}$	$E'_{25°C}$ (GPa)	$E'_{-100°C}$ (GPa)	$E''_{25°C}$ (MPa)	$T_{\beta}^{E''}$ (℃)	E''_{max} (MPa)
LDPE	-	0.16	37.7	76.9	0.16	0.20	2.6	32.0	-20.3	110.0
LDPE/$W_{UN/20/0}$	-	0.16	43.2	71.4	0.15	0.42	3.5	60.8	-19.2	140.0
LDPE/$W_{180/20/0}$	180.0	0.15	44.7	77.7	0.14	0.44	3.5	60.0	-18.3	140.0
LDPE/$W_{200/20/0}$	200.0	0.15	47.0	68.7	0.14	0.55	4.1	73.0	-18.3	160.0
LDPE/$W_{UN/37/0}$	-	0.14	49.1	76.7	0.12	0.76	4.8	91.7	-16.8	180.0
LDPE/$W_{180/37/0}$	180.0	0.14	49.9	76.3	0.12	0.73	4.6	89.0	-17.1	170.0
LDPE/$W_{200/37/0}$	200.0	0.15	45.5	68.9	0.13	0.91	5.4	119.0	-15.5	200.0
LDPE/$W_{UN/20/2}$	-	0.15	49.8	78.7	0.13	0.44	3.6	60.0	-19.5	140.0
LDPE/$W_{180/20/2}$	180.0	0.16	50.3	71.8	0.14	0.59	4.1	79.0	-17.7	160.0
LDPE/$W_{200/20/2}$	200.0	0.16	53.2	70.1	0.14	0.62	4.9	83.1	-18.5	165.0
LDPE/$W_{UN/37/2}$	-	0.15	49.8	67.4	0.13	0.73	4.7	95.2	-18.6	180.0
LDPE/$W_{180/37/2}$	180.0	0.15	54.4	66.4	0.12	1.05	5.7	126.0	-16.4	200.0
LDPE/$W_{200/37/2}$	200.0	0.15	53.1	61.6	0.12	1.06	5.7	123.0	-16.0	200.0
LDPE/$W_{UN/37/6}$	-	0.15	56.2	61.4	0.11	1.03	5.4	118.0	-16.9	200.0
LDPE/$W_{180/37/6}$	180.0	0.16	56.8	59.2	0.12	0.95	5.2	113.0	-17.7	190.0
LDPE/$W_{200/37/6}$	200.0	0.16	55.6	62.1	0.13	0.86	4.9	110.0	-17.8	180.0
LDPE/$W_{UN/37/10}$	-	0.16	59.2	61.8	0.12	1.00	5.5	116.0	-18.9	200.0
LDPE/$W_{180/37/10}$	180.0	0.16	58.6	59.5	0.12	0.87	4.9	102.0	-19.2	180.0
LDPE/$W_{200/37/10}$	200.0	0.16	58.1	69.8	0.13	0.85	4.9	106.0	-18.6	170.0

4.3.2.4 Mechanical properties

Polymer surfaces are usually physically weak and readily disintegrate under mild pressure after biological attack [196]. It has been shown that the changes in the mechanical properties of LDPE films by soil burial occur in three stages comprising of: a first period of rapid change, followed by a period of slow change, and finally, a third period of rapid change [197]. Furthermore, deterioration of mechanical properties could result from attack by micro organisms or from existing soil chemistry, which could cause hydrolysis and oxidation. This soil chemistry is extensively controlled by the availability of oxygen and microbial action [189]. Therefore, any observable mechanical deterioration of the physical structure of a moulded polymer would then, be a result of the physical, chemical, or biological impacts; either individually or jointly, in a synergistic manner (oxidation, heat, radicals, radiations, acids, solvents enzymes etc). However, for the inert PE, enzymatic cleavage of C-C bond resulting from a true enzymatic degradation of a long, straight olefin chain should not be expected since such endo-enzymes (n-alkane C-C endo-hydrolase) do not occur in nature. On the other hand, fungal hyphea can penertrate the cellulose rich wood in WTC and cause mechanical deterioration of the material through cracking due to biophysical or biochemical actions (Figure 4.82a) [198]. It is a known fact that strength properties are the most sensitive indicators of fungal decay in wood. However, this concept does not necessarily apply in WTC. Furthermore, wood filler tends to increase the stiffness of WTC and may therefore be a useful indicator of fungal decay in WTC [192] when changes in mechanical properties are measured after WTC is exposed to fungal environment. In this section, the mechanical properties of the buried samples are examined and compared with the dry as-moulded samples to ascertain the effect of heat treatment and MAPE level on the resistance of the composites to mechanical deterioration. It should be mentioned that detailed biological actions leading to the properties observed were not conducted.

Tensile properties

For most practical applications envisaged for WTC, in contact with soil, tensile properties are the most relevant practical criteria. Therefore, a study of the behaviour of buried composites during tensile testing is useful in determining the usefulness of the material.

Tensile modulus

The tensile modulus of the dry as-moulded and buried samples is given in Figure 4.88. No depreciation in tensile modulus, upon soil burial, was seen in the neat LDPE. Tensile modulii values of 0.231 GPa and 0.232 GPa were obtained for the dry as-moulded and buried LDPE respectively. It is possible that the hydrophobic nature of LDPE might have prevented fungal activities (Figure 4.81, page 185) that could have altered the tensile modulus. However, the tensile moduli of the composites decreased with soil burial, to various extents. This is closely related to the cracks on the surface of the composites due to fungal activities (Figure 4.82, page 186). Although the decrease was largely marginal in all the composites studied, untreated WTC presented the highest reduction in tensile modulus (7%). It has been suggested that biodegradation of the natural components in WTC could lead to increased porosity, thereby facilitating the access of free oxygen, enzymes (produced by microorganisms) and free radicals into the polymer bulk, significantly promoting further degradation step [199]. This almost certainly reduces the stiffness of the material, resulting in lower modulus. Incorporation of MAPE did not improve the tensile modulus of buried samples (Figure 4.89). This is in line with earlier reports where addition of compatibiliser to blends of

LDPE/starch showed no appreciable influence on the biodegradation of the samples [200].

Tensile strength

The buried LDPE has a tensile strength value of 9.16 MPa, similar to that recorded in the dry as-moulded sample (9.14 MPa). Figure 4.90 presents the tensile strength of the dry as-moulded and buried composites as a function of wood content and heat treatment. A general improvement in tensile strength was observed in all the composites studied, irrespective of the wood content and treatment temperature. It is expected that tensile properties of the composites should deteriorate with outdoor soil burial [189]. However, it has been reported [201] that short term exposure to wood decay fungi may improve the interfacial adhesion and reinforcement of WTC, attributable to the reinforcing effect of the fungal hyphae present in the interfacial gaps between wood filler and polymer matrix. Therefore, it is possible that the period of exposure (9 months) of this material was not sufficient to cause the expected decline in tensile strength, a consequence of the observed trend. Conversely, tensile strength is found to decrease with soil burial in compatibilised samples (Figure 4.91). The possibility of improved interfacial adhesion in compatibilised composites could mean that hyphae growth, which is alleged to result in improved reinforcement on short term fungal exposure, may be absent (Figure 4.92).

Tensile strain

Again, the tensile strain of the buried neat LDPE (90.89%) was relatively the same as the dry as-moulded sample (91.41%). Figure 4.93 presents the tensile strain of the heat-treated and untreated composites with varying wood content. The tensile strain of buried samples was generally higher than the dry as-moulded samples. This may be a result of the exposure to the degradative elements in the soil. However, no particular trend was observed with respect to treatment temperature. Incorporation of MAPE reduced the tensile strain of the composites (Figure 4.94).

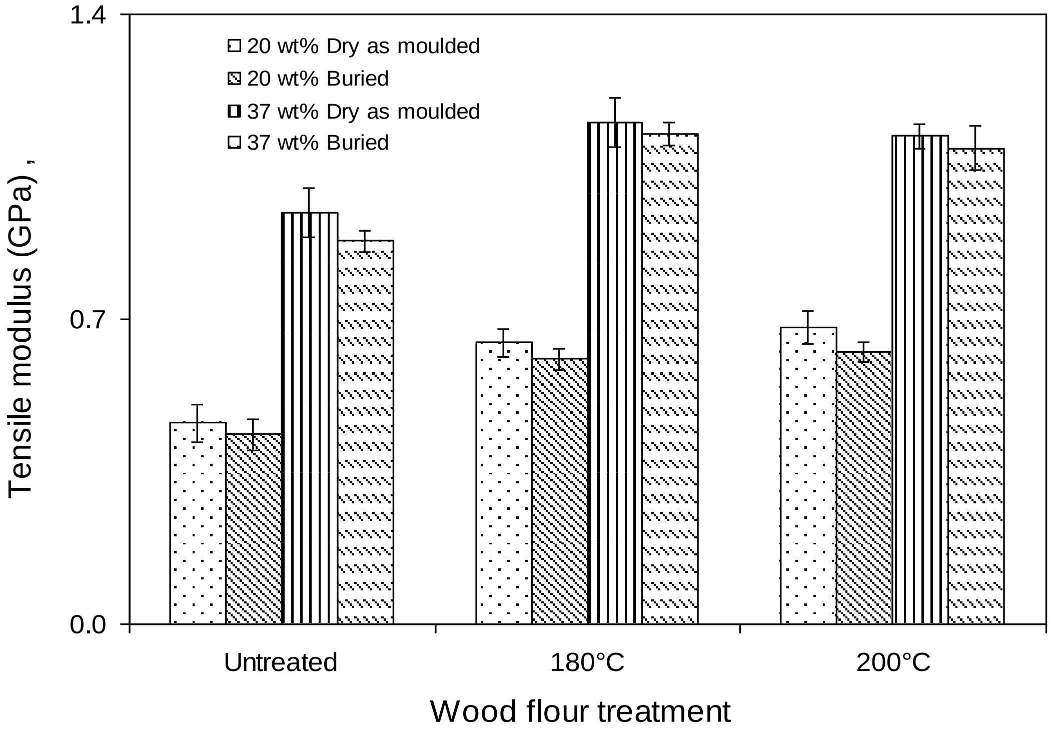


Figure 4.88: Tensile modulus of dry as-moulded and buried composites as a function of wood content and heat treatment

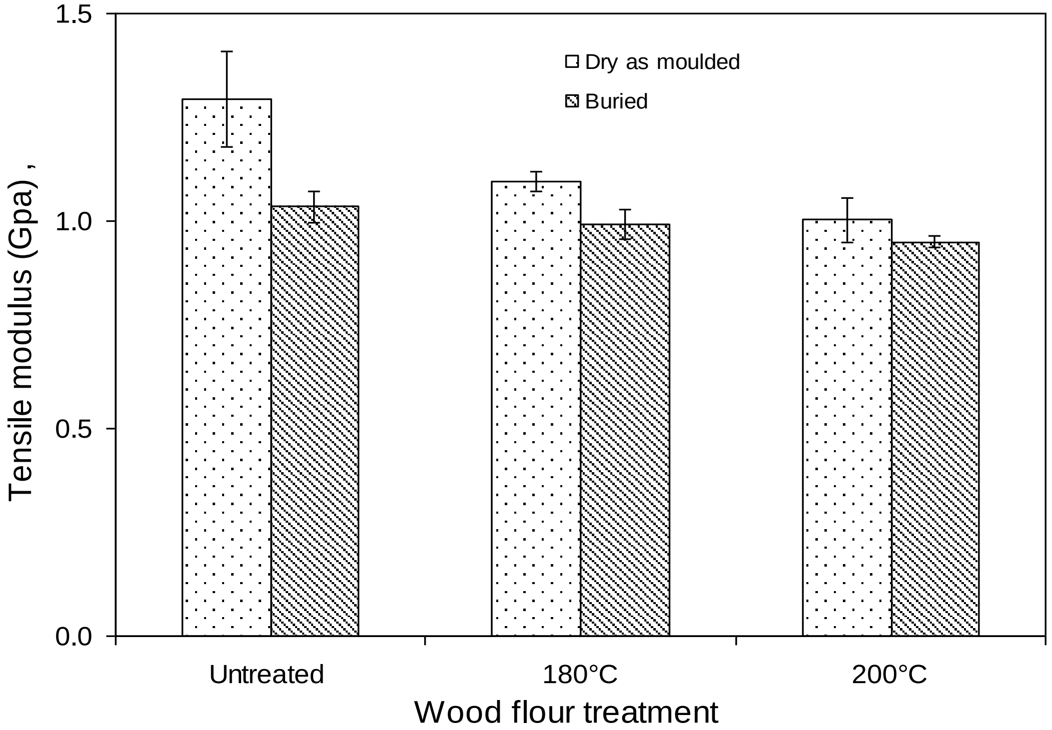


Figure 4.89: Tensile modulus of 37 wt% buried and dry as-moulded composites with 6% MAPE

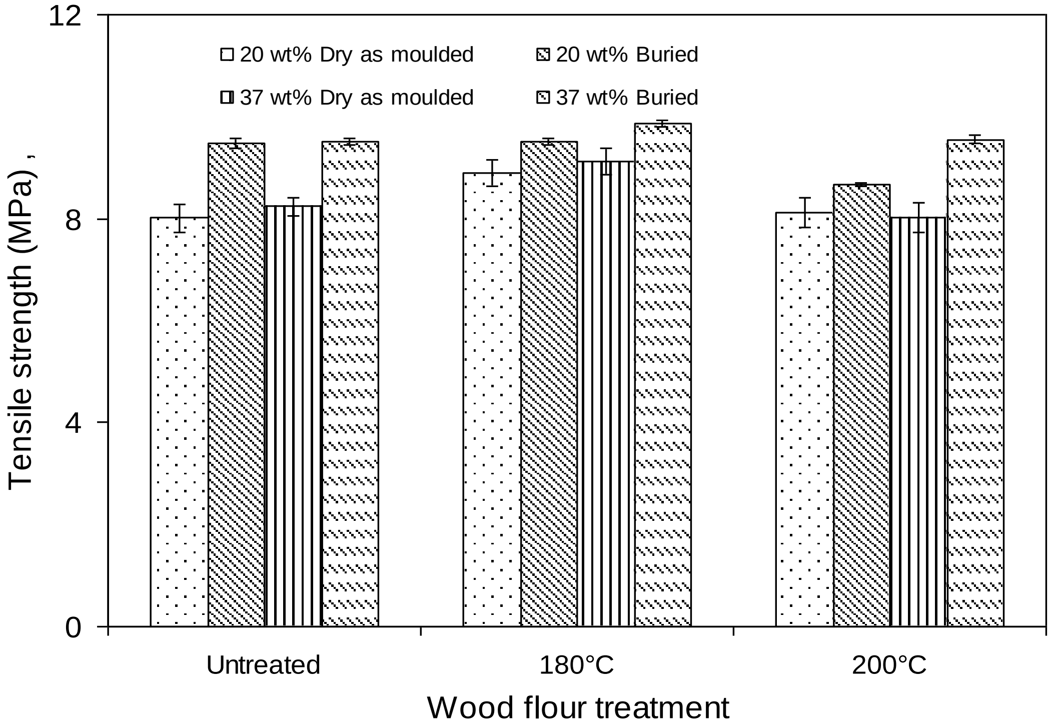


Figure 4.90: Tensile strength of dry as-moulded and buried composites as a function of wood content and heat treatment

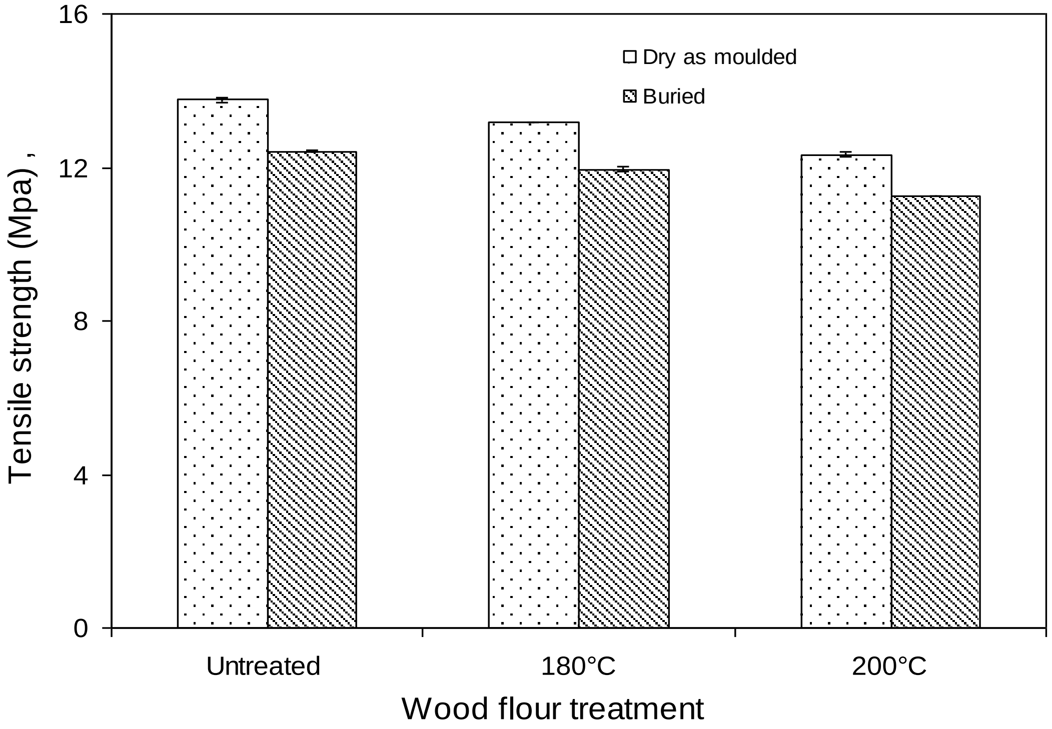


Figure 4.91: Tensile strength of 37 wt% buried and dry as-moulded composites with 6% MAPE

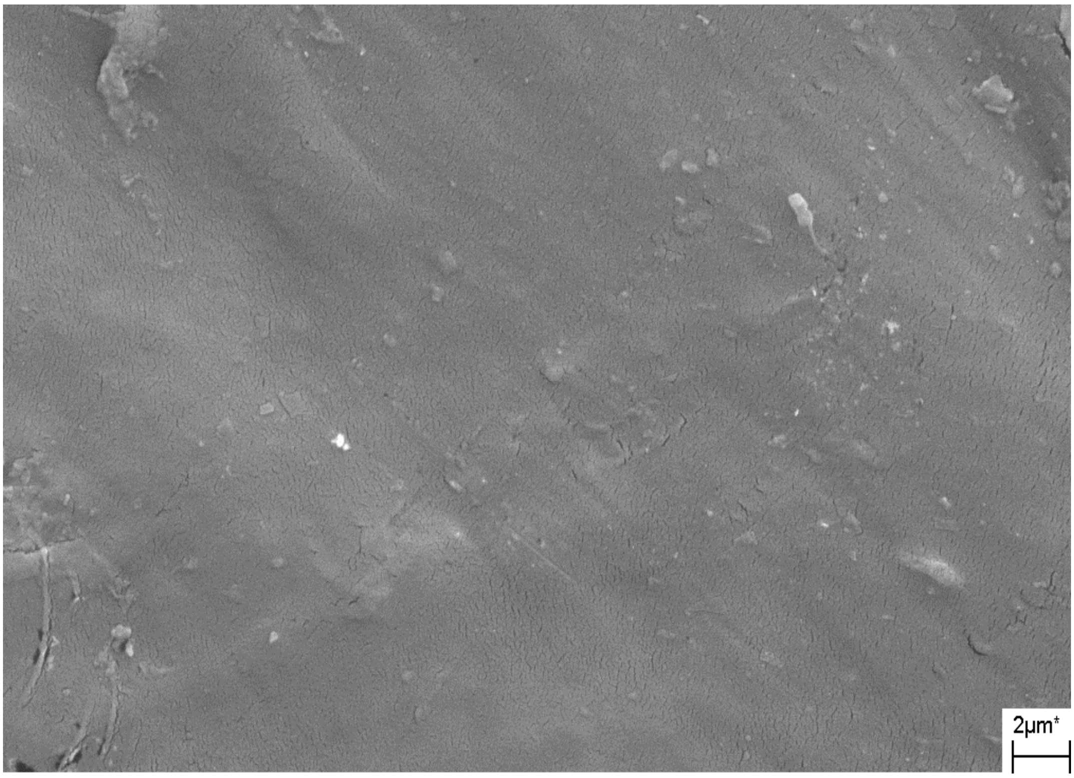


Figure 4.92: SEM micrograph of surface of buried 37 wt% untreated wood composite containing 6% MAPE showing sparse fungal growth

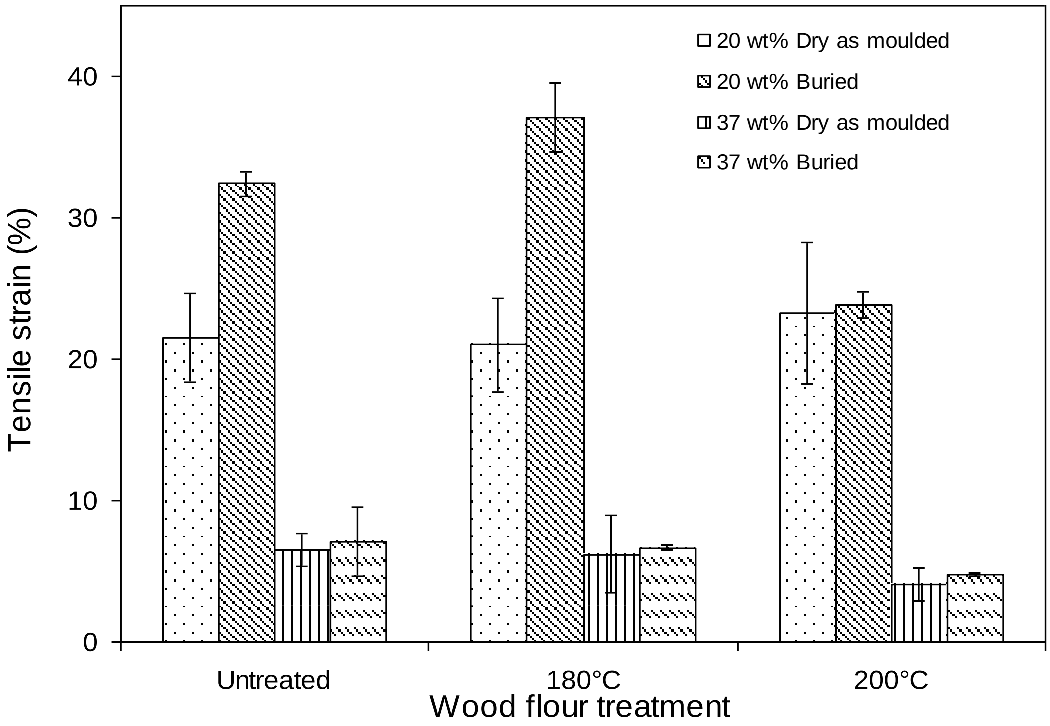


Figure 4.93: Tensile strain of dry as-moulded and buried composites as a function of wood content and heat treatment

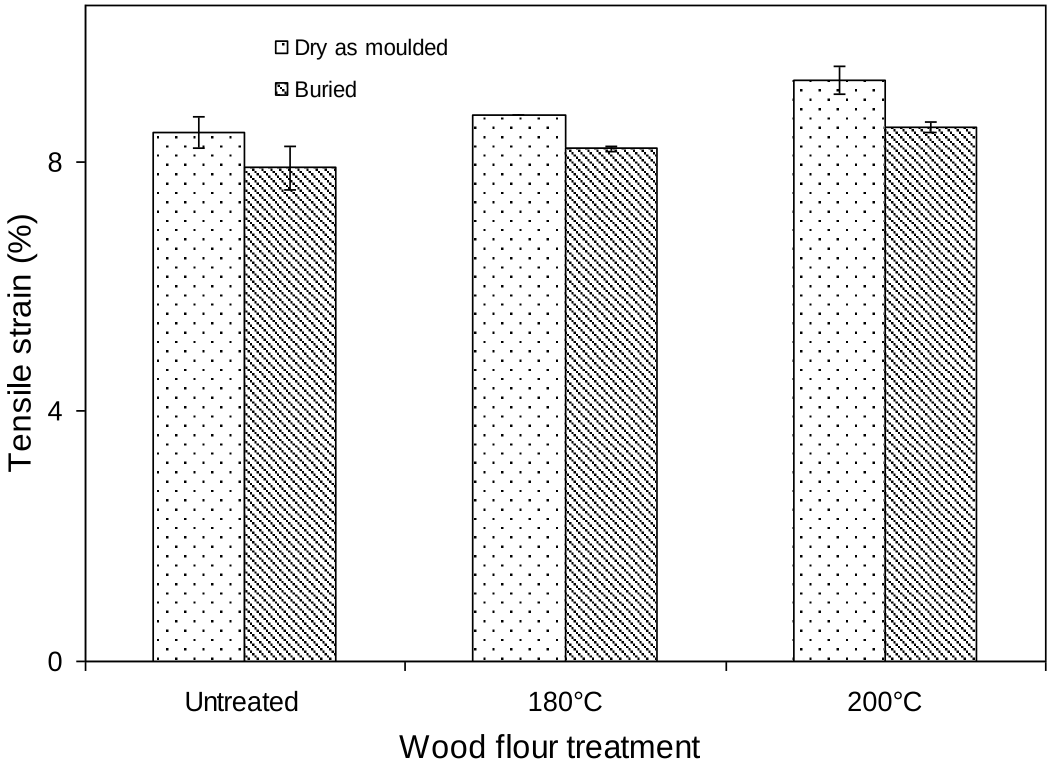


Figure 4.94: Tensile strain of 37 wt% buried and dry as-moulded composites with 6% MAPE

Flexural properties

Flexural modulus

Figure 4.95 presents the flexural modulus of the composites as a function of wood content and treatment temperature. No significant change in the flexural modulus of LDPE was observed, following out door burial. Value of 0.121 GPa was obtained for the dry as-moulded LDPE while 0.122 GPa is recorded for the buried sample. As with tensile modulus, there was a general decrease in flexural modulus of the buried composites, relative to the dry as-moulded composites. Again, buried composites made from untreated wood flour displayed a more prominent reduction when compared to the heat-treated composites. In the composites containing 37 wt% wood flour, a 30% decrease is observed in the untreated WTC, while a 9% decrement was recorded in composites containing 180°C treated wood flour. Composites made from 200°C treated wood flour showed no observable changes. As mentioned before, improved compatibility of composites made from heat-treated wood flour, relative to the untreated wood flour, which offered better resistance to fungal decay, may be accountable for this observation. Similar observations were reported in compression moulded untreated wood flour polyethylene composites exposed to the brown-rot fungus (*Gleoophyllum traebum*) for a period of 12 weeks [193]. In addition, incorporation of MAPE showed the same trend observed in the uncompatibilised system, although the rate of decrease was lower in the untreated WTC (Figure 4.96).

Flexural strength

The buried LDPE showed the same flexural strength value (7.15 MPa) as the dry as-moulded sample, indicating that soil burial did not change the flexural strength of the LDPE. In Figure 4.97, the flexural strength of dry as-moulded and buried composites are presented. Flexural strength of the buried composites reduced slightly, when compared to the dry as-moulded composites. Once more, the effect of the heat-treated wood flour in resisting the effect of fungal activities was more pronounced. Addition of MAPE did not improve the flexural strength of the buried composites (Figure 4.98).

Flexural displacement

The variation of flexural displacement of the dry as-moulded and buried composites is shown in Figure 4.99. Flexural displacement was generally higher in buried samples than the dry as-moulded samples. This is expected because interfacial degradation as a result of fungal activities should increase the displacement at yield of the composites. This was also observed in the composites containing MAPE (Figure 4.100).

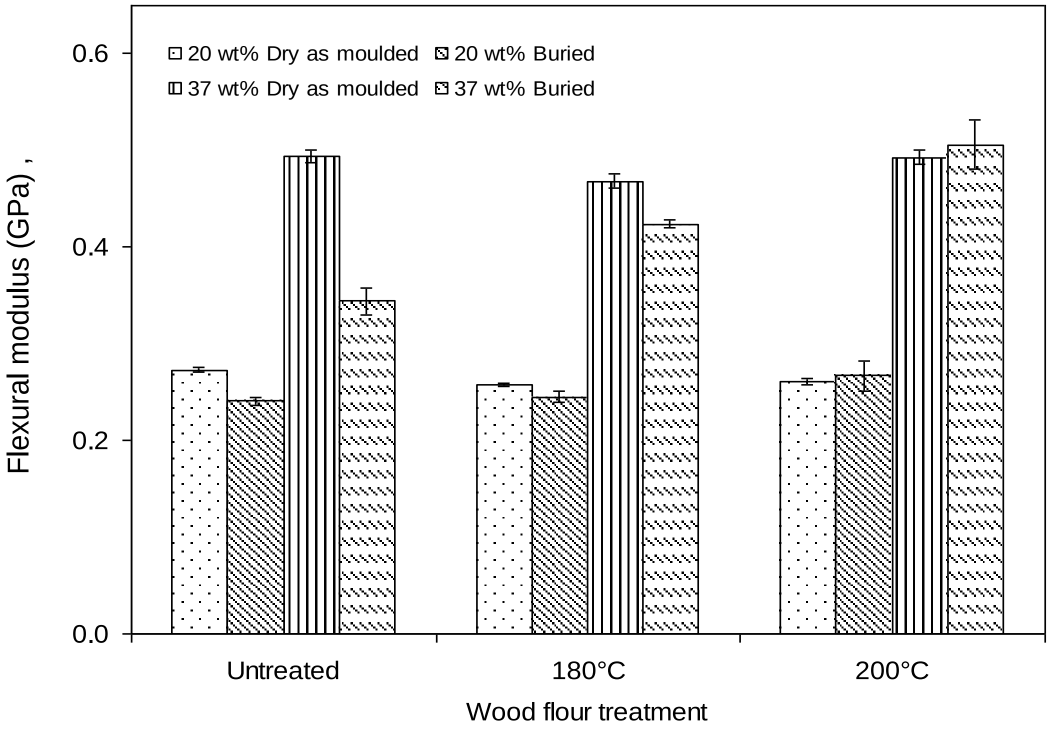


Figure 4.95: Flexural modulus of dry as-moulded and buried composites as a function of wood content and heat treatment

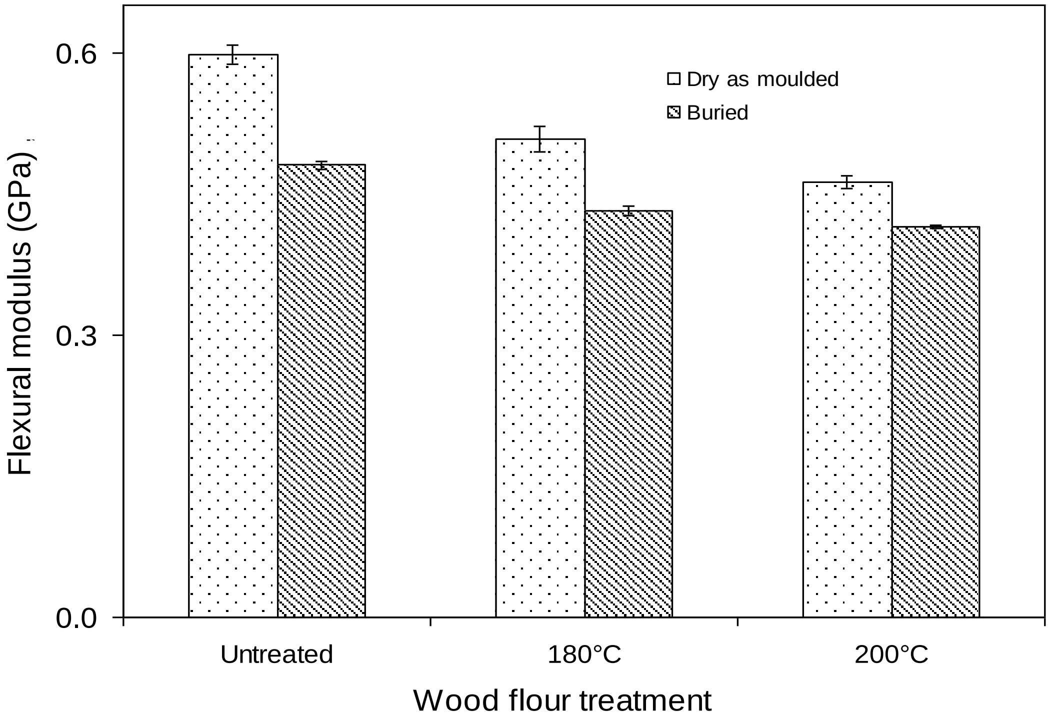


Figure 4.96: Flexural modulus of 37 wt% dry as-moulded and buried composites with 6% MAPE

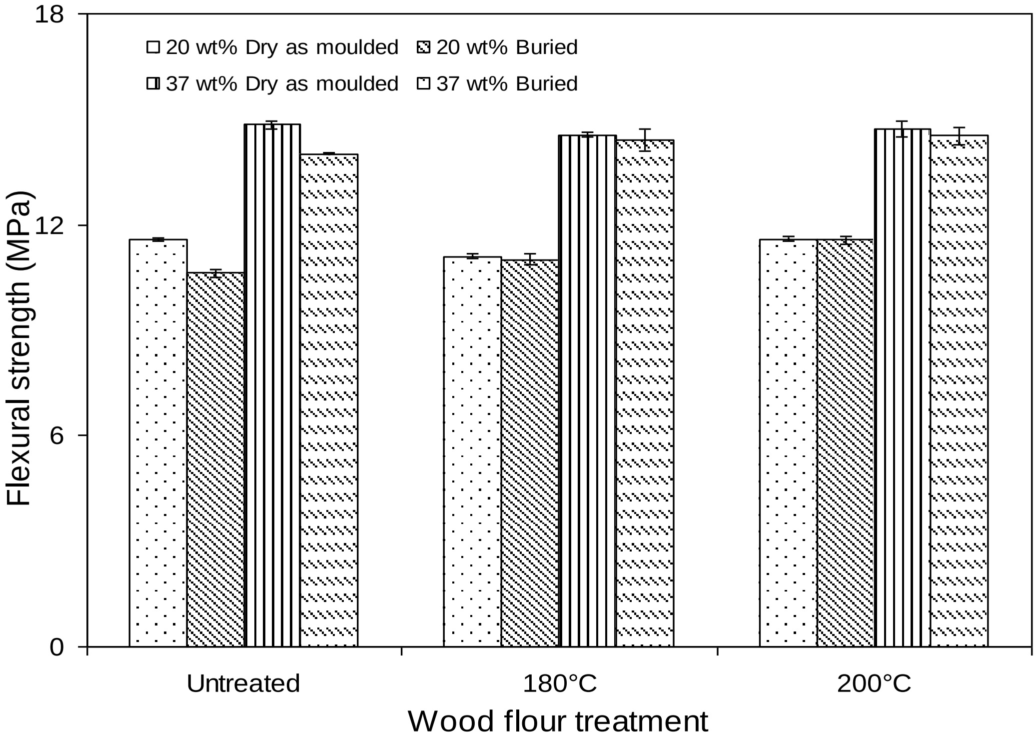


Figure 4.97: Flexural strength of dry as-moulded and buried composites as a function of wood content and heat treatment

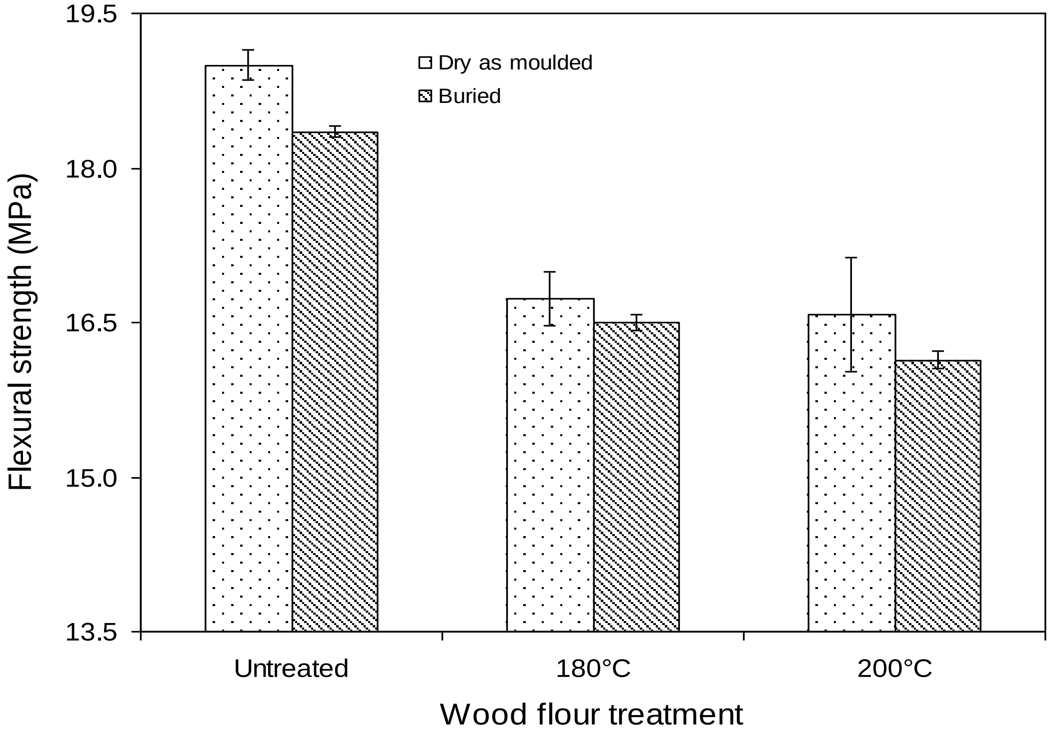


Figure 4.98: Flexural strength of 37 wt% dry as-moulded and buried composites with 6% MAPE

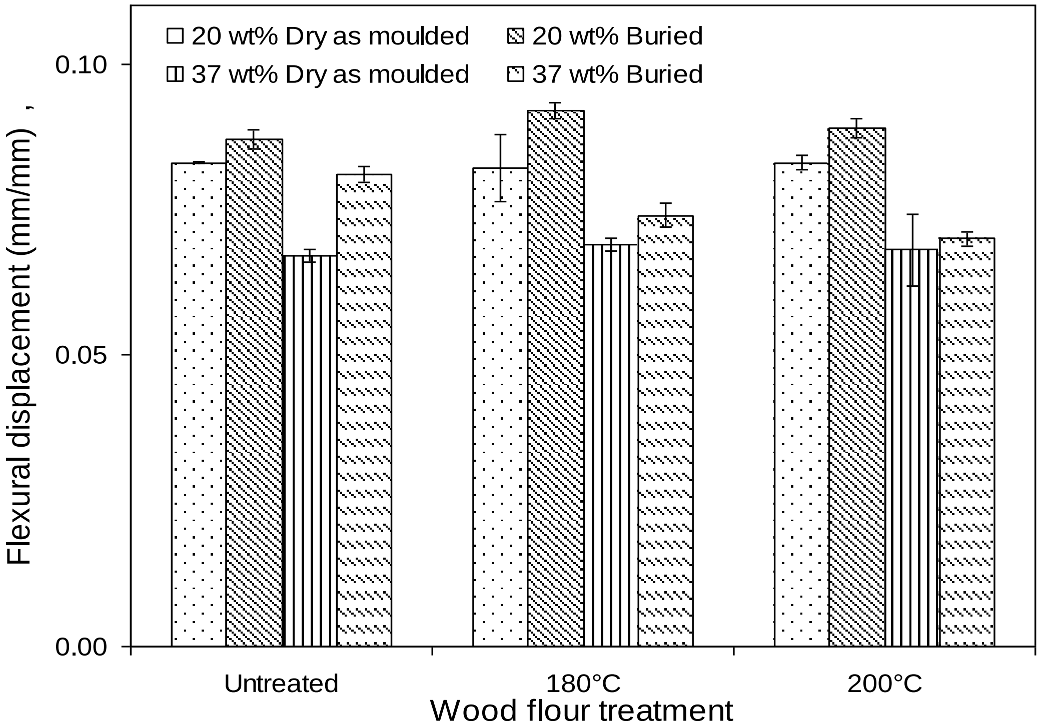


Figure 4.99: Flexural displacement of dry as-moulded and buried composites as a function of wood content and heat treatment

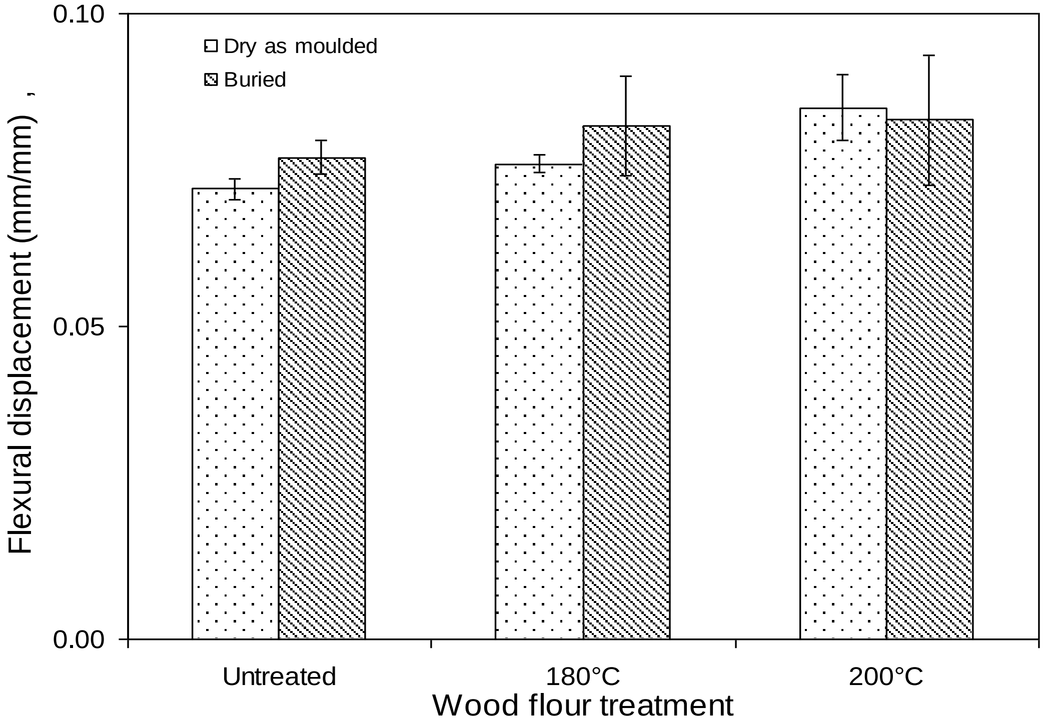


Figure 4.100: Flexural displacement of 37 wt% dry as-moulded and buried composites with 6% MAPE

Impact properties

Peak load, P

There is a slight reduction in the *P* value of LDPE after soil burial. Values of 282.0 N, 233.0 N, 193.1 N and 145.4 N were obtained in the buried samples while 266.6 N, 225.3 N, 184.5 N and 137.4 N are recorded in the dry as-moulded samples for a/D ratios of 0.1, 0.2, 0.3 and 0.4, respectively. The fact that there is no visible degradation in the LDPE may account for this observation. As was observed in the wet composites, the peak load of the buried composites was higher than those of the dry as-moulded ones (Figure 4.101). This increase is higher with increasing wood content and treatment temperature. This is rather surprising as it would mean that the ageing process, due to soil burial somewhat toughened the composites. Rather unexpected, is the highest values displayed by the WTC with high wood flour loading. It has been observed that the major sources of toughness in composites, consisting of ductile matrix and particle reinforcements, are matrix-related, including energy dissipation attributable to shear yielding of the matrix. Also, the interface-related toughening mechanism may augment the toughness contributions credited to the matrix-related composites under favourable conditions [202, 203]. With the possibility of hyphea growth at the interface, as mentioned before and the chances that this could further reinforce the composites system, a resultant increase in P is expected. The addition of MAPE did not influence P appreciably in the buried composites, relative to the dry as-moulded ones (Figure 4.102).

Critical stress intensity factor, K_c

The K_c values of LDPE remain essentially the same after burial. Values of 1.67 MPa.m$^{0.5}$ and 1.65 MPa.m$^{0.5}$ were obtained for the dry as-moulded and buried samples respectively. Again, this is an indication that soil burial had no significant deteriorative effect on LDPE. Meanwhile, the K_c values of the composites changed to various extents, as presented in Figure 4.103. As observed with P, K_c increased with wood content and treatment temperature. Once again, this result is unanticipated as it would imply that soil burial, which is expected to degrade the composites and rendered them more brittle, actually led to increases in fracture toughness. However, considering the amount of water absorbed during soil burial (Appendix A3), it is possible that, as with the moisture saturated samples, the composite system became pliable, thereby increasing the K_c. Similar results were obtained in aged poly(hydroxybutyrate) [204]. The addition of MAPE presents no identifiable trend (Figure 4.104).

Energy to failure, W

In the neat LDPE, W was insignificantly lower in the buried samples when compared to the dry as-moulded samples. The dry as-moulded samples recorded values of 4.62 J, 3.48 J, 3.17 J and 2.13 J, while 4.63 J, 3.47 J, 2.98 J and 2.06 J were recorded in the buried samples for a/D ratios 0.1, 0.2, 0.3 and 0.4 respectively. Again, this indicated that LDPE was not severely degraded with soil burial. However, the composites showed a slight increase in *W* with soil burial, especially at lower wood content (Figure 4.105). A possible reasoning for this trend is that although wood flour is degradable, once it is compounded with LDPE, the degradability tendency will be lowered. This is because, at lower wood content (20 wt%), the wood particles are encapsulated by the LDPE and protected from attack by micro organisms. However, as the wood flour loading increased (37 wt%), complete wetting by the matrix was not be possible as some wood particles may be present, close to (or on) the surface of the composites. Therefore, the response of WTC containing high wood content to deterioration in mechanical properties, is expectedly higher than with lower wood flour loading. Furthermore, in composites containing 37 wt%, no observable changes in *W* were seen in the buried samples relative to the dry as-moulded samples. Also, no obvious difference in *W* was observed in the buried composites when compared with the dry samples, as far as heat treatment temperature is concerned. The trend in the coupled composites is similar to those of the uncoupled composites (Figure 4.106).

Critical strain energy release rate, G_c

The value of G_c in the neat LDPE had not changed appreciably with soil burial. The dry as-moulded LDPE, presented a G_c of 96.58 kJ.m^{-2}, while 95.70 kJ.m^{-2} was recorded for the buried sample. Again, this indicated that LDPE had not degraded with soil burial. As observed in the *W*, G_c values of composites containing 20 wt% wood flour did not change significantly with soil burial (Figure 4.107). The same reasoning given in *W*, can be applied here. On the other hand, G_c at fracture decreased as expected, signifying the fact that there was a reduction in fracture resistance with soil burial. Conversely, the G_c of buried composites containing MAPE is higher than their dry as-moulded counterparts, showing that with MAPE, the composites were able to retain the impact energy (Figure 4.108).

Due to its non-suitability in structural applications, the LDPE composites prepared in this study can be used as flower pots or for other domestic uses. Thus, its ability to retain its impact strength when in contact with soil, is very pertinent. Therefore, reduction of G_c values of uncoupled composites with soil burial confirmed that the ageing process in soil is detrimental.

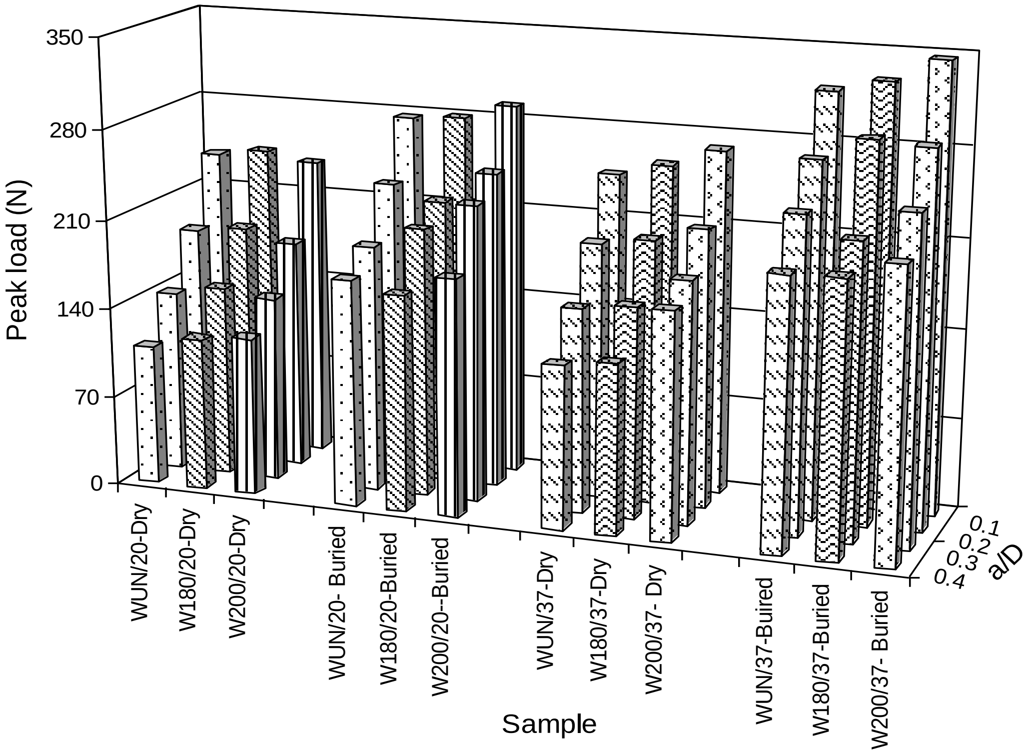


Figure 4.101: Peak load of dry as-moulded and buried samples as a function of wood content and heat treatment

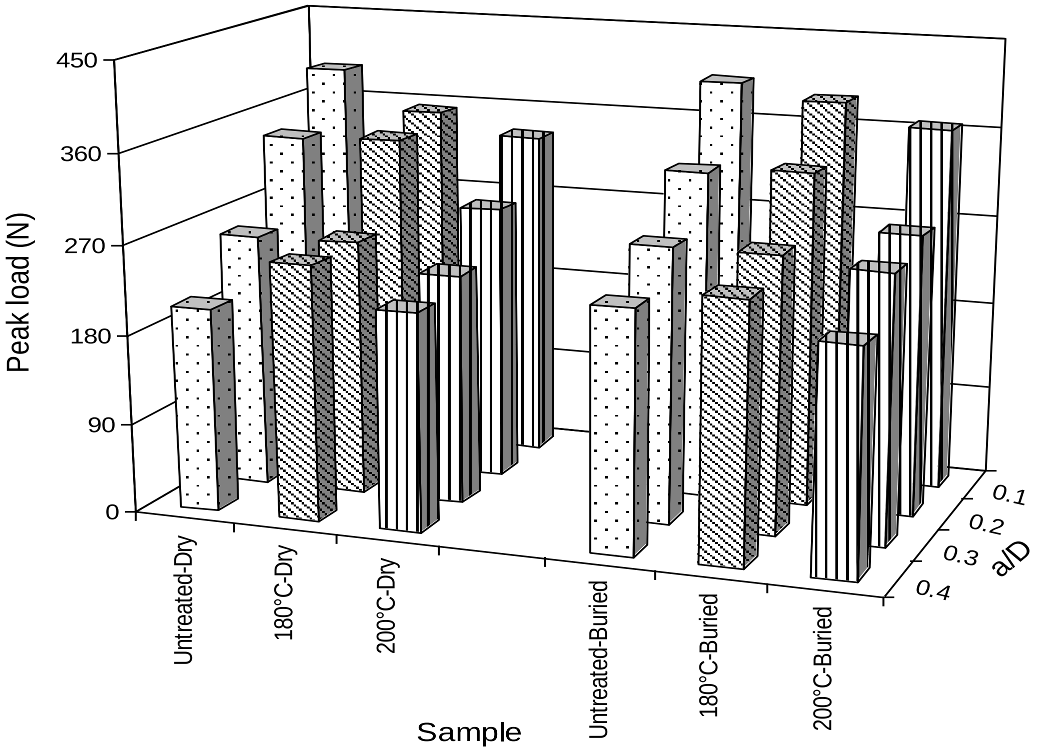


Figure 4.102: Peak load of 37 wt% dry as-moulded and buried samples containing 6% MAPE

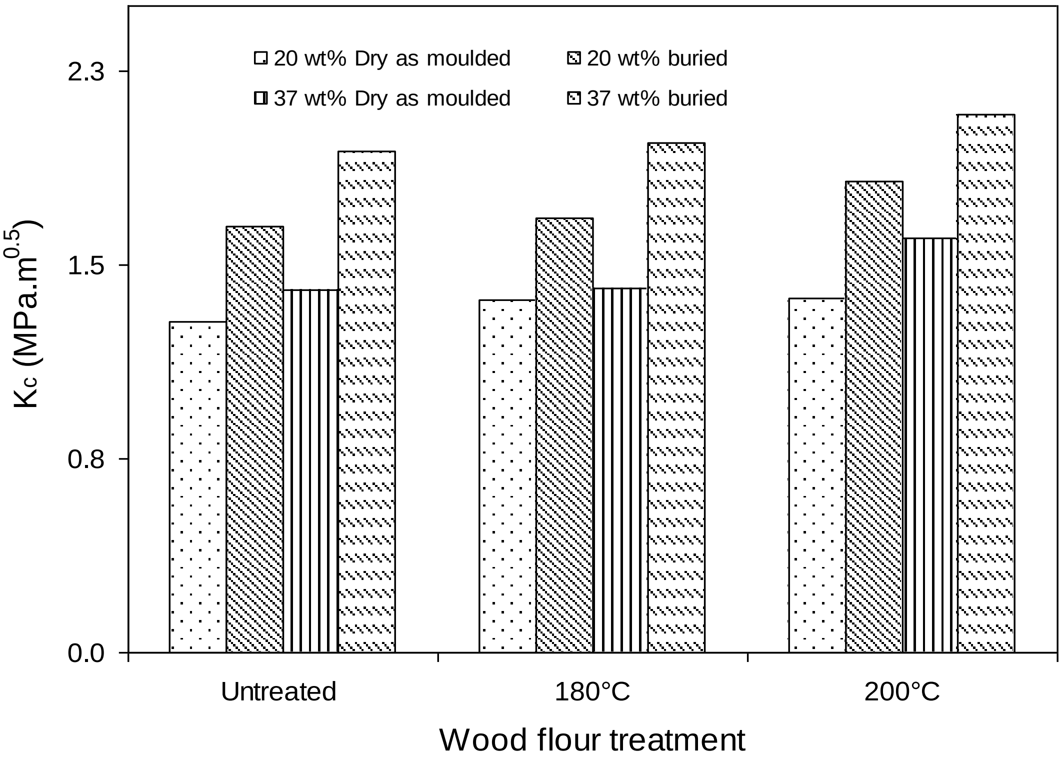


Figure 4.103: K_c of dry as-moulded and buried samples as a function of wood content and heat treatment

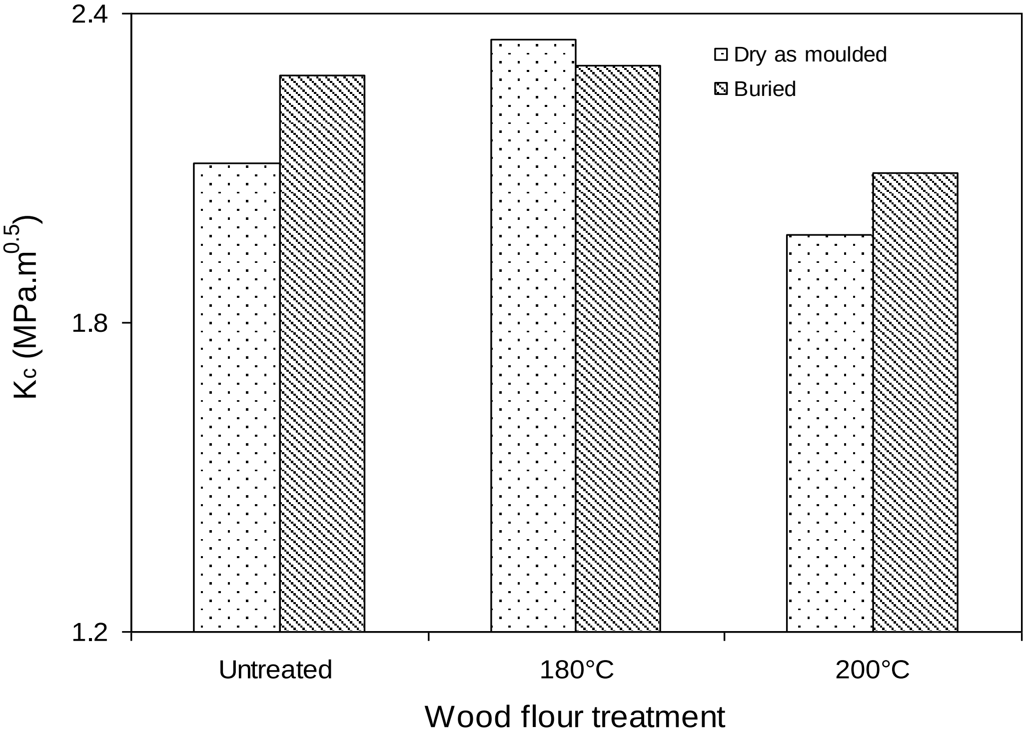


Figure 4.104: K_c of 37 wt% dry as-moulded and buried samples containing 6% MAPE

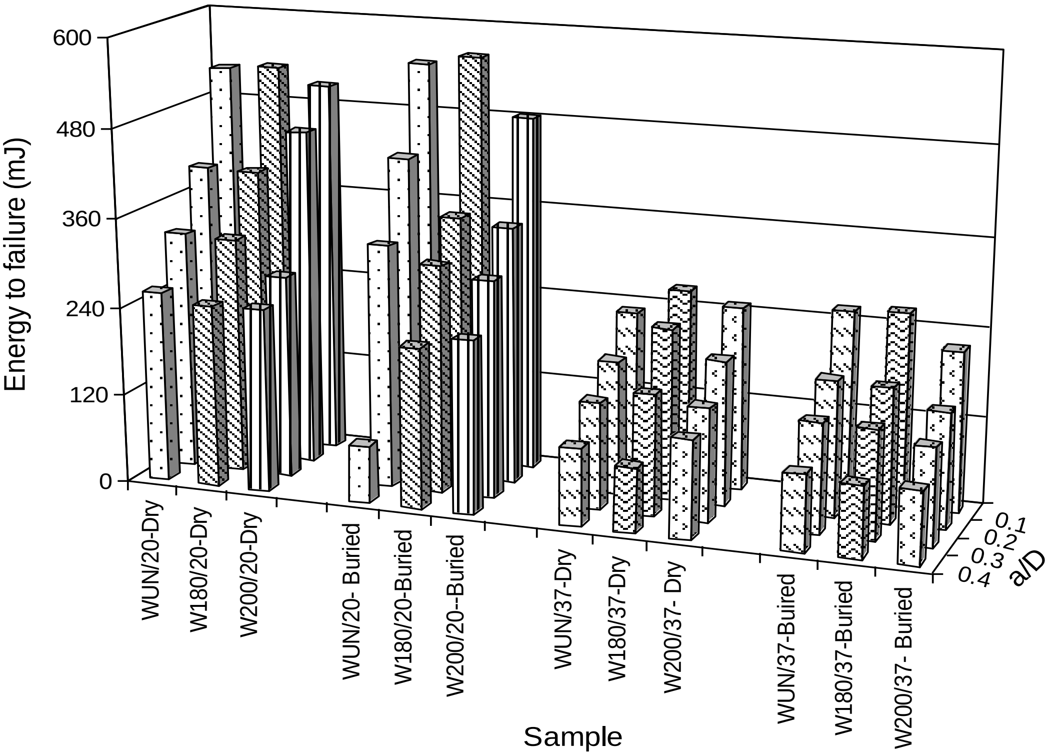


Figure 4.105: Energy to failure of dry as-moulded and buried samples as a function of wood content and heat treatment

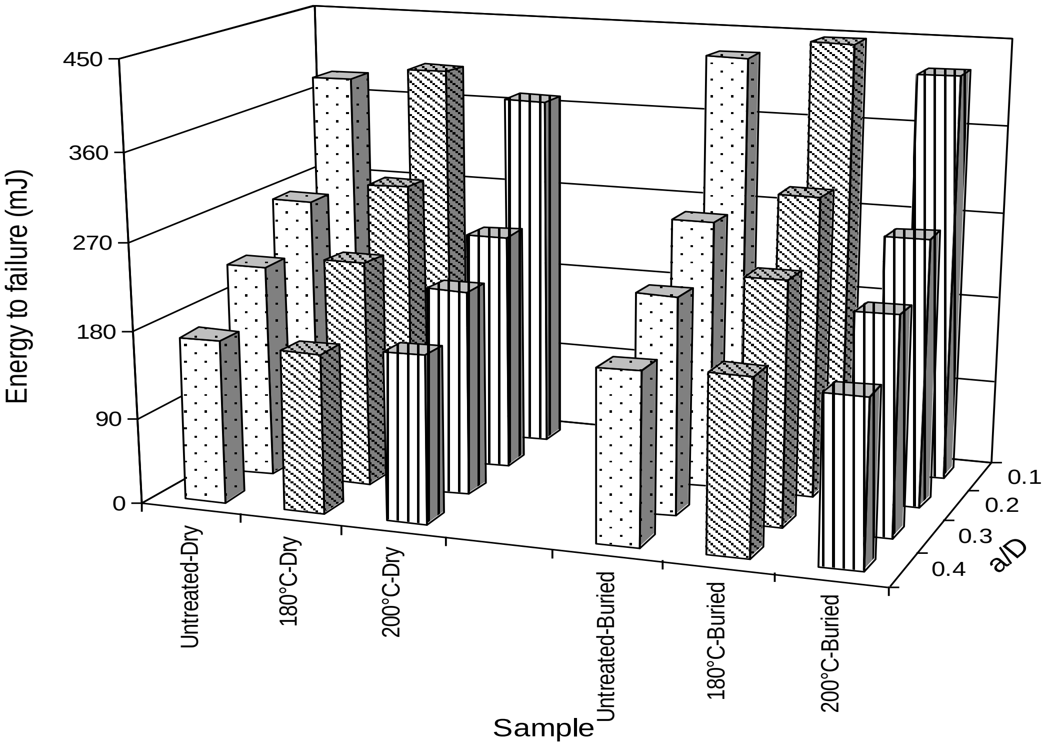


Figure 4.106: Energy to failure of 37 wt% dry as-moulded and buried composites with 6% MAPE

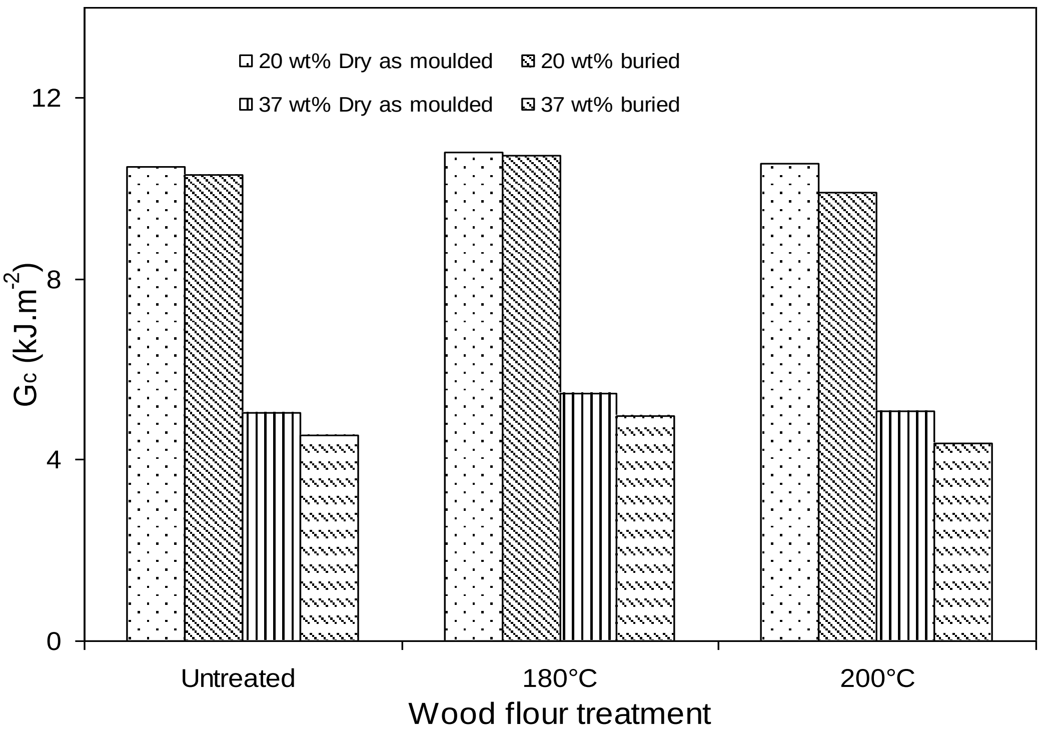


Figure 4.107: G_c of dry as-moulded and buried samples as a function of wood content and heat treatment

Figure 4.108: G_c of 37 wt% dry as-moulded and buried samples with 6% MAPE

4.3.3 Outdoor weathering

Weathering has been defined as the undesirable change produced in a material by outdoor exposure. It is particularly severe for organic materials, such as polymers, because it combines the photo-physical and photo-chemical effects of ultraviolet (UV) radiation photons from sunlight with the oxidative effects of atmospheric oxygen and hydrolytic effects of water (in the form of humidity, rain, dew, frost, snow or hail) [205]. Other elements of the outdoor weathering are temperature and atmospheric pollutants. Photo-oxidation is an effective natural weathering mechanism that uses atmospheric oxygen and radiation from sunlight. It has been reported that the photodegradation of polyolefin is caused mainly by the introduction of chromophores, such as catalyst residues, hydroperoxide groups, carbonyl groups and double bonds during manufacture. Carbonyl groups have been identified as the main light absorbing species responsible for the photochemically-induced reactions of polymers exposed to UV radiation [206]. Most WTC products are used in outdoor environment. This presents a harsh service situation that puts the structural integrity of the material to test. Furthermore, exposure of WTC to the outdoor environment affects not only the polymeric material itself but also other components, such as fillers within the matrix. Complex interactions of the combination of weather factors with the polymer and its components result in irreversible changes in the chemical structures and physical properties in a manner that generally changes the appearance and mechanical properties and reduce the useful life of the material [188]. To serve satisfactorily, WTC must meet the requirements of general use in terms of sustaining their function with minimum change in properties when utilised in a wide range of situations including use under severe weather conditions. Therefore, in this section, composites made from untreated and heat-treated wood flour were subjected to outdoor weathering in order to evaluate the response of the materials to the elements of the outdoor environment in terms of changes in thermal, dynamic mechanical and mechanical properties.

4.3.3.1 Chemistry of outdoor weathering

When UV energy is absorbed by chromophores such as pigments or catalyst residues, there is breakage of bonds and hydrogen atoms are stripped from the polymer chain (RH) to form alkyl free radicals ($R^{\cdot}$). Oxygen then combines with the free-radical species to create new reactive species, including peroxide radicals and hydroperoxides, which can react with the polyolefin chain (RH), as shown in the following reactions [205, 207]:

$$O_2 + R^{\cdot} \rightarrow ROO^{\cdot} \qquad (4.34)$$

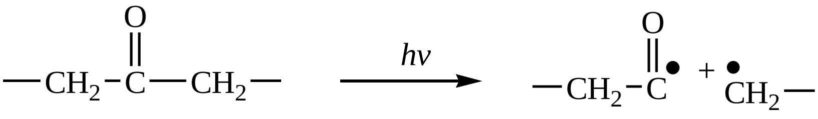
$$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \qquad (4.35)$$

Because of the chain nature of these reactions, even small concentrations of free radicals can result in significant amounts of oxidative degradation. The primary oxidative product, the hydroperoxide, is thermally and photochemically unstable and decomposes to produce two radicals, each of which can participate as R in the chain process:

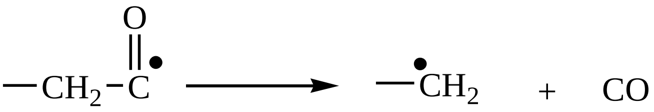
$$ROOH \rightarrow RO^{\cdot} + HO^{\cdot} \qquad (4.36)$$

The presence of carbonyl groups in a degraded polymer indicates that oxidation has taken place and also means that the material is vulnerable to further degradation because these groups are photo-labile.

In addition to oxidation initiation by the photolysis of hydroperoxide groups, another major contributor of photodegradation of polymer is ketone photolysis, which proceeds through two major reactions called Norrish type I (free radical generation and no chain cleavage) and Norrish type II (chain cleavage), as shown in the following equations [205]:

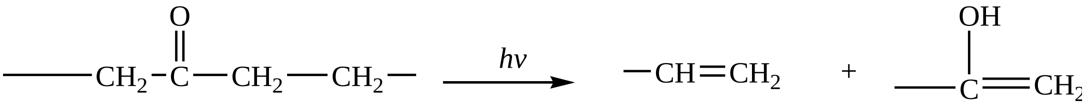


$$-\mathrm{CH_2}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_2}- \xrightarrow{h\nu} -\mathrm{CH_2}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{}^{\bullet} + {}^{\bullet}\mathrm{CH_2}- \qquad (4.37)$$



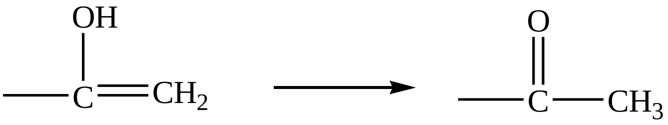
$$-\mathrm{CH_2}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{}^{\bullet} \longrightarrow -{}^{\bullet}\mathrm{CH_2} + \mathrm{CO} \qquad (4.38)$$

Norrish type I reaction



$$-\mathrm{CH_2}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH_2}- \xrightarrow{h\nu} -\mathrm{CH}=\mathrm{CH_2} + -\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}=\mathrm{CH_2}$$

(4.39)



$$-\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}=\mathrm{CH_2} \longrightarrow -\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_3} \qquad (4.40)$$

Norrish type II reaction

If the degradation of the carbonyl groups proceeds via Norrish type I reaction (Equations (4.37) and (4.38)), the resulting radicals that form can attack the polymer, and may lead to termination via cross-linking or chain scission. If the degradation proceeds according to a Norrish type II mechanism (Equations (4.39) and (4.40)), carbonyl groups and terminal vinyl groups are formed and chain scission occurs. Furthermore, the carbonyl group that forms is capable of further degradation.

In the course of polyethylene photodegradation, chain scission and cross-linking mechanisms compete. Chain scission lowers the molecular weight, whereas, cross-linking raises the molecular weight by increasing the bonding between polymer chains [206]. The formation of carbonyl and vinyl groups can be considered as a direct indication of main chain scission [208]. It has been reported [209] that the weathering of polyethylene results in an increase in crystallinity, indicating that scission has taken place. The shorter chains produced during chain scission are readily mobile and can crystallize more readily, leading to an increase in crystallinity and the attendant embrittlement. Conversely, cross-linking does not increase polymer crystallinity [206]. Although chain scission occurs in the amorphous phase of the polymer, imperfect crystalline regions degrade because of cross-linking [210].

FTIR was used to verify the occurrence of surface oxidation of the samples. In the aged LDPE, a band appears at 1,714 cm^{-1}, but this is absent in the dry as-moulded LDPE [Figure 4.109]. This indicates that the carboxylic acid generated [206] could have resulted from Norrish type I reaction where peracids break down to form hydroxyl radicals and polymer carboxy radicals, which in turn break down to form carboxylic acids [211]. This band also appeared in the WTC (1,733 cm^{-1}), but shifted to higher values (1,738 cm^{-1}) in aged WTC and could indicate chain scission. Previous studies [211] have shown that the main products of polyethylene photo-oxidation are carboxylic acids and ketones with lesser amounts of hydroperoxides. The ketones can further react by either a Norrish type II mechanism following H-abstraction from the γ-carbon or decompose into fragments with unsaturated polymer chain end and a carbonyl group end. Although an evidence of cross-linking could not be observed in the FTIR spectra, a possibility that cross-linking and chain scission happened concurrently during photo-oxidation of polyethylene, cannot be ruled out.

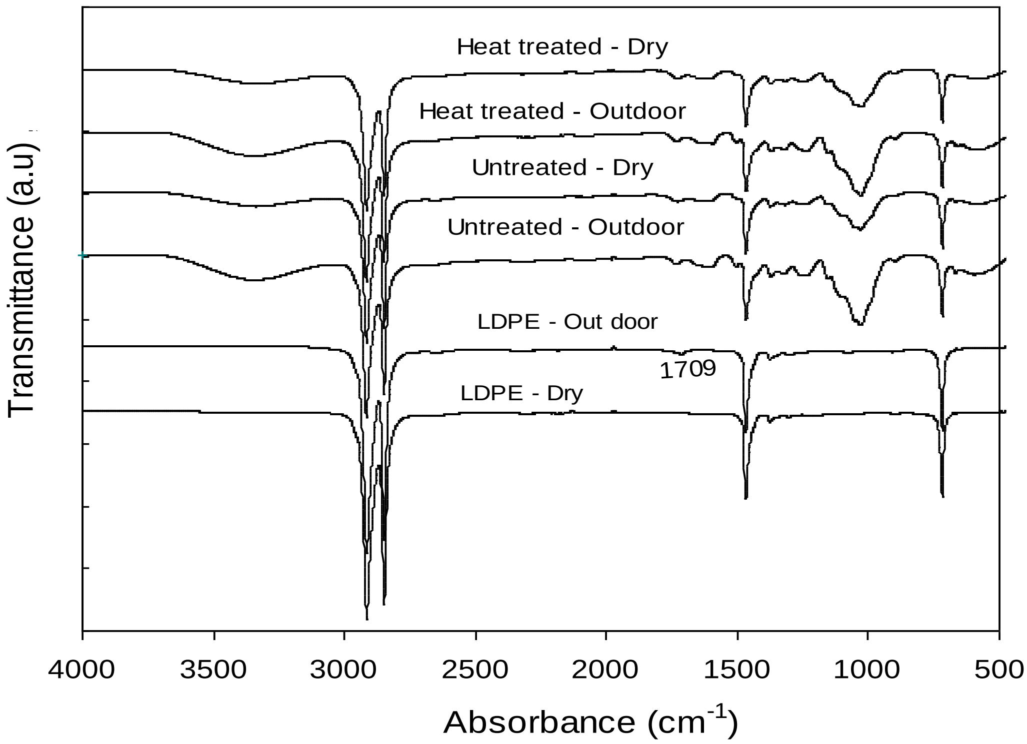


Figure 4.109: FTIR of the surface of 37 wt% composites made from untreated and heat-treated wood flour exposed to the outdoor environment

4.3.3.2 Physical appearance

The neat LDPE changed colour from white to light yellow on exposure to outdoor environment. This could be the result from the effects of depolymerisation caused by exposure to light. Polyethylene has been found to be susceptible to light, which induces depolymerisation. Depolymerisation hardens and embrittles the material, inducing a yellowing colouration and a general loss of optical properties [212]. Visual assessment of the composites indicated that the dry as-moulded specimens appear dark brown to chocolate in colour depending on the wood content and treatment temperature. However, after outdoor exposure for 9 months, the colour changed to light grey (Figure 4.110), with the composites containing higher wood content showing a greater difference in colour and a fibrous appearance due to loss of aesthetic appeal. This must have resulted from the degradation of the wood components by UV radiation. It has been observed that exposure to the outdoor environment affects not only the polymeric material itself, but also other components within the matrix. All wood components are susceptible to degradation by UV radiation. However, lignin is responsible for the UV absorption in wood because of the presence of chromophoric functional groups like phenolics, O-H groups, double bonds and carbonyl groups. UV light degrades lignin into water-soluble compounds that are washed-off from the wood with rain, leaving a cellulose-rich surface with a fibrous appearance [213]. Furthermore, UV radiation can lighten WTC by causing the surface of the polymer matrix to crack, creating a whitening effect and to a larger extent, by bleaching the wood particles. In addition, the presence of water aggravates the bleaching effect of UV radiation by accelerating the oxidation reactions and causing the wood particles to swell, creating more openings for light penetration. Besides, water can remove some water soluble extractives that impart colour to the wood particle [214].

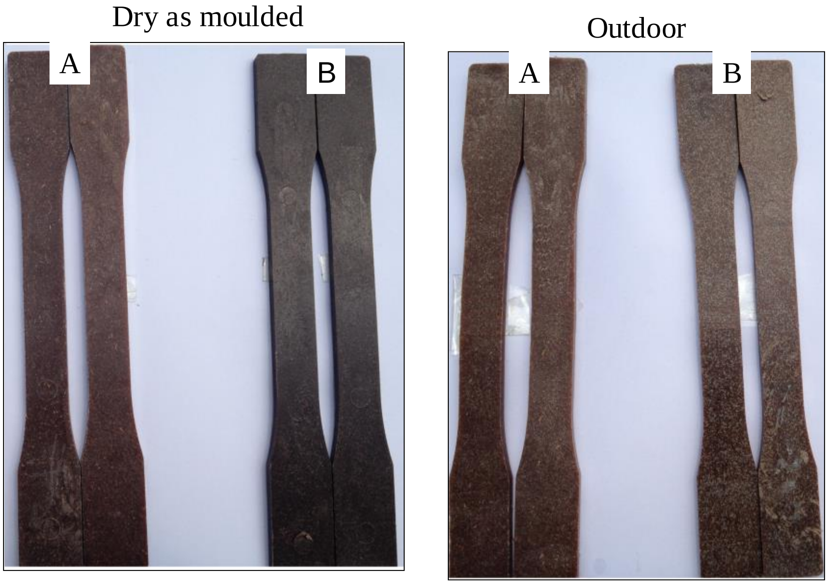


Figure 4.110: Visual appearance of dry as-moulded and outdoor weathered A): untreated and B): 200°C treated composites

From Figure 4.110, it can be seen that the heat-treated WTC changed colour more than the untreated sample. It has been observed that the darker the colour of a material, the higher the absorbed UV radiations [188]. Also, photodegradation of wood has been observed to begin with the lignin-rich middle lamella, with longer exposure resulting in the degradation of the secondary cell walls [215]. Therefore, it is not surprising that composites made from wood flour treated at 200°C containing higher lignin content (Table 4.1, page 53) displayed a highly profound change in colour, relative to the untreated sample, on outdoor exposure.

Figures 4.111and 4.112 present the scanning electron micrographs of the surfaces of un-aged LDPE, outdoor exposed LDPE, untreated and heat-treated WTC. From the figures, it that can be observed that outdoor weathering has destroyed the aesthetic appeal of the samples’ surfaces. The surface of the aged LDPE (Figure 4.111b) has been eroded when compared to the un-aged sample (Figure 4.111a). It has been reported [216] that photodegradation by chain scission can occur at the tie molecule region. Tie molecules are polymer molecules that form part of a folded crystalline region and extend through an amorphous region into another crystalline region. Decrease in the tie molecules density has been found to increase environmental stress cracking [217], which may be responsible for the eroded surface. The surface of the composites from untreated and heat-treated wood flour were also weather-beaten to different extents, with cracks appearing prominently (Figures 4.112a-c). Weathering results in the destruction of WTC surface as a result of the absorption of water by the wood particles exposed at the surface and the consequent swelling. In addition, upon UV exposure, the polymer matrix cracks. Together, these result in a flaky and cracked surface [213].

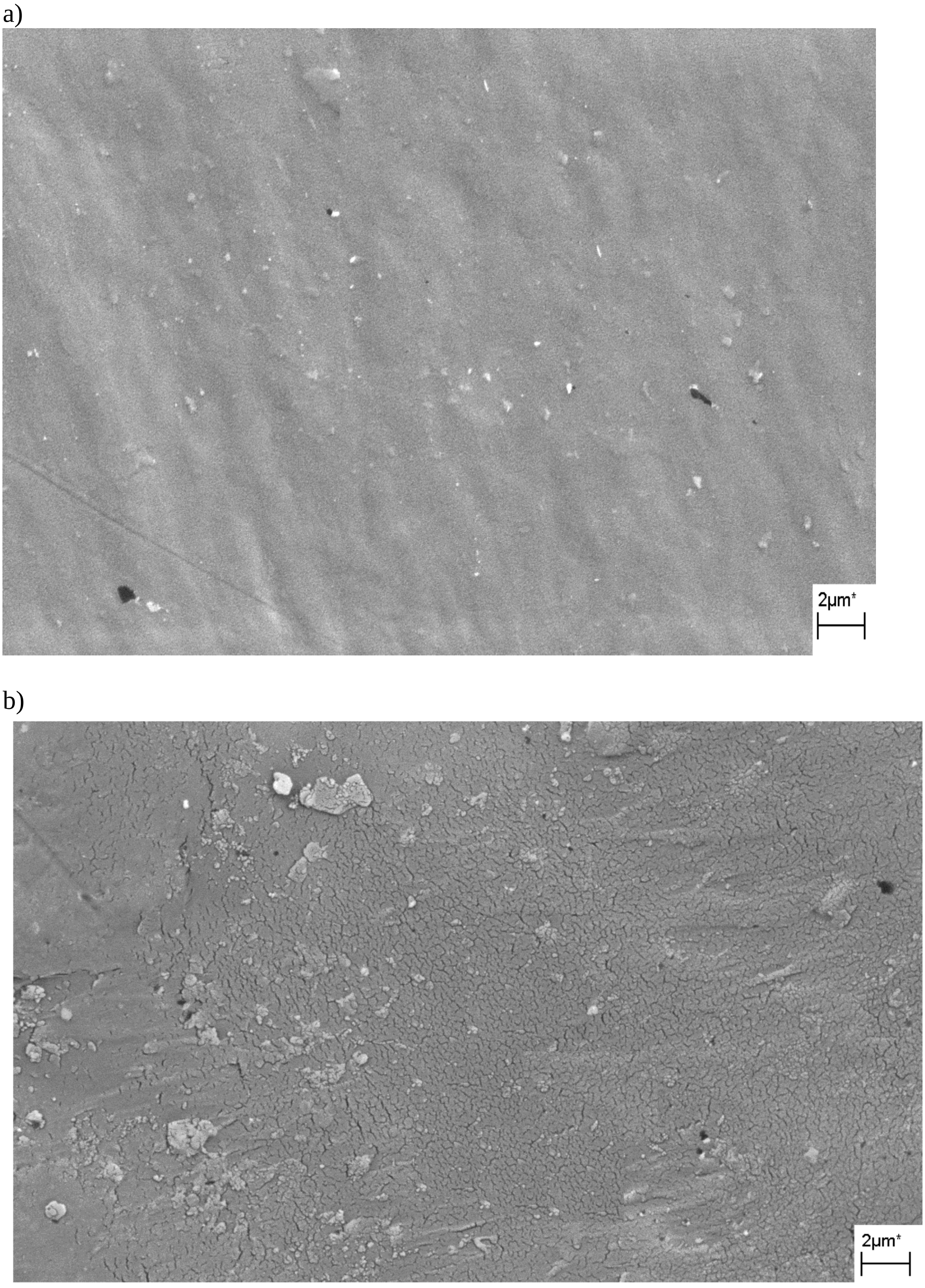
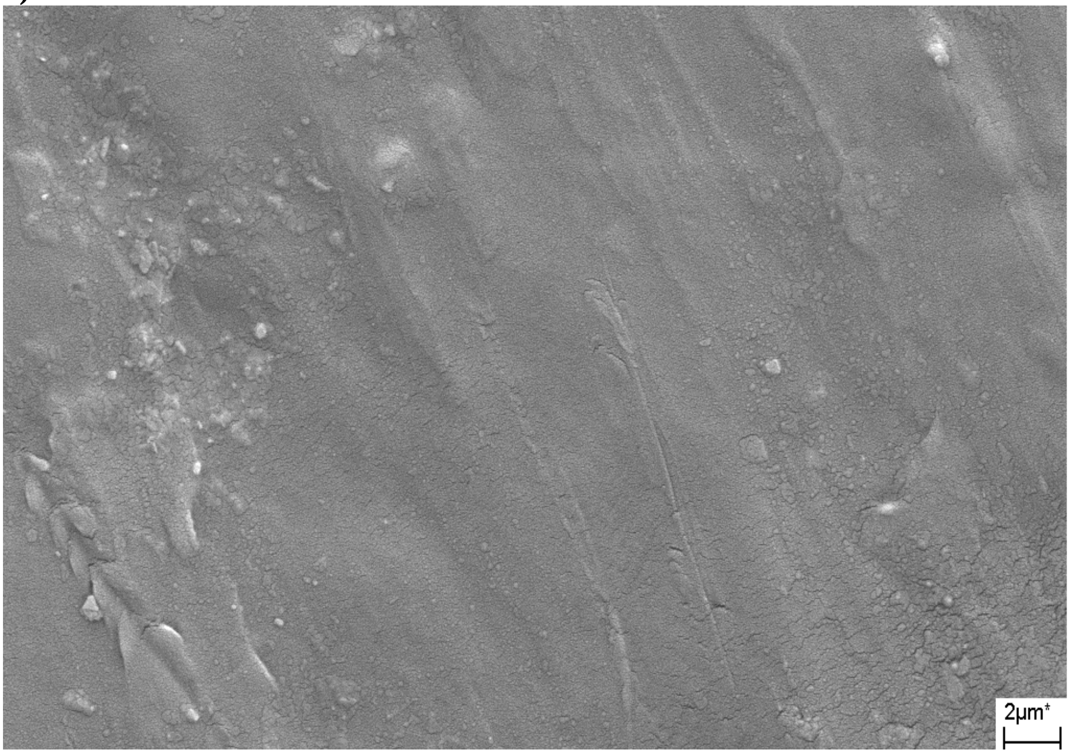


Figure 4.111: SEM micrograph of the surfaces of a): un-aged LDPE and b): outdoor aged LDPE

a)



b)

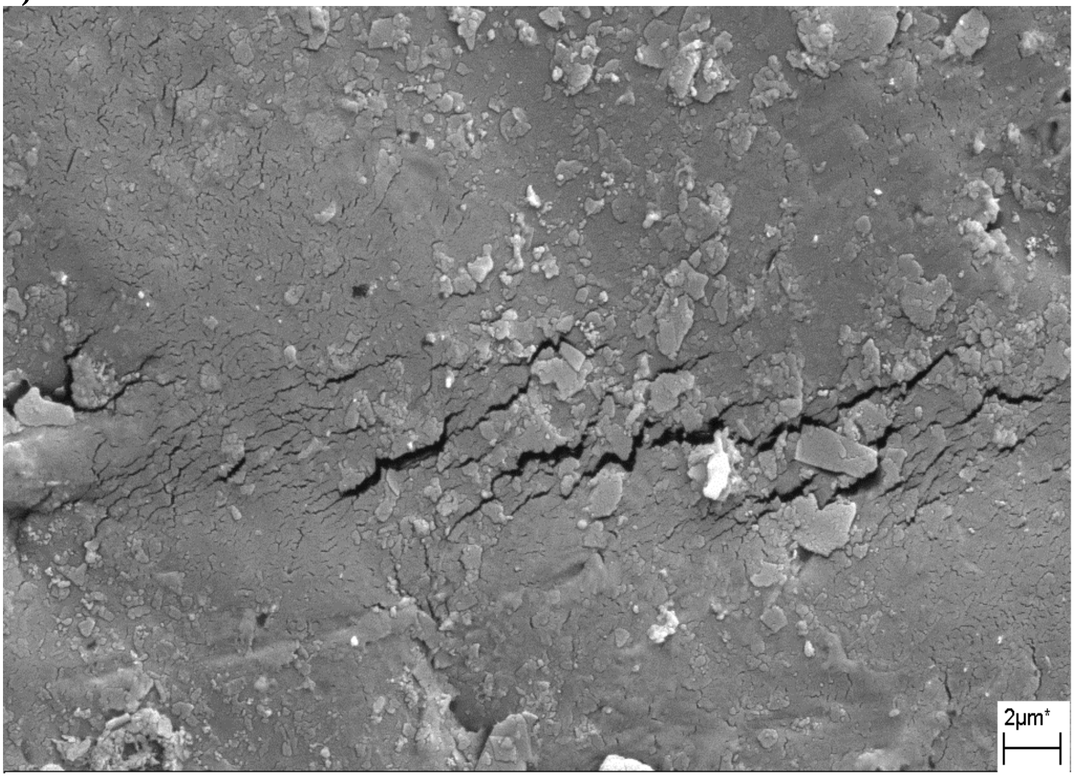


Figure 4.112 cont'd

c)

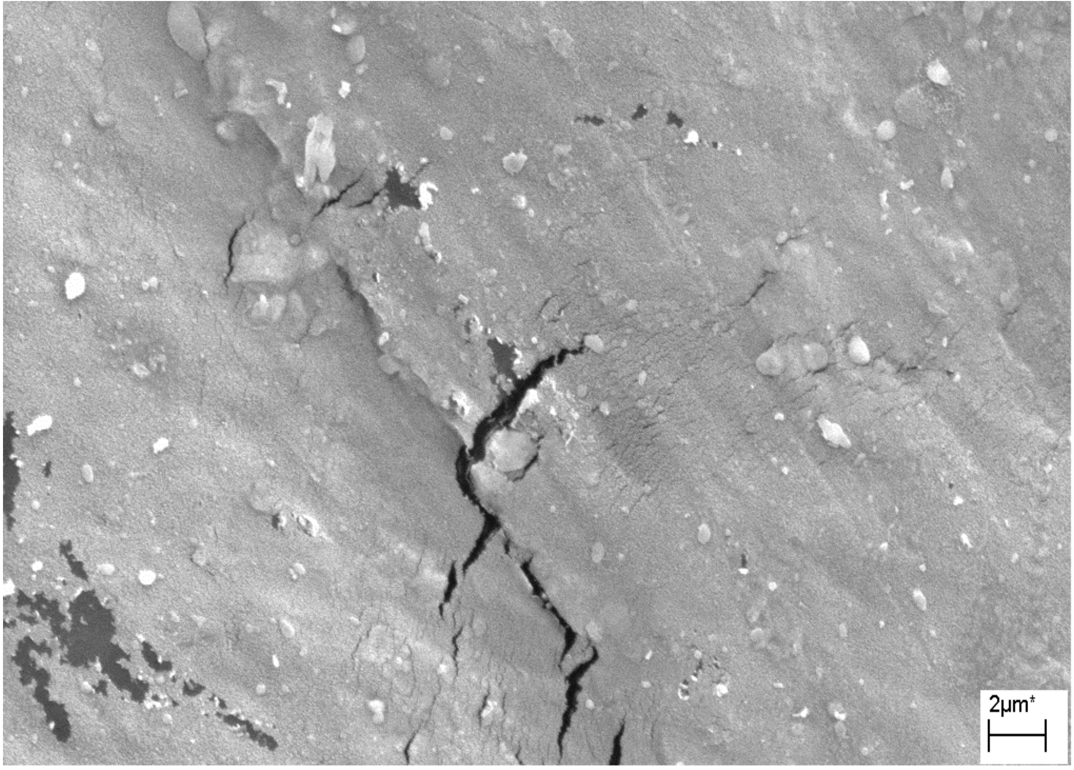


Figure 4.112: SEM micrograph of the surfaces of a): un-aged WTC, b): untreated and c): 200 °C treated WTC exposed to outdoor aging

4.3.3.3 Thermal properties

Thermogravimetric analysis, TGA

The TGA/DTG curves of dry as-moulded and outdoor weathered LDPE and 37 wt% composites are shown in Figures 4.113a and b. Extracted data from these curves and those of 20 wt% are presented in Table 4.12. The samples absorbed water on exposure to the outdoor environment, as shown by the peak around 100°C. 2.96%, 2.18% and 2.31% moisture evaporated from the 37 wt% composite made from untreated, 180°C and 200°C treated wood flour respectively. In all the samples, the thermal stability of the exposed samples decreased marginally relative to the unexposed samples. T_p, and $T_{50\%}$ values slightly decreased in the outdoor weathered LDPE when compared to the exposed sample. Also, the same trend is observed in the composites at different filler loadings. This small decrease in thermal stability may be as a result of the formation of low molecular weight species during oxidative degradation of the materials [218]. Although the changes in molecular weight of the exposed samples were not determined, it is possible that the period of exposure to the elements of the outdoor environment in this study is not sufficient to cause appreciable chain scission required for substantial decrease in the molecular weight and consequently, the thermal stability. Since the degradation of PE is a slow process, it has been suggested that a period of more than one year is needed for noticeable photo-oxidation of PE to take place [219]. Furthermore, although geographical location plays a role in the duration of exposure, samples of PE films have been exposed for a period of three years in order to study its photo-degradability [220]. A definite trend could not be established with respect to heat treatment. In addition, incorporation of MAPE showed no identifiable trend (Figure 4.113b).

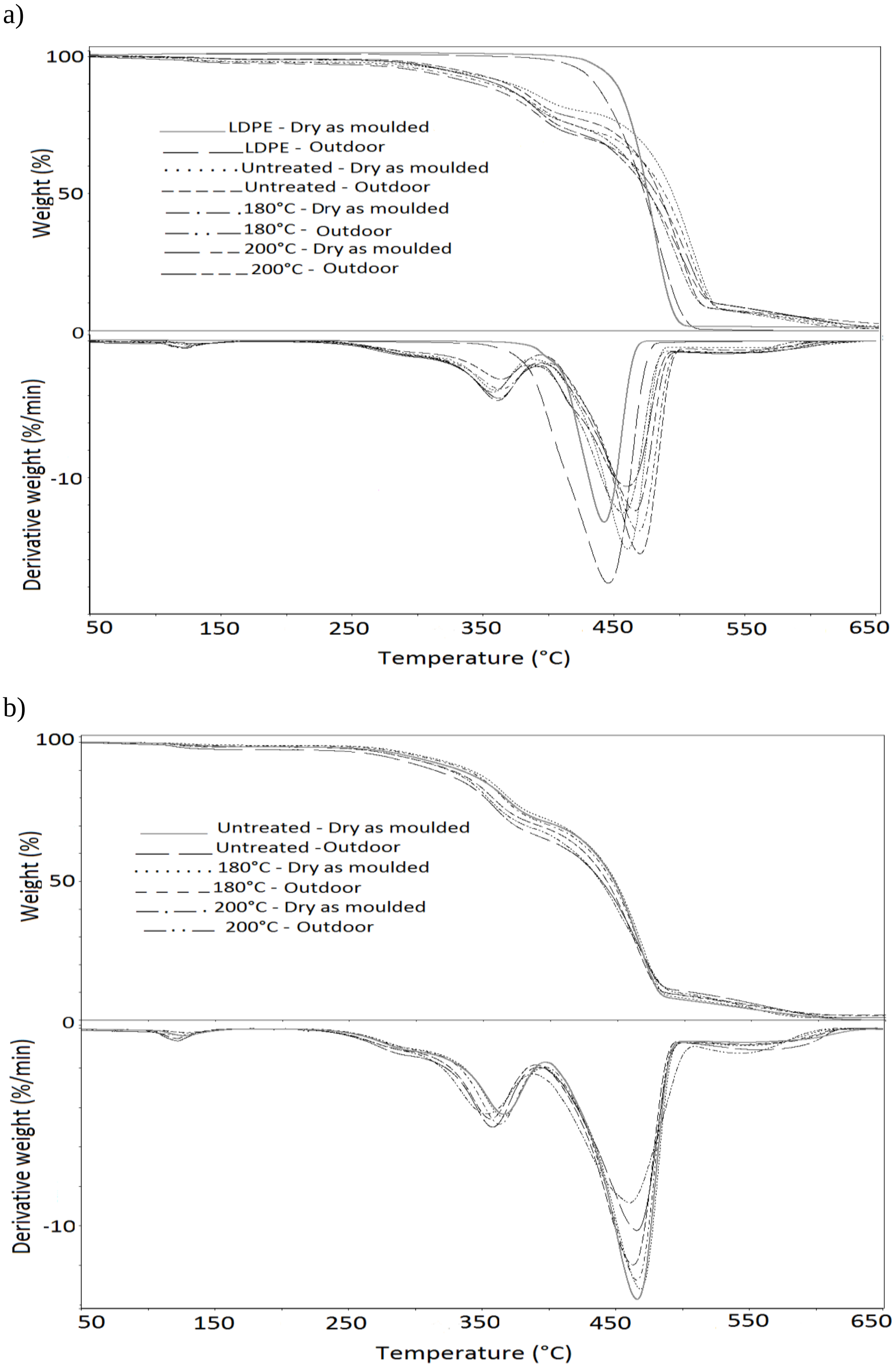


Figure 4.113: TGA/DTG of outdoor aged and un-aged LDPE and 37 wt% untreated and heat-treated WTC containing: a) 0% and b) 6% MAPE

Table 4.12: TGA data of samples exposed to outdoor weathering

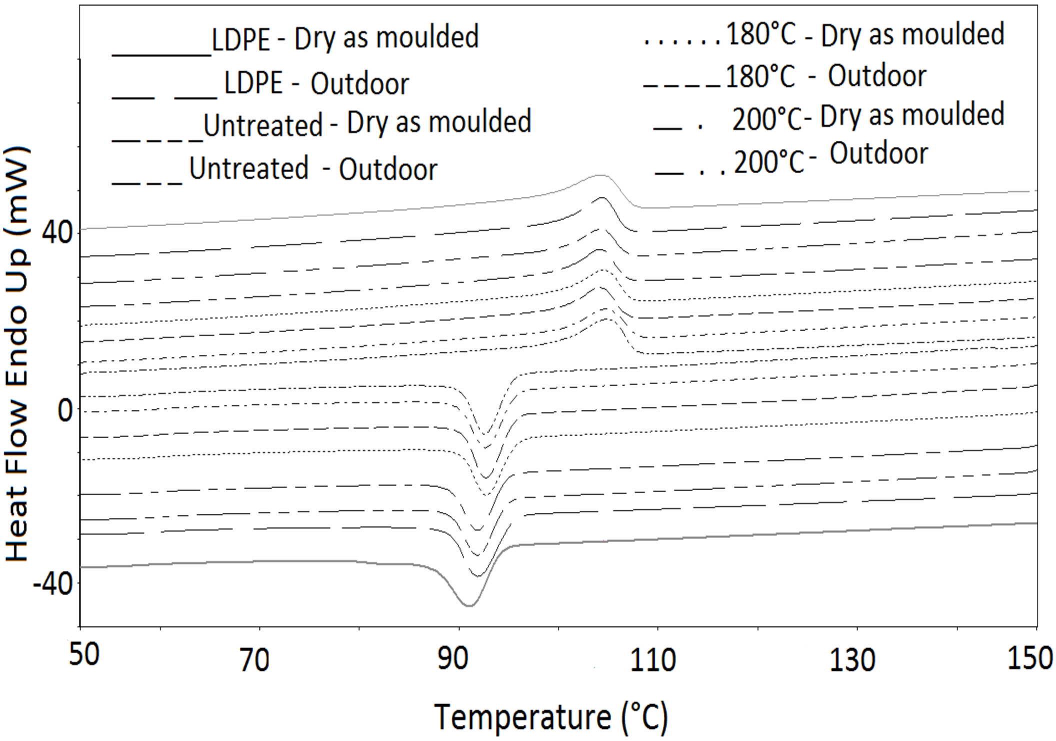
Sample	Wood treatment temperature (°C)	T_p (°C)	Onset temperature, T_{onset} (°C)	$T_{50\%}$ (°C)	Degradation temperature (°C)
LDPE	-	443.6	390.0	420.7	345.3-474.0
LDPE/$W_{UN/20/0}$	-	461.8	387.2	451.3	274.0-505.9
LDPE/$W_{180/20/0}$	180.0	467.8	389.7	453.8	260.6-500.0
LDPE/$W_{200/20/0}$	200.0	465.0	417.9	451.0	239.0-500.0
LDPE/$W_{UN/37/0}$	-	449.9	392.4	445.9	235.2-503.1
LDPE/$W_{180/37/0}$	180.0	460.9	362.9	440.4	232.0-500.6
LDPE/$W_{200/37/0}$	200.0	460.4	379.0	382.1	232.7-498.5
LDPE/$W_{UN/20/2}$	-	444.4	405.4	442.5	245.4-501.9
LDPE/$W_{180/20/2}$	180.0	451.1	421.6	445.0	252.4-500.0
LDPE/$W_{200/20/2}$	200.0	450.2	401.1	437.2	217.4-502.6
LDPE/$W_{UN/37/2}$	-	451.0	388.3	440.5	221.0-503.4
LDPE/$W_{180/37/2}$	180.0	459.1	404.2	441.9	216.1-507.4
LDPE/$W_{200/37/2}$	200.0	461.8	400.1	435.4	222.7-502.8
LDPE/$W_{UN/20/6}$	-	450.2	370.7	422.1	240.1-497.9
LDPE/$W_{180/20/6}$	180.0	457.4	406.0	445.3	241.6-499.0
LDPE/$W_{200/20/6}$	200.0	460.1	402.2	439.8	245.8-506.8
LDPE/$W_{UN/37/6}$	-	466.3	382.1	437.1	221.0-500.0
LDPE/$W_{180/37/6}$	180.0	465.4	400.0	441.7	237.5-499.0
LDPE/$W_{200/37/6}$	200.0	468.9	390.2	444.7	222.3-505.4
LDPE/$W_{UN/20/10}$	-	455.3	373.3	427.4	236.9-501.1
LDPE/$W_{180/20/10}$	180.0	468.7	422.1	460.9	233.5-498.8
LDPE/$W_{200/20/10}$	200.0	461.2	423.1	449.6	246.0-497.5
LDPE/$W_{UN/37/10}$	-	468.5	384.6	437.3	231.6-501.0
LDPE/$W_{180/37/10}$	180.0	467.2	399.0	444.3	239.9-500.3
LDPE/$W_{200/37/10}$	200.0	460.6	411.2	446.1	232.9-498.8

Differential scanning calorimetry, DSC

Figure 4.136 presents the DSC cooling and second heating thermograms of dry as-moulded and outdoor exposed samples. Data extracted from these curves and those of the 20 wt% filler level are presented in Table 4.13. Generally, the T_m and T_c of LDPE and composites with different filler loadings showed insignificant change on outdoor exposure. However, ΔH_m increased in the outdoor weathered WTC, relative to the dry as-moulded samples, indicating that more energy is required for melting. On the other hand, composites made from untreated wood flour exhibit a marginal decrease in ΔH_m in the outdoor weathered samples. Decrease in ΔH_m of weathered polypropylene has been attributed to a combined effect of the reduction in molecular sizes and increasing concentration of chemical defects caused by the photodegradation [221]. Other than that, a clear trend could not be established with the addition of MAPE. Values of $-\Delta H_c$ decreased generally in the 20 wt% weathered samples, relative to the dry as-moulded ones, especially at 0% and 2% MAPE additions. In the weathered composites containing 37 wt%, a general increase in $-\Delta H_c$ is observed. Incorporation of MAPE at 6% and 10% seem to increase the $-\Delta H_c$ values of the weathered composites, irrespective of the wood content.

A 100% increase in X_c is observed in the LDPE exposed to the outdoor environment when compared with the dry as-moulded samples (compare Table 4.3 and Table 4.13). Weathering of LDPE films has been found to result in an increase in crystallinity and has been shown to indicate chain scission of polyethylene during photodegradation, which is mainly attributed to secondary crystallization, localized exclusively in the amorphous phase. Chain scissions resulting from Norrish type I and II reactions decreased the density of entanglements in the amorphous phase, allowing the shorter molecules to crystallize due to their higher mobility [209], with a consequent increase in the crystallinity of the material. Composites containing heat-treated wood flour also exhibited the same trend. This is expected because of the presence of carbonyl peaks and the growth of vinyl peaks (Figure 4.109, page 224), which is suggestive of chain scission. Composites made from 37 wt% wood flour treated at 200°C displayed a 129% increase in X_c. By contrast, composites containing the same level of untreated wood flour show a decrement in X_c. A possible reasoning for this behaviour is the mechanism of photodegradation in composites containing untreated wood flour is more complex than that in the heat-treated samples. Reports [208] have shown that while chain scission (which increases X_c) is an important mode of polyethylene degradation, cross-linking also takes place concurrently under favourable conditions. Cross-linking reduce the free radicals taking place during the oxidation process, with the radicals combining together to elongate the polymer chain, increasing its molecular weight, with the attendant reduction in X_c. On the other hand, judging by the FTIR intensity of the carbonyl peak in outdoor weathered untreated WTC (Figure 4.109, page 224), it is possible that the photo-oxidation by chain scission is predominant in this category of composites. Therefore, increase in the amount of oxidation products can cause great damage to the tie molecules [216], resulting in breakdown of crystallisation [206]. In the composites containing MAPE, X_c remained relatively unchanged at all MAPE levels (Figure 4.114b and Table 4.13), indicating that outdoor exposure had no influence on the crystallinity of the compatibilised composites. In addition, it is likely that these composites have, predominantly, undergone cross-linking, which resulted in no net change in X_c [206].

a)



b)

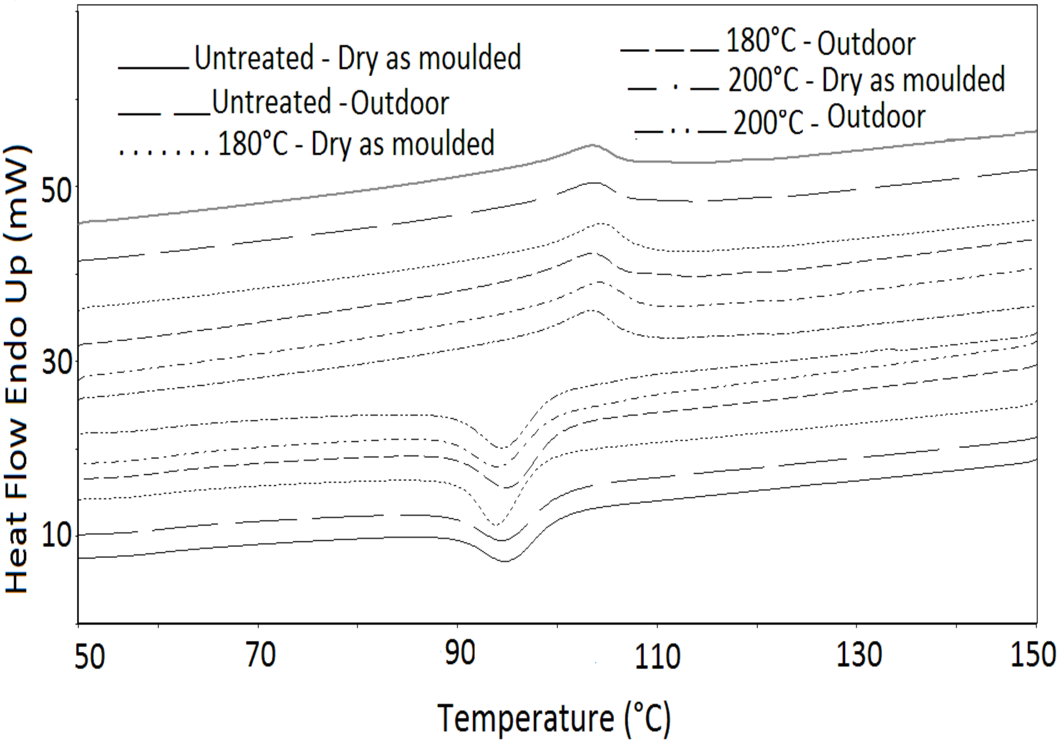


Figure 4.114: DSC thermograms of LDPE and 37 wt% untreated and heat-treated outdoor aged WTC containing: a) 0% and b) 6% MAPE

Table 4.13: DSC data of outdoor weathered samples

Sample	Treatment temperature (°C)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	$-\Delta H_c$ (J/g)	X_c (%)
LDPE	-	104.1	91.0	86.3	73.1	29.5
LDPE/$W_{UN/20/0}$	-	104.1	92.2	50.3	92.2	21.5
LDPE/$W_{180/20/0}$	180.0	104.2	92.5	43.1	50.5	18.4
LDPE/$W_{200/20/0}$	200.0	104.5	92.8	41.5	44.0	17.7
LDPE/$W_{UN/37/0}$	-	104.5	92.1	36.6	40.8	19.8
LDPE/$W_{180/37/0}$	180.0	104.2	92.6	36.5	38.9	19.8
LDPE/$W_{200/37/0}$	200.0	104.7	92.0	29.7	36.4	16.1
LDPE/$W_{UN/20/2}$	-	104.1	94.7	34.5	42.0	14.7
LDPE/$W_{180/20/2}$	180.0	103.8	93.9	35.2	44.2	15.0
LDPE/$W_{200/20/2}$	200.0	104.3	93.7	33.8	38.5	14.4
LDPE/$W_{UN/37/2}$	-	103.8	93.7	28.9	31.9	15.7
LDPE/$W_{180/37/2}$	180.0	103.2	94.2	22.7	25.4	12.3
LDPE/$W_{200/37/2}$	200.0	103.9	94.0	25.6	32.8	13.9
LDPE/$W_{UN/20/6}$	-	103.5	95.1	27.5	39.9	11.7
LDPE/$W_{180/20/6}$	180.0	103.1	95.0	27.9	34.4	11.9
LDPE/$W_{200/20/6}$	200.0	103.2	95.5	26.2	40.7	11.2
LDPE/$W_{UN/37/6}$	-	103.4	94.7	17.0	26.5	9.2
LDPE/$W_{180/37/6}$	180.0	103.2	95.2	18.4	34.1	10.0
LDPE/$W_{200/37/6}$	200.0	103.4	94.7	20.9	30.6	11.3
LDPE/$W_{UN/20/10}$	-	103.2	94.6	19.1	39.5	8.1
LDPE/$W_{180/20/10}$	180.0	102.7	94.6	21.6	38.2	9.2
LDPE/$W_{200/20/10}$	200.0	103.1	94.4	22.4	33.3	9.6
LDPE/$W_{UN/37/10}$	-	102.9	94.5	19.6	26.9	10.6
LDPE/$W_{180/37/10}$	180.0	104.2	92.6	18.0	33.0	9.8
LDPE/$W_{200/37/10}$	200.0	102.7	94.6	16.9	29.9	9.2

4.3.3.4 Dynamic mechanical properties

As was observed in the thermal properties of outdoor weathered samples, it is expected that natural outdoor aging should have an effect on the visco-elastic behaviour of the samples. Therefore, an assessment of the dynamic mechanical properties of the weathered samples is carried out in order to determine the extent of interaction of the factors of outdoor weathering with the macromolecular structure of the composites.

Storage modulus

The storage modulus of the dry as-moulded and outdoor exposed composites made from 37 wt% heat-treated and untreated wood flour is presented in Figure 4.115. The storage modulus of the exposed LDPE is lower relative to the dry as-moulded sample. $E'_{25°\mathrm{C}}$ and $E'_{-100°\mathrm{C}}$ decreased by 8% and 34% respectively when compared with the un-aged LDPE. This implies that outdoor exposure has reduced the stiffness of the material. Photodegradation of the LDPE by the elements of the outdoor conditions is believed to be responsible for this behaviour. This trend is also repeated in the composites, which show a decrement in $E'_{25°\mathrm{C}}$ and $E'_{-100°\mathrm{C}}$ to different extents (Table 4.14). A reduction in $E'_{25°\mathrm{C}}$ and $E'_{-100°\mathrm{C}}$ to the tune of 16% is observed in the exposed composites containing 37 wt% untreated and 180°C treated wood flours. There is no observable change in the storage modulus of exposed composites containing heat-treated wood flour at 200°C. Although the extent of reduction in the composites is lower than that of the LDPE, the same mechanism of photodegradation which tends to destroy the molecular structure of the LDPE may also have degraded the interfacial adhesion in the composites, thereby reducing the stiffening effect of the wood flour on the composites. The severity of the degradation in the neat LDPE relative to the composites means that the wood flour and in particular, wood flour treated at 200°C, had a stabilizing effect against photodegradation of the composites. The addition of MAPE at low content (2% and 6%) showed no particular trend in the $E'_{25^\circ\mathrm{C}}$ of the outdoor weathered composites, although an increase was observed at 10% MAPE level. Also, the incorporation of MAPE indicated no effect on the $E'_{-100^\circ\mathrm{C}}$ of the exposed samples when compared with the dry as-moulded samples as the values remained relatively the same at all MAPE levels used (Figure 4.115b).

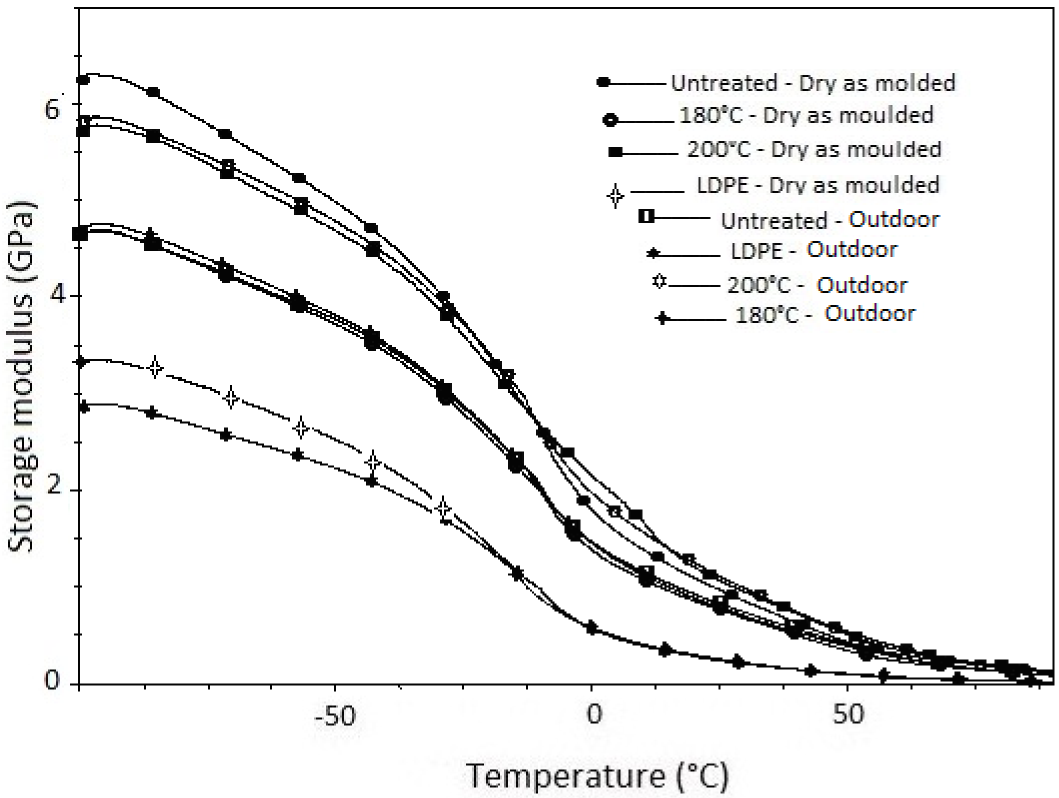
Loss modulus

The variation of loss modulus with temperature in dry as-moulded and outdoor weathered samples is presented in Figure 4.116. The $E''_{25^\circ\mathrm{C}}$ of the outdoor weathered LDPE is almost the same as the dry as-moulded sample, but a 14% drop in $E''_{\max}$ is recorded in the same sample. Possible formation of low molecular weight species in the outdoor weathered LDPE resulted in shorter polymer chains, with the attendant increase in free volume, leading to increased segmental mobility of the amorphous polymer chains. However, $T_{\beta}^{E''}$ increased in the aged LDPE when compared with the dry as-moulded samples, indicating that higher energy is required for the $T_{\beta}^{E''}$ transition. This seems strange, as the production of low molecular weight species in aged LDPE should result in lower temperature for $T_{\beta}^{E''}$ transition. On the other hand, photodegradation by chain scission has been reported to take place, mainly in the amorphous region of the polymer chains [209]. Therefore, depletion of the amorphous segment represent increased crystallinity, which perhaps, led to lower segmental mobility and consequently, increased $T_{\beta}^{E''}$. Values of $E''_{25^\circ\mathrm{C}}$ decreased in the aged composites containing untreated and 180°C treated wood flours, but remained relatively the same in composites made from 200°C treated wood flour at all compositions studied. The only identifiable effect of outdoor aging on the $E''_{\max}$ of the composites is in the samples containing 37 wt% untreated wood flour, where a decrement in $E''_{\max}$ was observed with outdoor weathering. No particular trend in $E''_{\max}$ could be established in composites containing heat-treated wood flour. The values of $T_{\beta}^{E''}$ remained comparatively unchanged in all the outdoor aged samples relative to the dry as-moulded specimen. Also, incorporation of MAPE gave no clear trend in $E''_{25°\mathrm{C}}$, while $E''_{\max}$ remained unchanged in all the coupled outdoor exposed samples (Figure 4.116b).

Tan delta

Tan delta curves of dry as-moulded and outdoor exposed samples containing 37 wt% wood flour at different treatment temperatures are presented in Figure 4.117. $Tan\ \delta_{\max}$ value of the outdoor weathered LDPE (0.17) is almost the same as the dry as-moulded sample (0.16). Photodegradation have increased the damping in the LDPE, resulting in this observation. Temperature at $\tan\delta_{\max}$ dropped slightly in the exposed LDPE, while values of $tan\,\delta_{25°C}$ increased marginally, indicative of increased free volume in the exposed LDPE. In the composites, $\tan\delta_{\max}$ values of samples exposed to the outdoor environment remained comparatively the same with the dry as-moulded samples (compare Table 4.4, page 80 with Table 4.14). However, the values of $\tan\delta_{25°\mathrm{C}}$ and the temperature at $\tan\delta_{\max}$ showed no identifiable trend with regards to filler loading, heat treatment or MAPE content (Figure 4.117b) when compared with the unexposed composites. The $W_{\sqrt{2}}$ of weathered LDPE is relatively the same as the un-aged sample, a sign that the width of tan delta do not change significantly with aging. However, $W_{\sqrt{2}}$ value increased in all the aged composites relative, to the un-aged samples (Table 4.14).

a)



b)

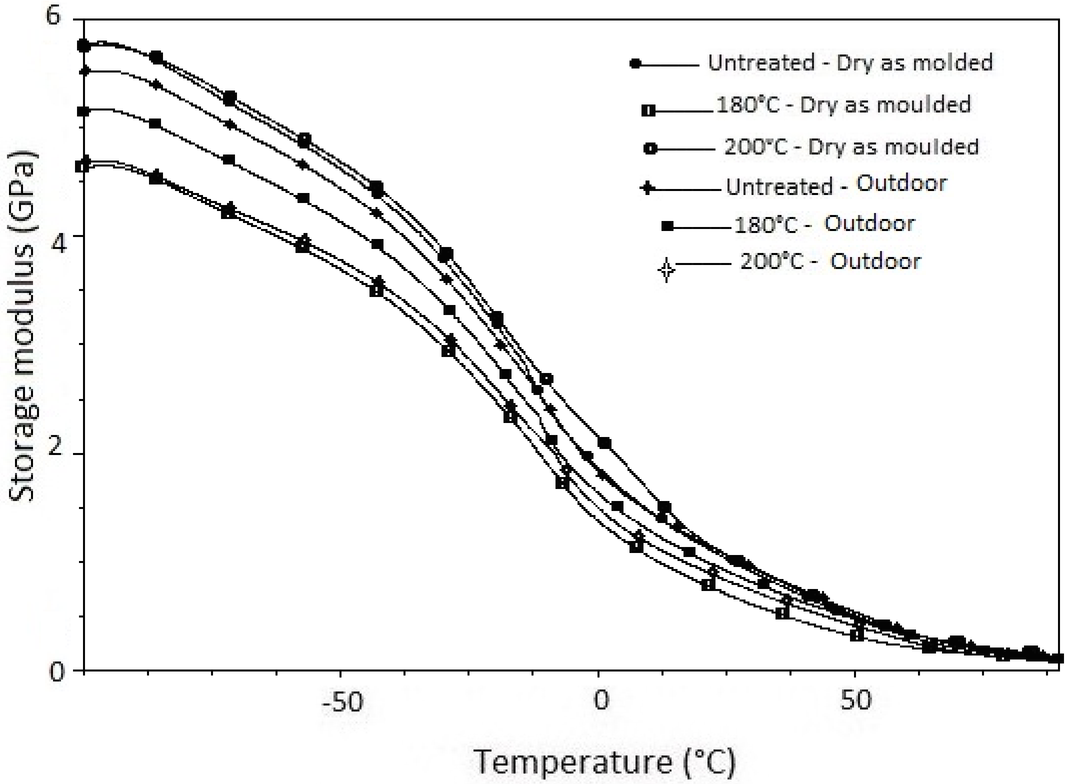
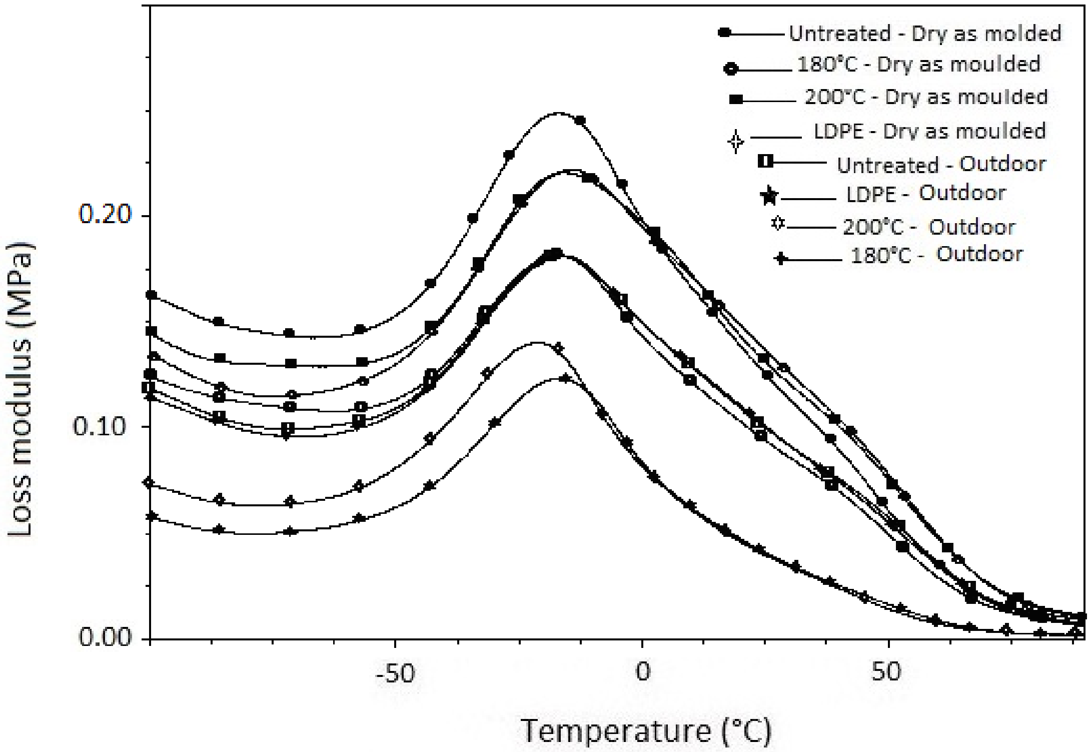


Figure 4.115: Storage modulus curves of dry as-moulded and outdoor exposed LDPE and composites containing 37 wt% wood flour and: a) 0% and b) 6% MAPE

a)



b)

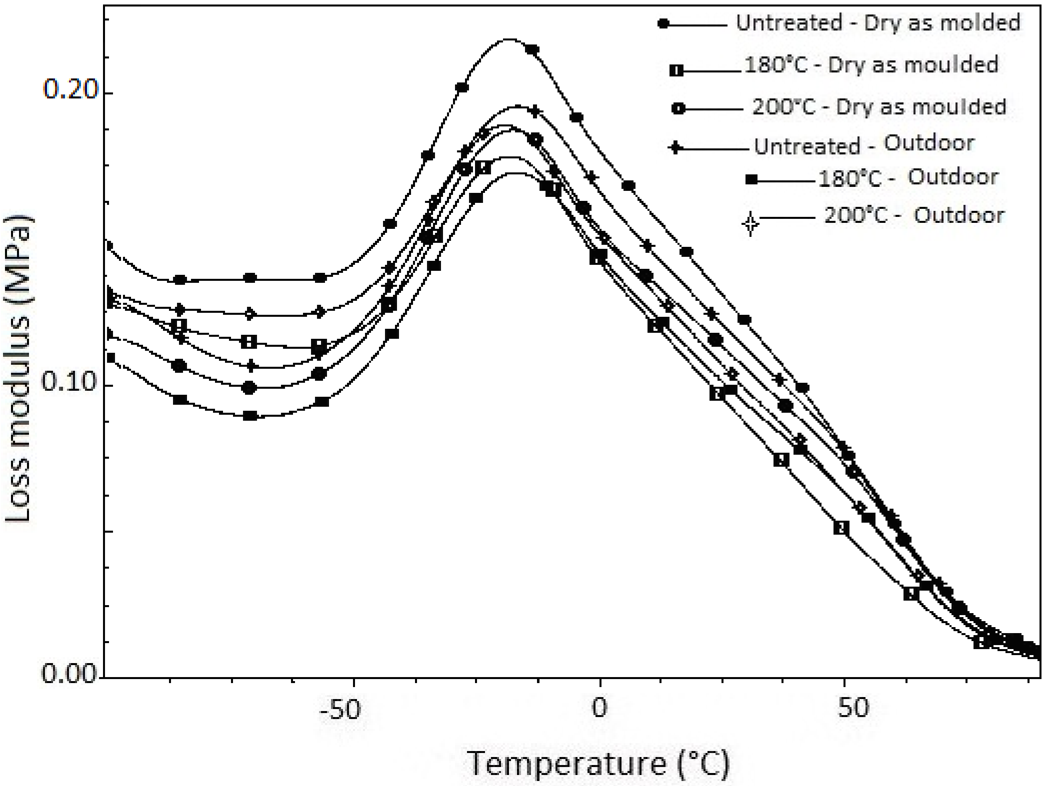
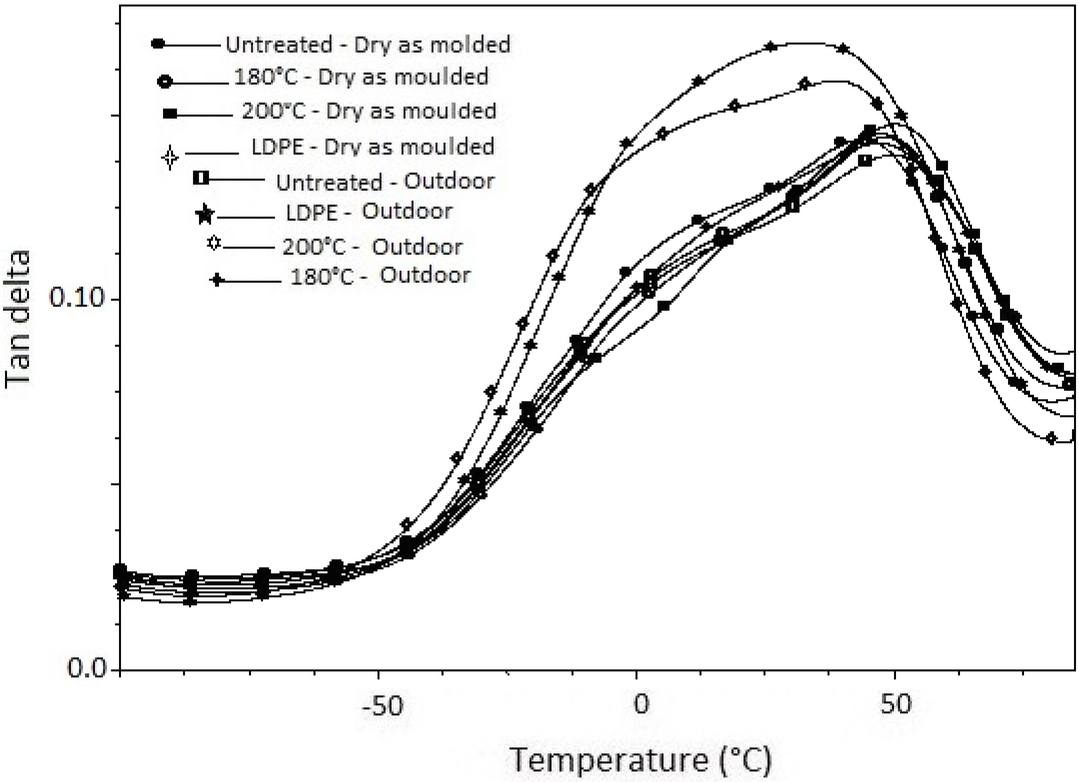


Figure 4.116: Loss modulus curves of dry as-moulded and outdoor exposed LDPE and composites containing 37 wt% wood flour with: a) 0% MAPE and b) 6% MAPE

a)



b)

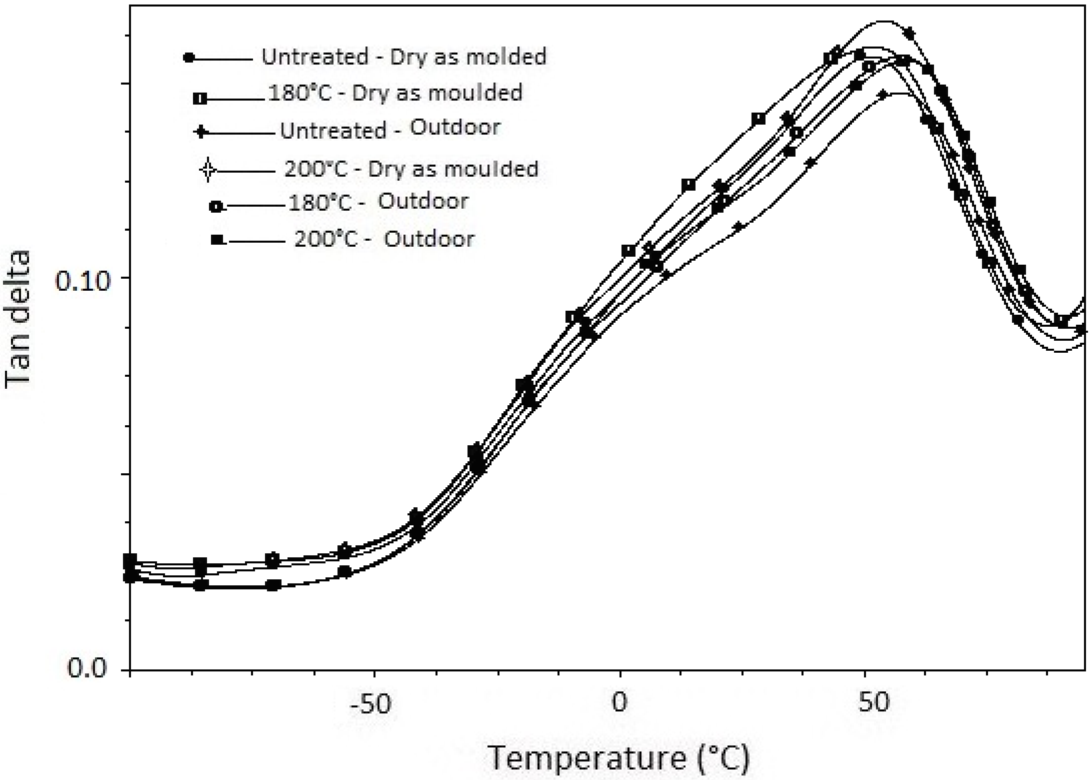


Figure 4.117: Tan delta curves of dry as-moulded and outdoor exposed LDPE and composites containing 37 wt% wood flour and: a) 0% and b) 6% MAPE

Table 4.14: DMA data of outdoor weathered samples

Sample	Wood treatment temperature (°C)	$Tan\delta$				Storage modulus E'		Loss modulus E"		
		$Tan\ \delta_{\max}$	Temperature at tan $\delta_{\max}$ (℃)	$W_{\sqrt{2}}$	$Tan\delta_{25°C}$	$E'_{25°C}$ (GPa)	$E'_{-100°C}$ (GPa)	$E''_{25°C}$ (MPa)	$T_{\beta}^{E''}$ (℃)	$E''_{\max}$ (MPa)
LDPE	-	0.17	33.8	73.2	0.17	0.24	2.9	41.0	-16.9	120.0
LDPE/W$_{UN/20/0}$	-	0.15	50.5	75.1	0.14	0.49	3.7	67.0	-17.9	150.0
LDPE/W$_{180/20/0}$	180.0	0.16	41.5	70.4	0.15	0.41	3.4	61.0	-17.8	140.0
LDPE/W$_{200/20/0}$	200.0	0.16	44.9	65.3	0.15	0.54	4.0	79.0	-17.9	160.0
LDPE/W$_{UN/37/0}$	-	0.14	49.8	73.1	0.12	0.82	4.6	99.0	-16.8	180.0
LDPE/W$_{180/37/0}$	180.0	0.14	46.7	71.4	0.13	0.79	4.7	101.0	-16.2	180.0
LDPE/W$_{200/37/0}$	200.0	0.15	47.3	66.0	0.12	1.11	5.8	132.0	-14.2	220.0
LDPE/W$_{UN/20/2}$	-	0.15	48.5	74.7	0.13	0.48	3.7	65.0	-18.1	150.0
LDPE/W$_{180/20/2}$	180.0	0.16	51.6	68.9	0.13	0.63	4.0	82.0	-18.6	160.0
LDPE/W$_{200/20/2}$	200.0	0.16	48.3	69.5	0.14	0.58	4.2	78.0	-17.5	160.0
LDPE/W$_{UN/37/2}$	-	0.14	53.2	67.8	0.12	0.84	4.8	99.0	-17.1	180.0
LDPE/W$_{180/37/2}$	180.0	0.14	61.1	66.4	0.12	1.09	5.6	133.0	-15.8	200.0
LDPE/W$_{200/37/2}$	200.0	0.14	53.4	68.2	0.12	0.84	5.9	99.0	-15.0	210.0
LDPE/W$_{UN/37/6}$	-	0.15	57.4	61.6	0.13	1.07	5.5	121.0	16.4	200.0
LDPE/W$_{180/37/6}$	180.0	0.16	57.4	62.3	0.12	0.91	4.8	113.0	-17.6	190.0
LDPE/W$_{200/37/6}$	200.0	0.16	58.4	66.2	0.12	0.83	4.7	100.0	-16.7	170.0
LDPE/W$_{UN/37/10}$	-	0.16	60.1	60.8	0.12	1.12	5.6	127.0	-17.6	200.0
LDPE/W$_{180/37/10}$	180.0	0.16	57.6	62.4	0.12	0.93	5.1	104.0	-18.3	190.0
LDPE/W$_{200/37/10}$	200.0	0.16	60.2	57.7	0.12	0.90	5.0	105.0	-18.5	180.0

4.3.3.5 Mechanical properties

It has been observed that weathering of polymeric materials depends on the specific wavelengths and amount of solar radiation the materials are capable of absorbing, the strength of their chemical bonds in relation to the photon energies of the solar radiation absorbed and the reaction processes promoted by heat, moisture and other weather factors following bond breakage. Complex interactions of the combination of weather factors with the polymer and its components in composites lead to permanent changes in the chemical structures and physical properties, in a way that generally changes the appearance and mechanical properties and reduces the useful life of the material [188]. Also, outdoor applications of WTC require that the materials withstand a wide variety of environmental factors including moisture, UV radiation, high temperatures, freeze-thaw cycles, mechanical action and biological invasion. In almost all cases, more than one of these factors act at the same time and in cycles. Swelling, warping, twisting, mould growth, decay, colour changes and connector failure are some of the problems often encountered from normal outdoor use [222]. These contribute to mechanical property losses by eroding the surface and increasing surface wettability. In this section, an evaluation of the mechanical performance of outdoor weathered composites, relative to the dry as-moulded samples, was conducted with a view to assessing the extent of mechanical properties deterioration following outdoor weathering.

Tensile properties

Tensile modulus

The tensile modulus of neat LDPE (0.231 GPa) increased slightly (0.224) after exposure to outdoor weathering. Though the chemical structure of LDPE consists of carbon and hydrogen atoms, constituting only C-C and C-H bonds, with no chromophores present, photodegradation of LDPE is possible but difficult by UV radiation. From the FTIR spectra (Figure 4.109), a sign of photodegradation is seen in the weathered LDPE. The possibility of a slight depolymerisation by chain scission may have eroded the surface (Figure 4.111b, page 227) and may be responsible for the reduced tensile modulus. Figure 4.118 presents the tensile modulus of dry as-moulded and outdoor exposed samples as a function of wood content and treatment temperature. On exposure to outdoor weathering, the tensile modulus decreased, with composites filled with 37 wt% wood flour exhibiting a significant drop in modulus. This is attributed to the deteriorating effect of the outdoor environment on the properties of WTC components by photodegradation. It has been reported [213] that changes in the mechanical properties of WTC after weathering are due to changes in the composite surface oxidation, matrix crystallinity changes and interfacial degradation. In addition, wood particles absorb water and swell and the polymer matrix cracks upon UV exposure, resulting in reduced tensile properties. These, in combination, result in a flaky, cracked composite surface with reduced mechanical properties. Therefore, the higher the wood content, the higher was the degradation. Heat-treated wood composites resisted deterioration in properties more than the heat-treated samples (Figure 4.118). Composites filled with 37 wt% untreated wood flour showed the highest decrement in tensile modulus (33%) after outdoor exposure. While those containing wood flour treated at 180°C and 200°C exhibited a decrement to the tune of 23% and 5% respectively. Reduced hydrophilicity of heat-treated wood composites because of reduced surface O-H relative to the untreated samples is responsible for this trend. This has reduced the tendency to absorb water and also, possibly reduced the UV absorption capacity (Figure 4.109, page 224). Even with the addition of MAPE, the tensile modulus of exposed samples is reduced relative to the dry as-moulded samples (Figure

4.119), with the untreated WTC still showing a higher rate of decrement.

Tensile strength

The tensile strength of the outdoor-aged LDPE (9.01 MPa) is slightly lower than the dry as-moulded ones (9.14). This is expected due to degradation by the elements of the outdoor weather (Figures 4.111b, page 227). Strangely, the tensile strength of the composites increased with exposure to outdoor weathering (Figure 4.120). A decrease in strength is expected because the composites are supposed to have aged from outdoor exposure (Figures 4.112 b and c). However, this is not the case in the present observation. It has been suggested that starch filled polyethylene, undergo a small increase in tensile strength in the very early stages of degradation, due to increased cross-linking as cleaved molecules relax into more stable configurations [223]. This result agrees with the findings of Leong *et. al*, [224] who observed an increase in tensile strength during the initial period of exposing talc/calcium carbonate filled polypropylene composites to tropical outdoor environment for six months. Reports have shown that increase in tensile strength of LDPE during aging might be a result of higher ordering of the amorphous phase and recombination of alkyl radicals from LDPE. The recombination reaction may be restricted to certain level of aging time and temperature and further the formation of free radicals caused by chain scission, causing a decrease in the value of its tensile strength [218]. It is possible that the duration of exposure in this experiment is not enough to have resulted in the depreciation of tensile strength. More so, predicting a polymer's useful life has been observed to be difficult because its mechanical properties can be a nonlinear function of aging time. Thus, extrapolation of short-term behaviour may not be an accurate predictor of long-term behaviour [225]. As with the dry as-moulded specimens, composites from wood flour treated at 180°C present the highest tensile strength values. On the other hand, a reduction in tensile strength is seen in outdoor aged composites containing MAPE (Figure 4.121).

Tensile strain

A decrement in the tensile strain is observed with outdoor exposure (Figure 4.122). Depolymerisation, surface cracking and increase in crystallinity may be responsible for this trend [224]. Tensile strain has been suggested to be a more sensitive proof of deterioration than tensile strength and is found to be most indicative of the deterioration of unoriented polymers by, for example, oxidative processes which is well known to lead to surface or bulk cracking and associated embrittlement [189]. However, no correlation could be made between the tensile strain and treatment temperature in relations to outdoor exposure. Again, no observable trend in tensile strain of exposed composites could be established with the incorporation of MAPE (Figure 4.123).

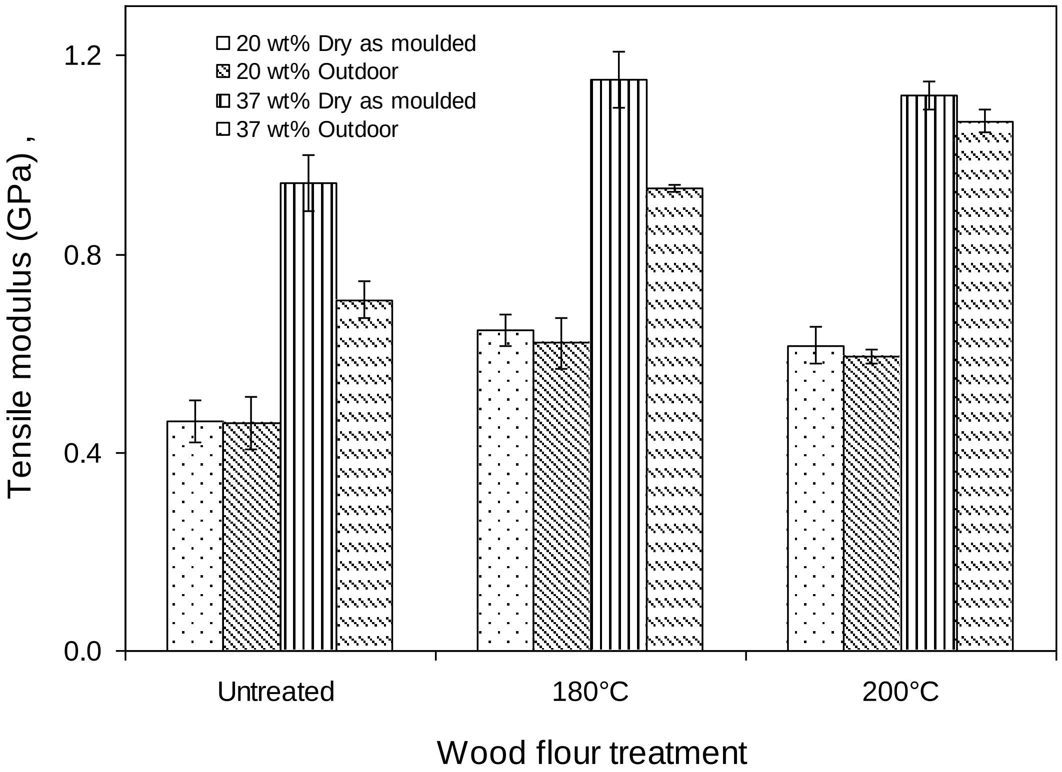


Figure 4.118: Tensile modulus of outdoor and dry as-moulded composites as a function of wood content and treatment temperature

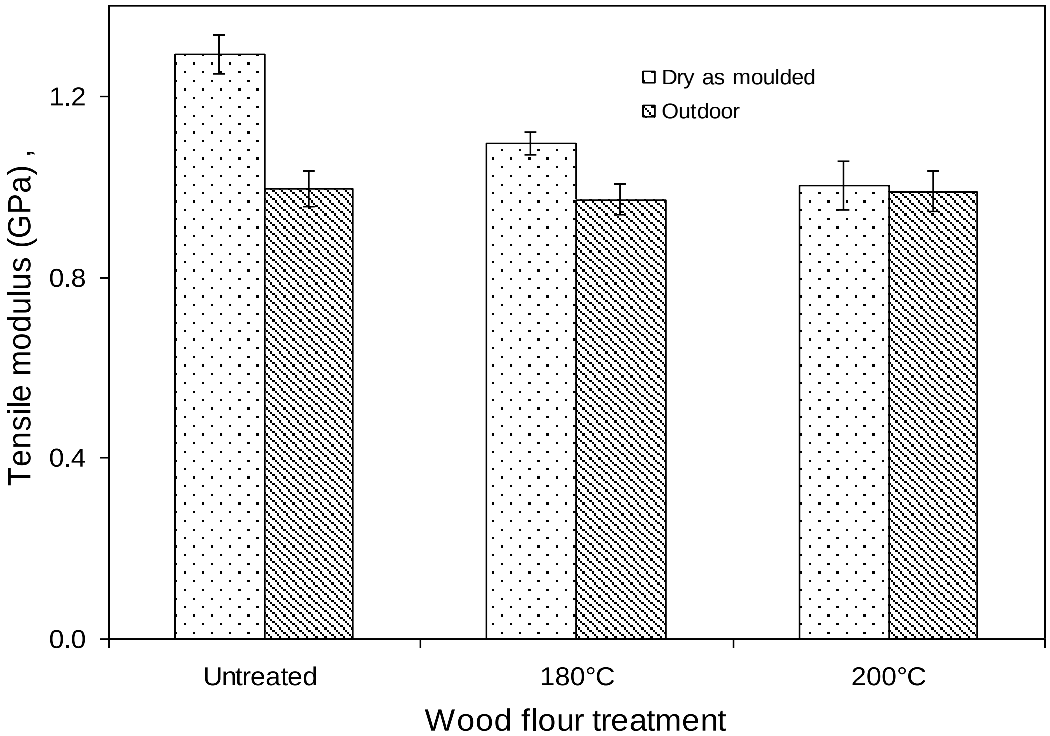


Figure 4.119: Tensile modulus of 37 wt% outdoor and dry as-moulded composites with 6% MAPE

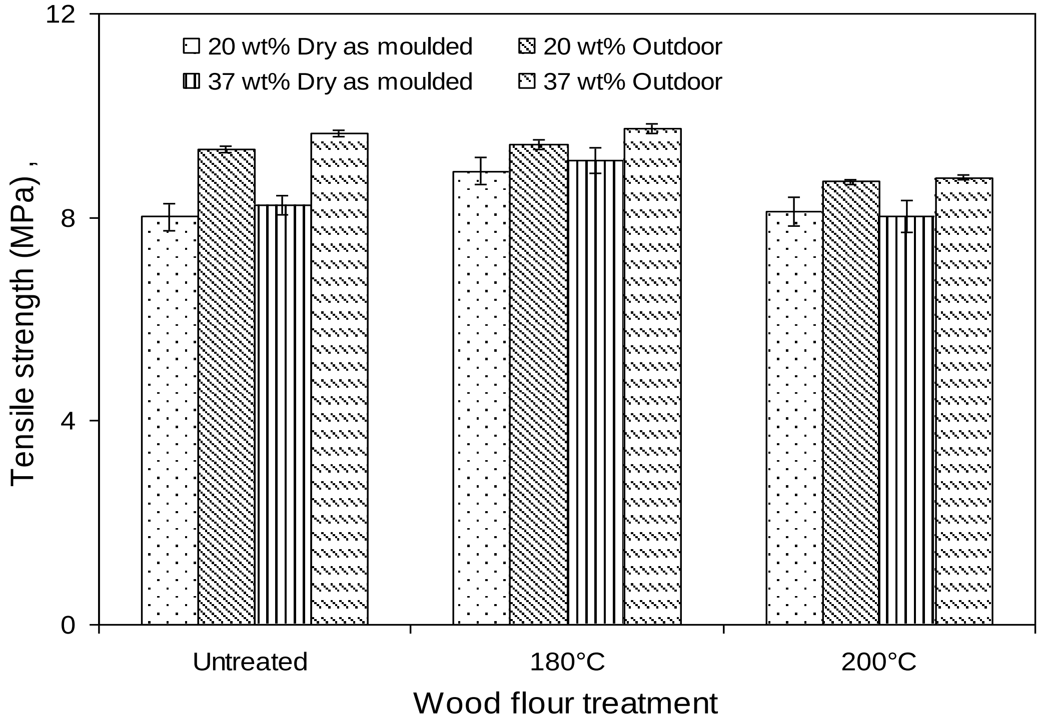


Figure 4.120: Tensile strength of outdoor and dry as-moulded composites as a function of wood content and treatment temperature

Figure 4.121: Tensile strength of 37 wt% outdoor and dry as-moulded composites with 6% MAPE

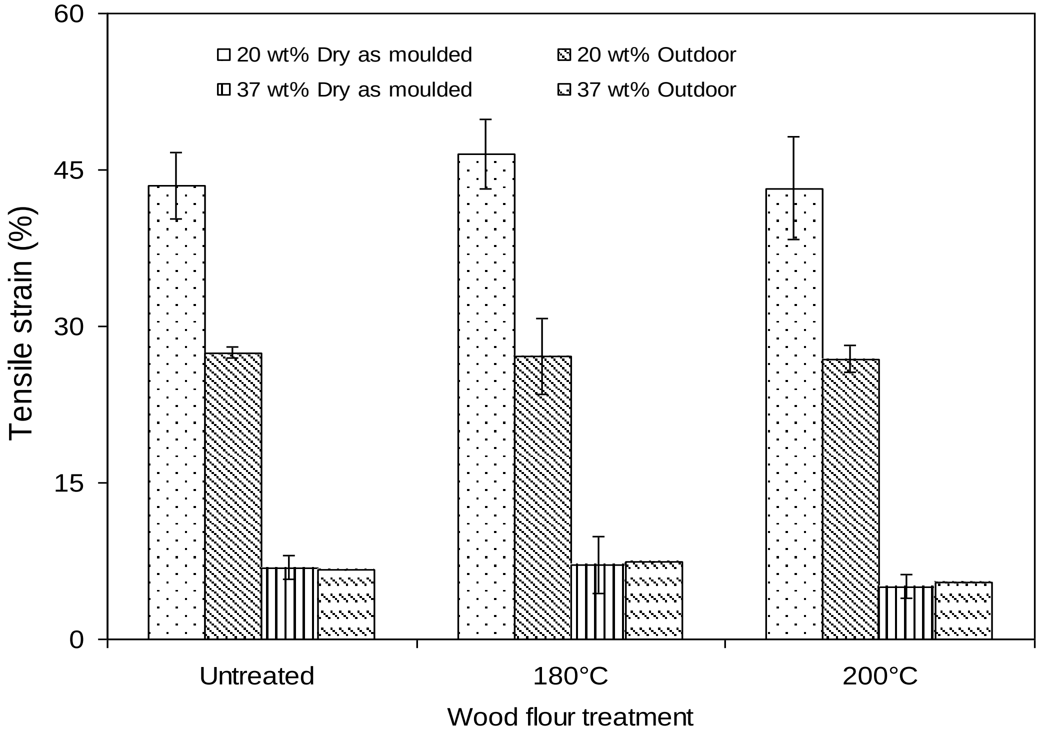


Figure 4.122: Tensile strain of outdoor and dry as-moulded composites as a function of wood content and treatment temperature

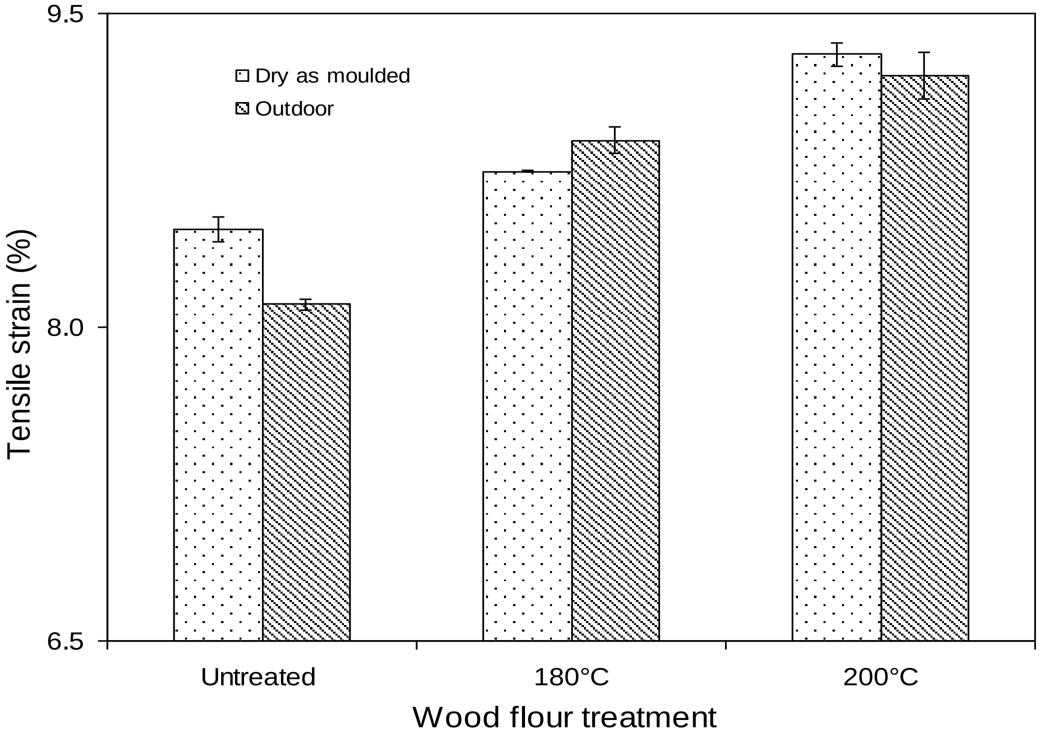


Figure 4.123: Tensile strain of 37 wt% outdoor and dry as-moulded composites with 6% MAPE

Flexural properties

Flexural modulus

Figure 4.124 presents the flexural modulus of the dry as-moulded and outdoor weathered composites as a function of wood content and heat treatment. The flexural modulus of the neat LDPE (0.121 GPa) showed no significant change with outdoor weathering (0.118 GPa). On exposure to outdoor weathering, the flexural modulus decreased in all compositions and with heat treatment condition, with the exception of samples made from wood flour treated at 200°C. Deterioration due to outdoor exposure could be responsible for this trend. The rate of decrease is higher in untreated wood composites relative to the heat-treated materials. The possibility of better interfacial adhesion between the wood fillers and the matrix in composites made from heat-treated wood flour may be responsible for this observation. Also, a decrease in flexural modulus is seen in outdoor weathered composites containing MAPE, with the weathered composites made form untreated wood flour showing a higher rate of decrease (Figure 4.125).

Flexural strength

The flexural strength of dry as-moulded LDPE (7.13 MPa) increased after outdoor aging (8.11 MPa). Surprisingly again, a slight increase in flexural strength of the composites is observed with outdoor exposure (Figure 4.126). The increment is higher in composites made from heat-treated wood composites relative to the untreated wood composites. The same reasons adduced for the increase in tensile strength may also be applicable in this case. On addition of MAPE, only a negligible increment is seen in the outdoor weathered composites (Figure 4.127).

Flexural displacement

Figure 4.128 presents the flexural displacement of the weathered and unweathered composites. The flexural displacement of the outdoor aged LDPE (0.097 mm/mm) is relatively the same as the dry as-moulded sample (0.098 mm/mm). From the figure, it can be seen that the flexural displacement increased marginally with outdoor weathering. Surface crazing and cracks developed on the surface of the composites as a result of outdoor exposure, which could aid premature failure, may be responsible for this behaviour. The same trend is detected in the composites containing MAPE (Figure 4.129).

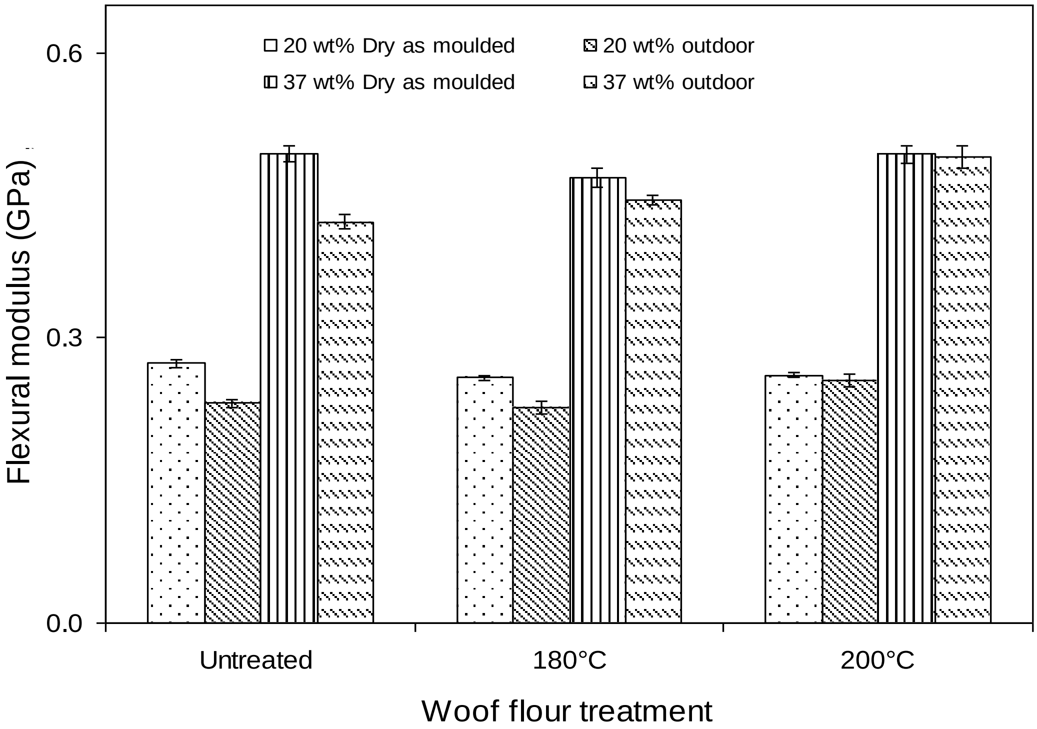


Figure 4.124: Flexural modulus of dry as-moulded and outdoor exposed samples as a function of wood content and treatment temperature

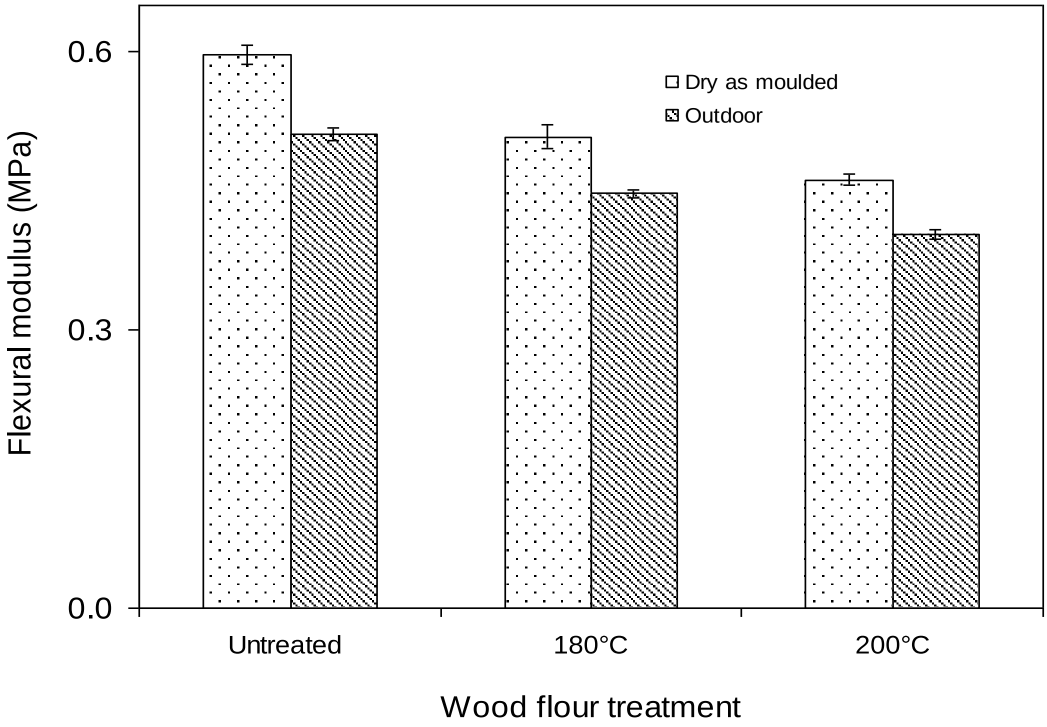


Figure 4.125: Flexural modulus of 37 wt% dry as-moulded and outdoor exposed samples with 6% MAPE

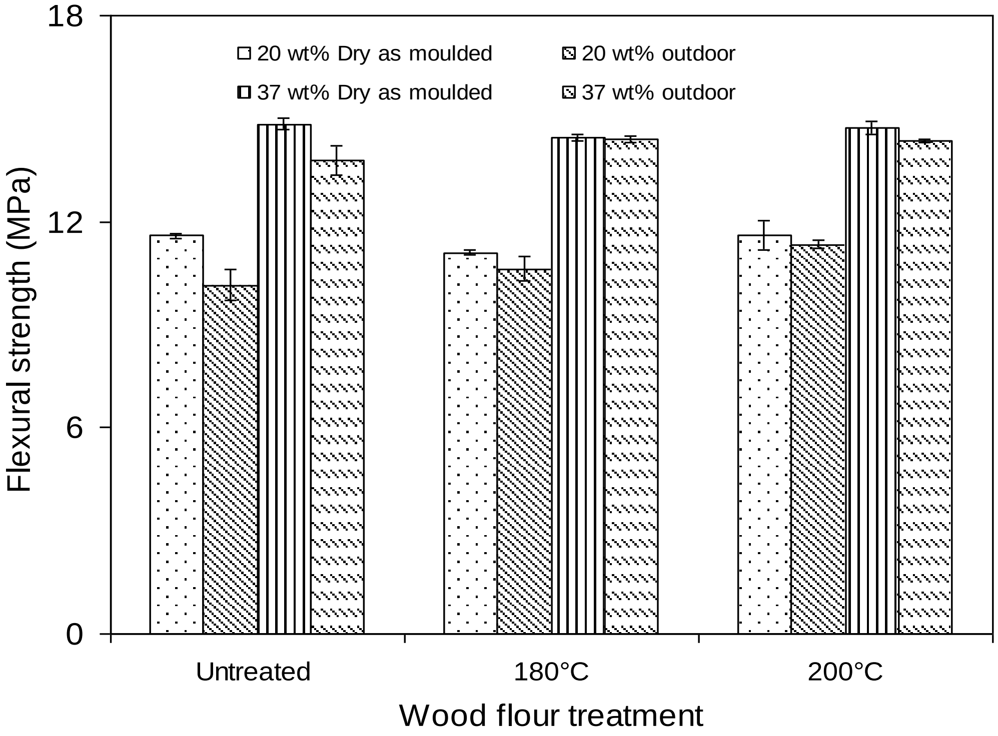


Figure 4.126: Flexural strength of dry as-moulded and outdoor exposed samples as a function of wood content and treatment temperature

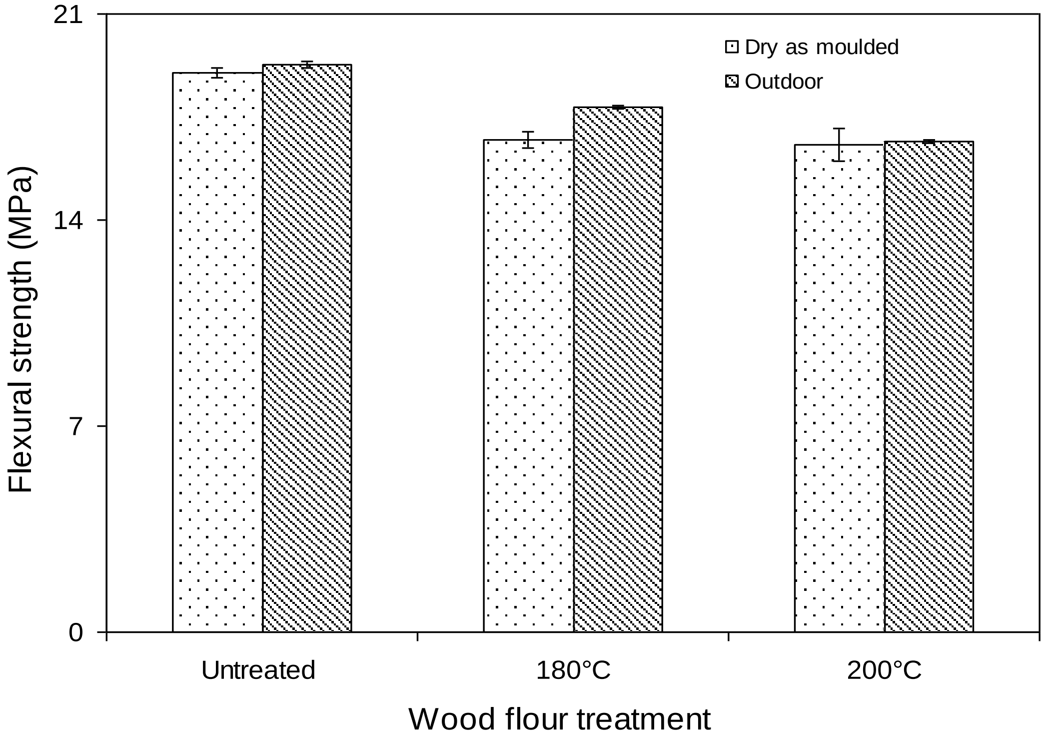


Figure 4.127: Flexural strength of 37 wt% dry as-moulded and outdoor exposed samples with 6% MAPE

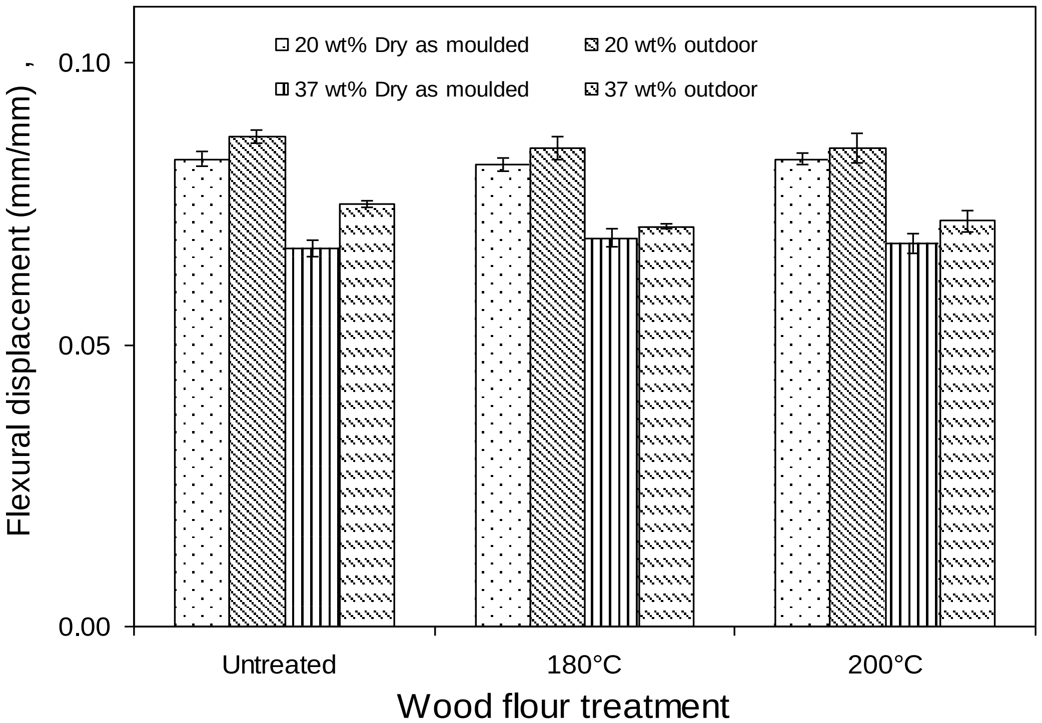


Figure 4.128: Flexural displacement of dry as-moulded and outdoor exposed samples as a function of wood content and treatment temperature

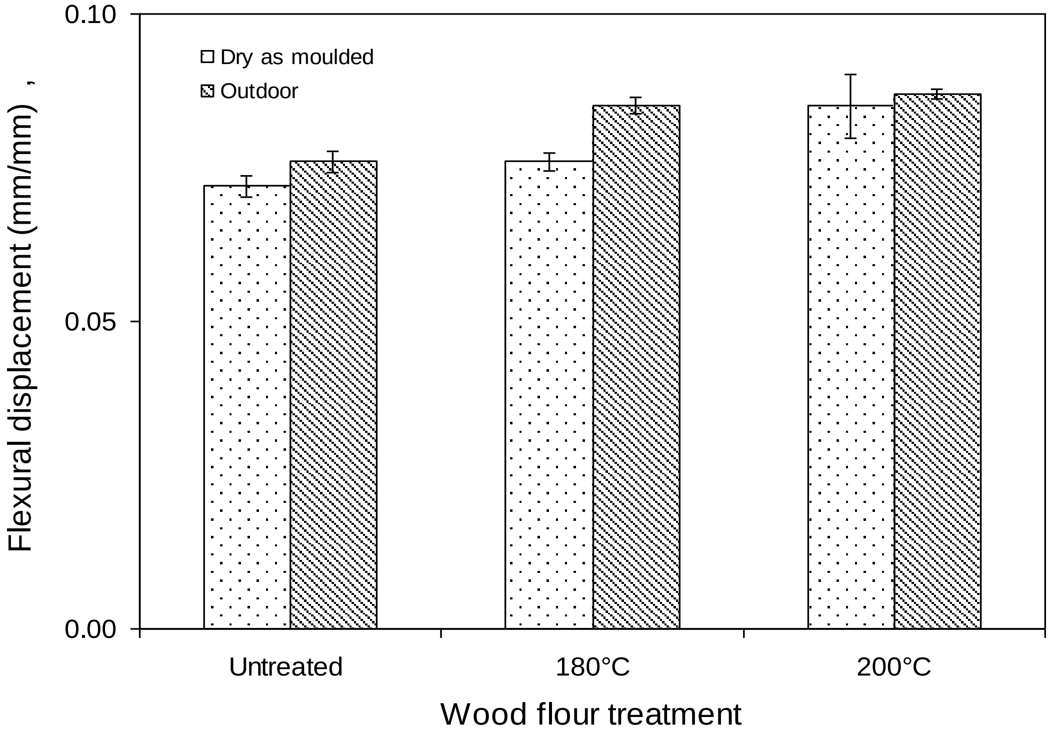


Figure 4.129: Flexural displacement of 37 wt% dry as-moulded and outdoor exposed samples with 6% MAPE

Impact properties

Peak load, P

The values of P in the dry as-moulded LDPE increased from 266.6 N, 225.3 N, 184.5 N, and 137.4 N to 283.3 N, 241.4 N, 198.9 N and 150.7 N for a/D ratios 0.1, 0.2, 0.3 and 0.4 respectively. This trend is presented in the composites (Figure 4.130). In the composites, the increment is more noticeable in the samples containing 37 wt% wood flour, while no appreciable increase is seen in composites made of 20 wt% wood content. It is expected that the P should drop on exposure to outdoor weathering, but the reverse is observed here. Although, it is not clear what is responsible for this trend, it is likely that the amount of water absorbed in the composites may have softened the system, making it more ductile, leading to increased P. In addition, cross-linking caused by photodegradation may also increase the maximum load needed for failure. Nevertheless, an obvious trend could not be found with regards to heat treatment temperature. On addition of 6% MAPE, only a marginal increase in P was observed in the composites following exposure to the natural outdoor environment (Figure 4.131).

Critical stress intensity factor, K_c

The K_c values of the neat LDPE did not change with outdoor exposure (1.7 MPa.m$^{0.5}$). The variation of K_c of untreated and heat-treated WTC with outdoor exposure is given in Figure 4.132. As observed in P, K_c increased with outdoor aging. Again, the fact that the composites absorbed over 50% water (Appendix A) on outdoor weathering when compared to the dry as-moulded samples, could mean that the system may have become softer and as a result, more ductile, thereby resisting brittle failure to different extents. Addition of MAPE gave no identifiable trend in K_c with outdoor aging (Figure 4.133).

Energy to failure, W

Energy to failure decreases marginally with aging in the LDPE. Values of 4.62 J, 3.48 J, 3.17 J and 2.12 J are obtained for the dry as-moulded samples while 4.28 J, 3.56 J, 2.79 J and 2.04 J are recorded in the outdoor aged samples for a/D ratios 0.1, 0.2, 0.3, 0.4 respectively. This is expected since the neat LDPE show signs of embrittlement (Figure 4.111b, page 227), resulting from a likelihood of increased crystallinity due to outdoor aging. Also, the composites show a slight decrement in W with outdoor exposure (Figure 4.134). Again, the propensity to brittle failure in weathered composites may be responsible for this behaviour. This is in agreement with previous studies where the impact energy of HDPE exposed to Canadian winter was found to decrease [226]. Furthermore, W increased in the outdoor weathered composites containing MAPE compared to the un-aged counterparts (Figure 4.135).

Critical strain energy release rate, G_c

The G_c values of the dry as-moulded LDPE (96.58 kJ.m^{-2}) also decreased slightly with outdoor exposure (91.10 kJ.m^{-2}). Once more, the possibility of matrix cracking, resulting from embrittlement, may be the reason for this behaviour. The same trend is exhibited by the composites (Figure 4.136), where a marginal decrease in G_c is observed with outdoor aging. This is in line with earlier reports where the impact strength of rice husk filled polyethylene composites was found to reduce with outdoor weathering and was attributed to the oxidation-induced embrittlement, due to UV absorption [227]. Incorporation of MAPE presents higher values of G_c in the outdoor weathered composites, relative to the dry as-moulded composites (Figure 4.137).

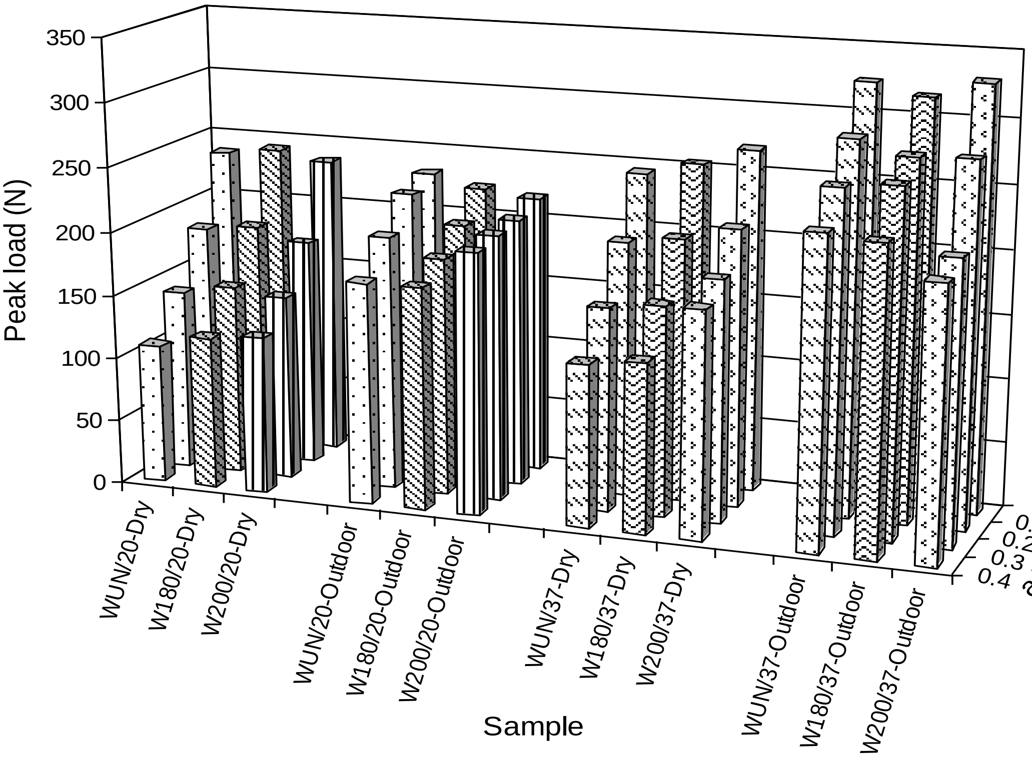


Figure 4.130: Peak load of dry as-moulded and outdoor exposed samples as a function of wood content and heat treatment

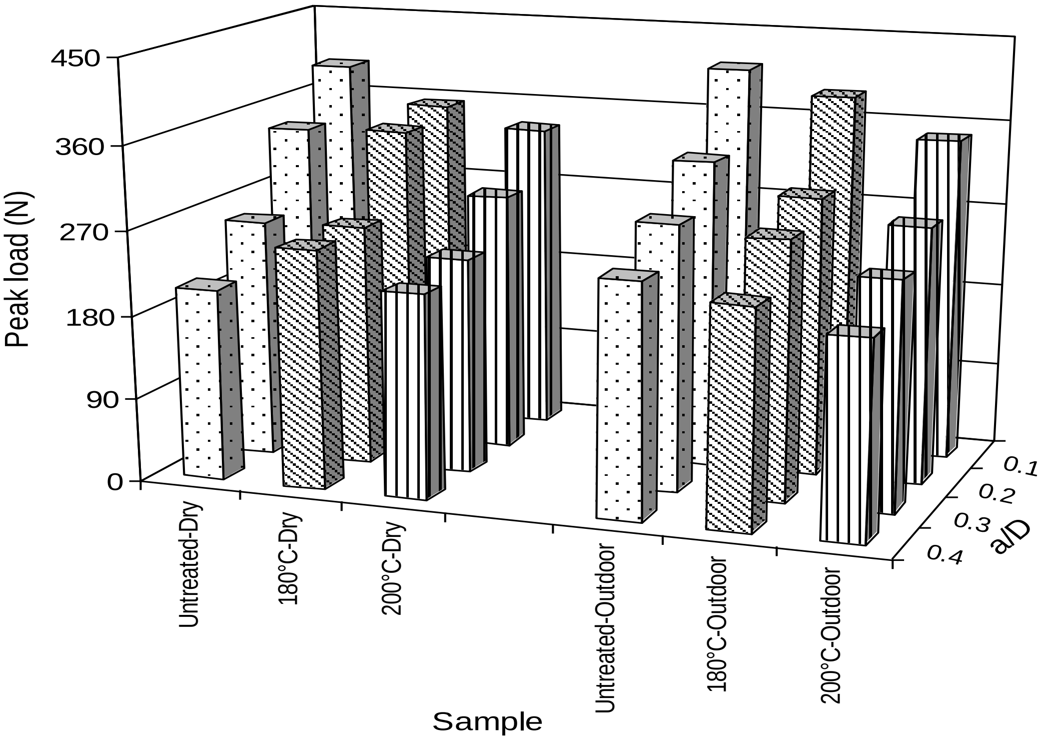


Figure 4.131: Peak load of 37 wt% dry as-moulded and outdoor exposed samples containing 6% MAPE

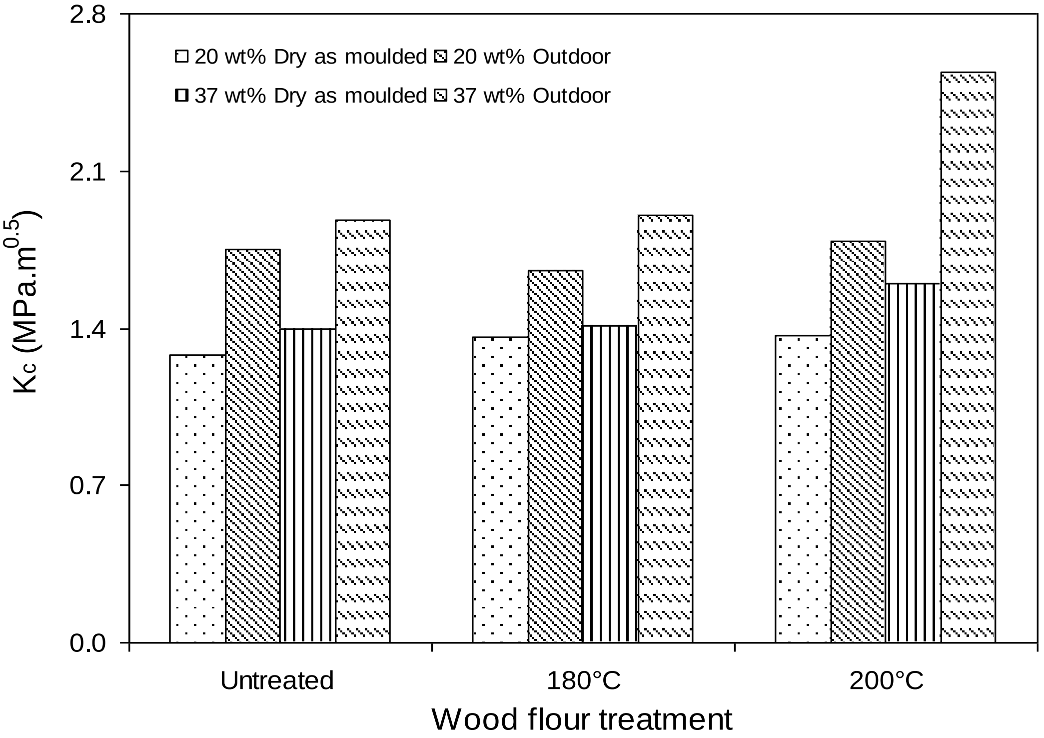


Figure 4.132: K_c of dry as-moulded and outdoor exposed samples as a function of wood content and heat treatment temperature

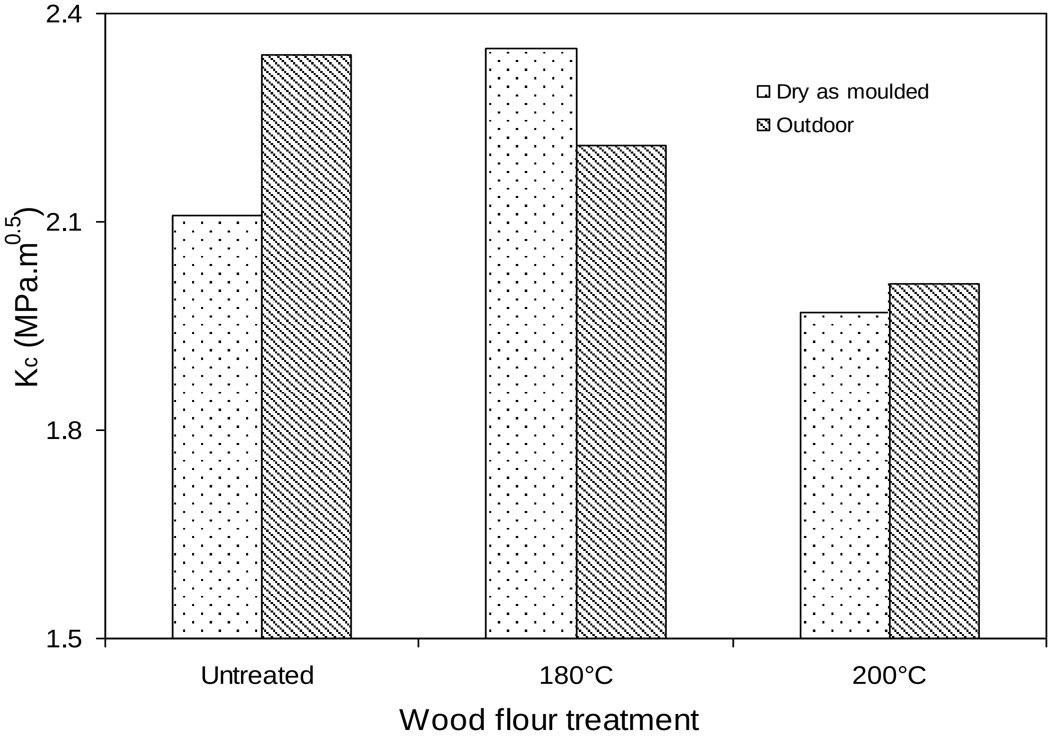


Figure 4.133: K_c of 37 wt% dry as-moulded and outdoor exposed samples containing 6% MAPE

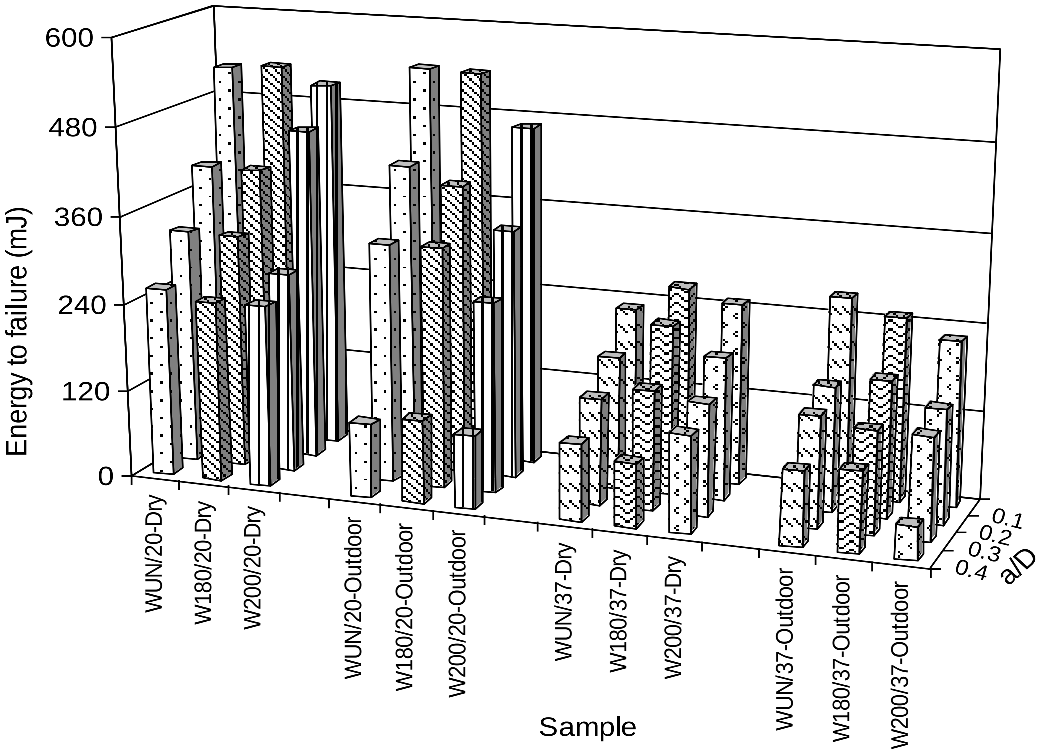


Figure 4.134: Energy to failure of dry as-moulded and outdoor exposed samples as a function of wood content and heat treatment

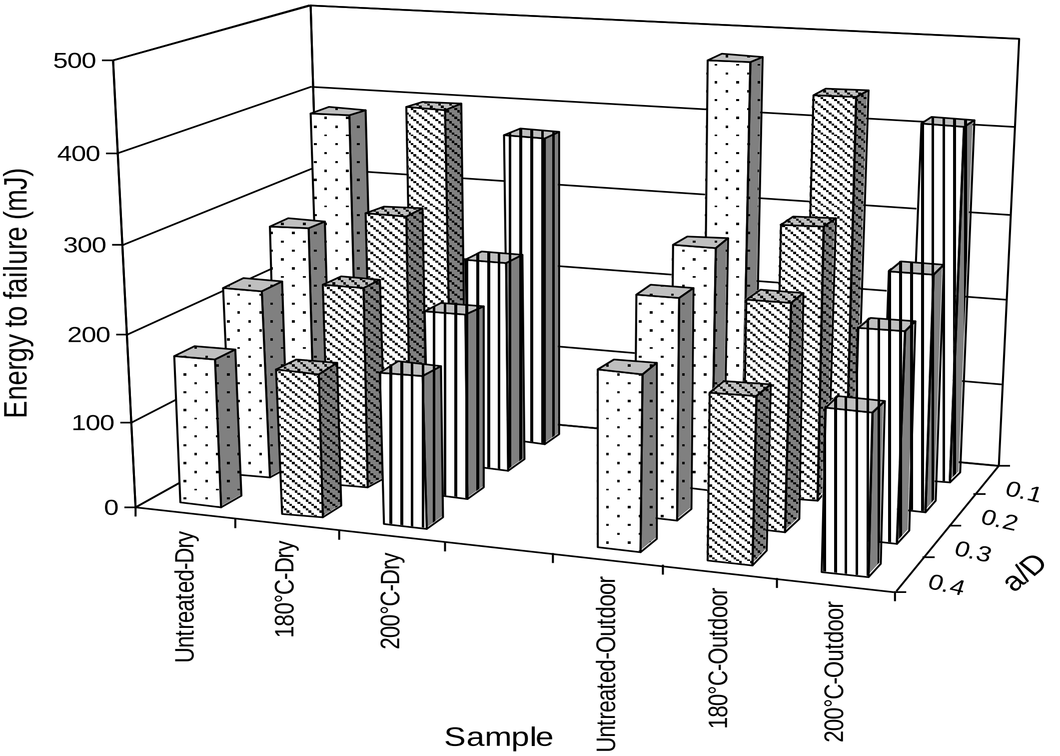


Figure 4.135: Energy to failure of 37 wt% dry as-moulded and outdoor exposed samples with 6% MAPE

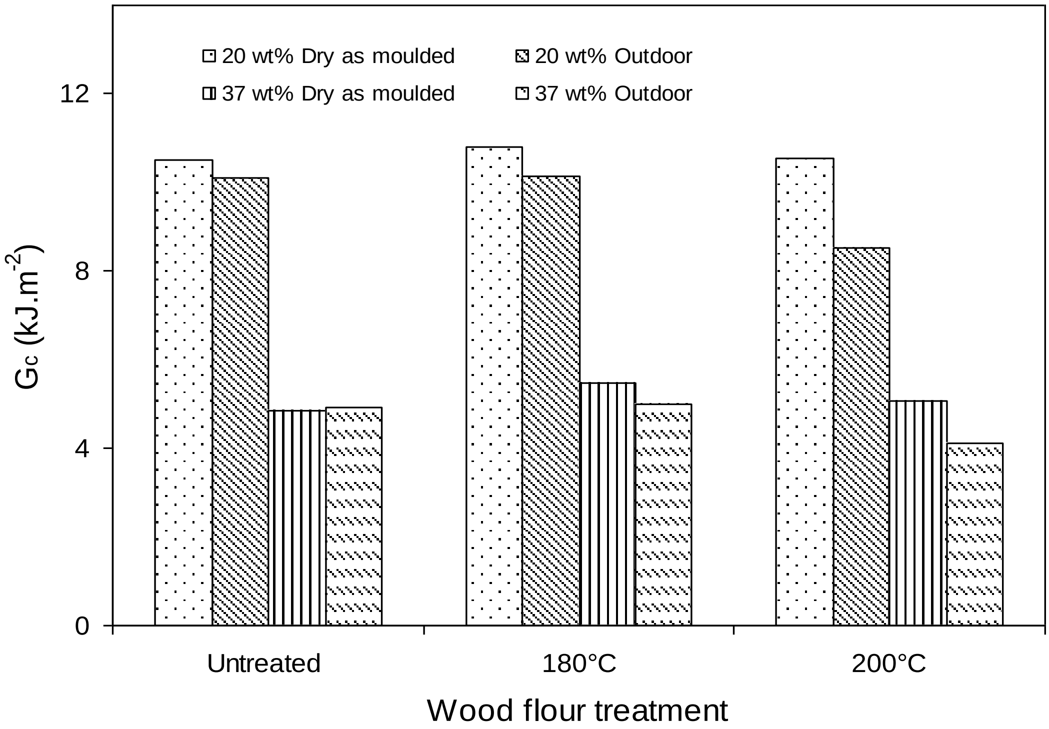


Figure 4.136: G_c of dry as-moulded and outdoor exposed samples as a function of wood content and heat treatment

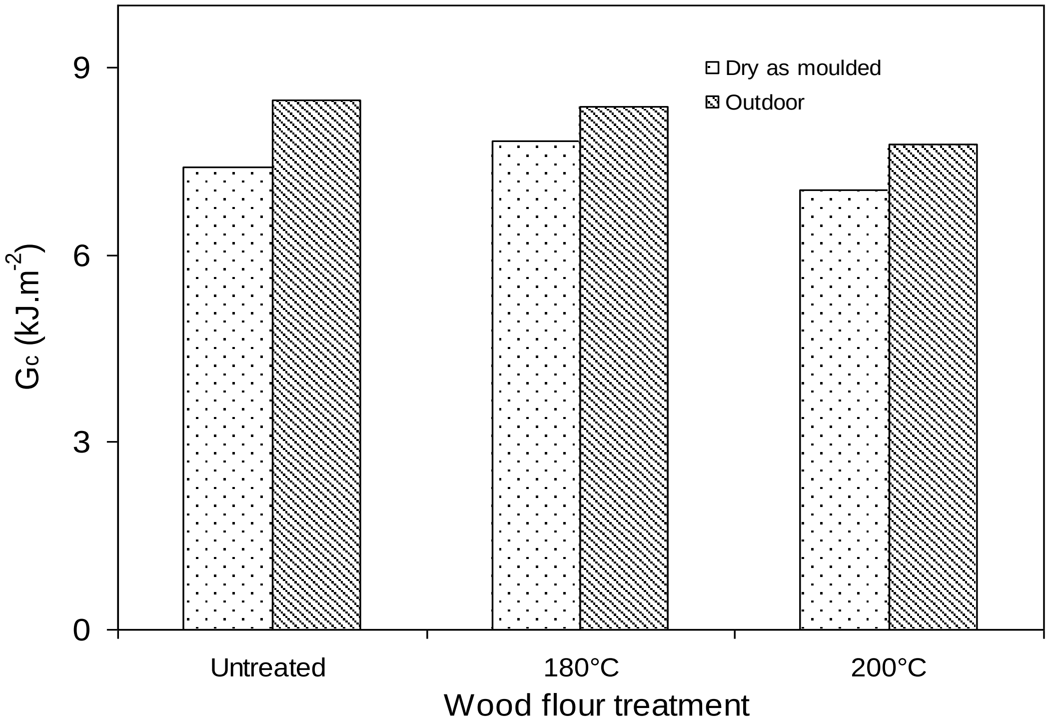


Figure 4.137: G_c of 37 wt% dry as-moulded and outdoor exposed samples containing 6% MAPE

4.3.4 Effect of the indoor environment

In this section, the effects of the indoor environment on the properties of the composites are investigated in order to determine the extent of degradation, if any. Since part of the intended applications of these composites is in the indoor environment, such as: cutlery holders and other domestic uses, determination of the material's response to the indoor situation was carried out in order to ascertain its applicability.

4.3.4.1 Physical appearance

The SEM micrographs of indoor exposed samples are presented in Figures 4.138 to 4.139. From the figures, there are no visible cracks on the surfaces of the samples. This is an indication that the indoor environment is not hostile to the samples.

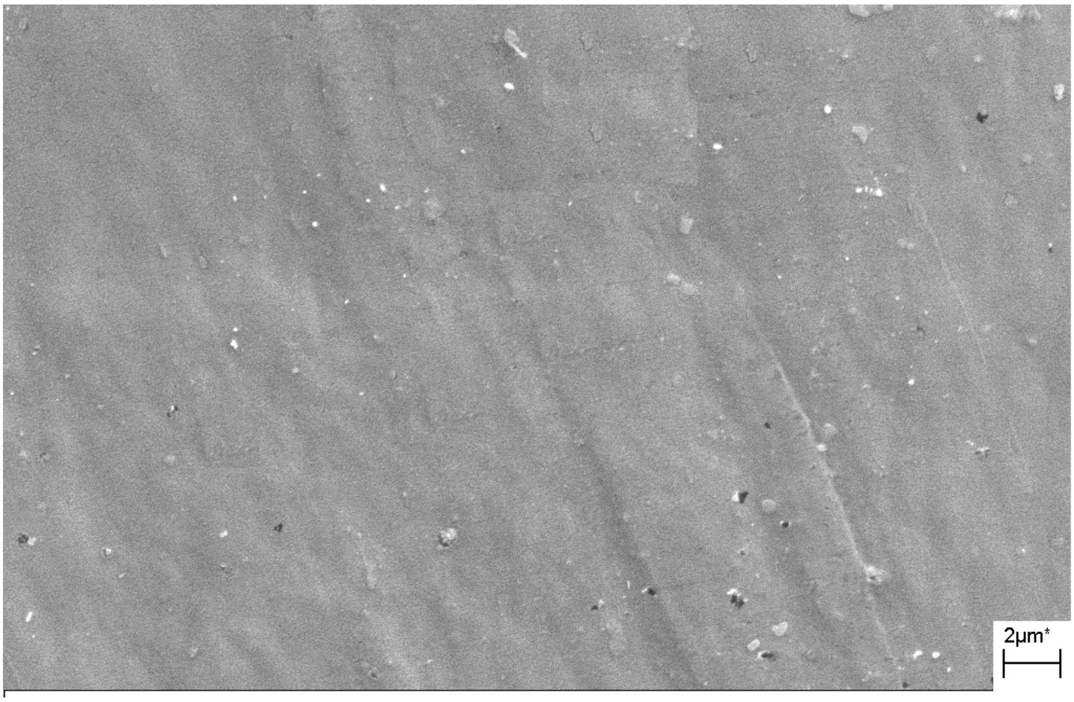


Figure 4.138: SEM micrograph of indoor exposed LDPE

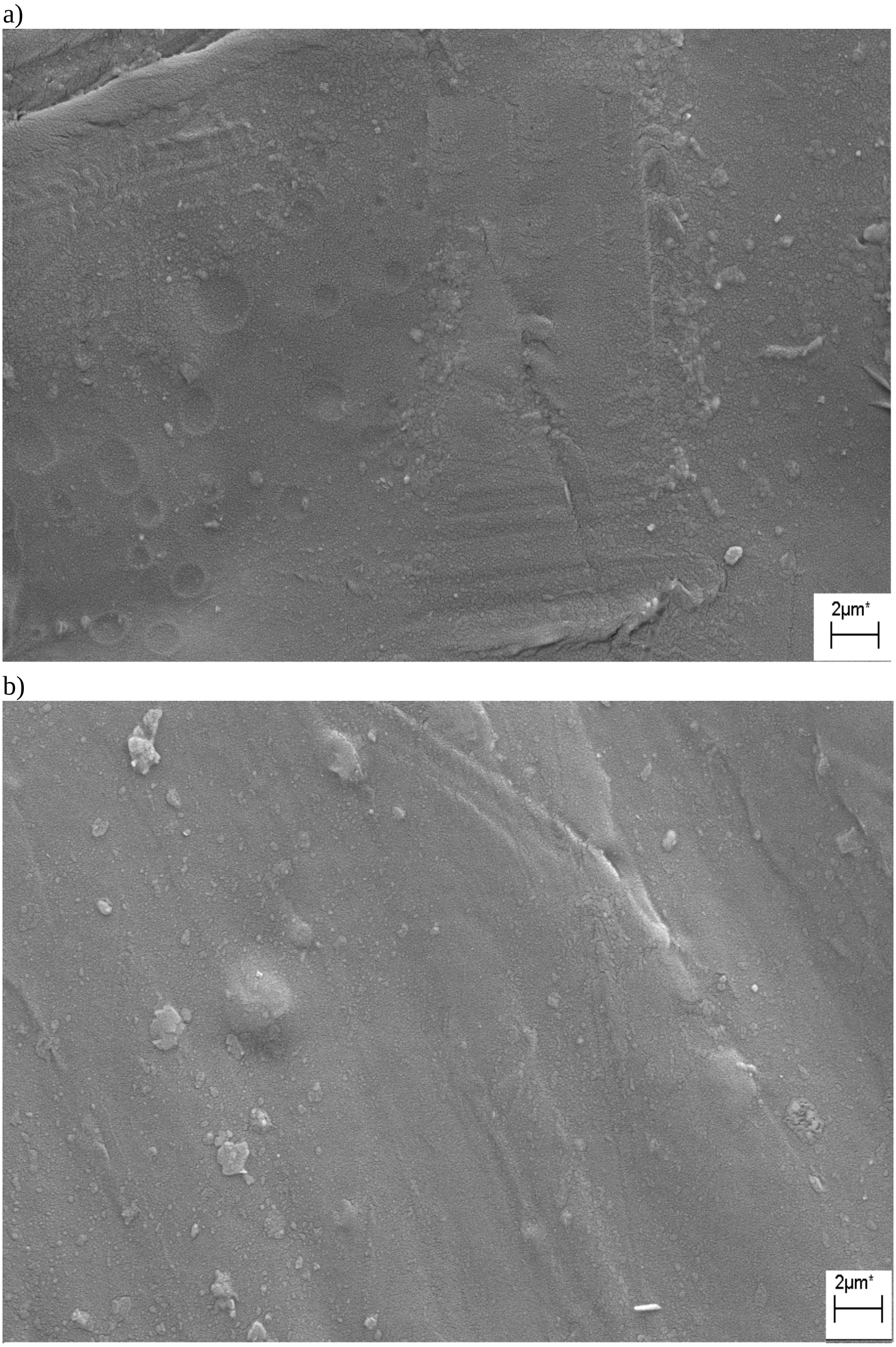


Figure 4.139: SEM micrograph of surfaces of indoor exposed composites containing: a) untreated and b) 200°C treated wood flour

4.3.4.2 Thermal properties

Thermogravimetric analysis, TGA

The TGA/DTG curves of dry as-moulded and indoor exposed samples containing 37 wt% wood flour are presented in Figure 4.140. Data extracted from these curves and those of 20 wt% wood content are given in Table 4.15. A peak at around 100°C show that 2.24%, 1.46% and 1.23% water evaporated from the 37 wt% indoor exposed composites made from untreated, 180°C and 200°C treated wood flour, respectively (Appendix A5). This indicates that the composites have absorbed moisture from the surrounding on exposure to the indoor environment, with the untreated WTC absorbing the highest amount of moisture. The thermal stabilities of the dry as-moulded and indoor exposed LDPE samples are relatively the same; as the curves overlapped. Also, from the table, it is clear that leaving the composites indoors has no marked effect on the thermal behaviour (Figure 4.140). There is no observable effect of the outdoor environment on: T_p, T_{onset}, $T_{50\%}$ and the degradation temperature range (Compare Table 4.2, page 57 and Table 4.15). The samples are not expected to undergo photodegradation as it is the case with the outdoor exposed samples. Therefore, an observable consequence of exposure to ambient environment should not be expected. The same trend is shown on addition of MAPE (Figure 4.140b).

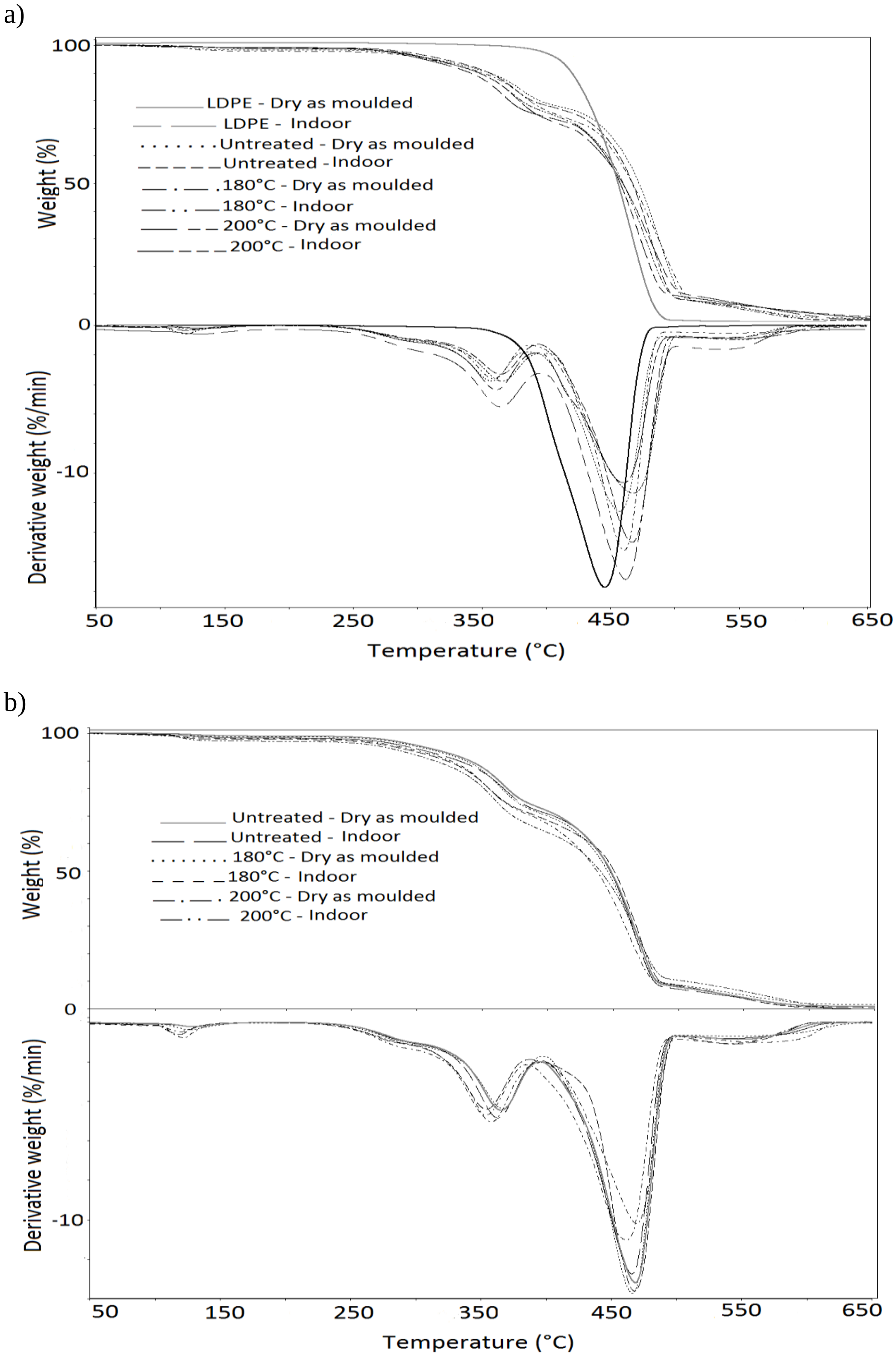


Figure 4.140: TGA/DTG curves of dry as-moulded and indoor exposed LDPE and 37 wt% untreated and heat-treated WTC containing: a) 0% and b) 6% MAPE

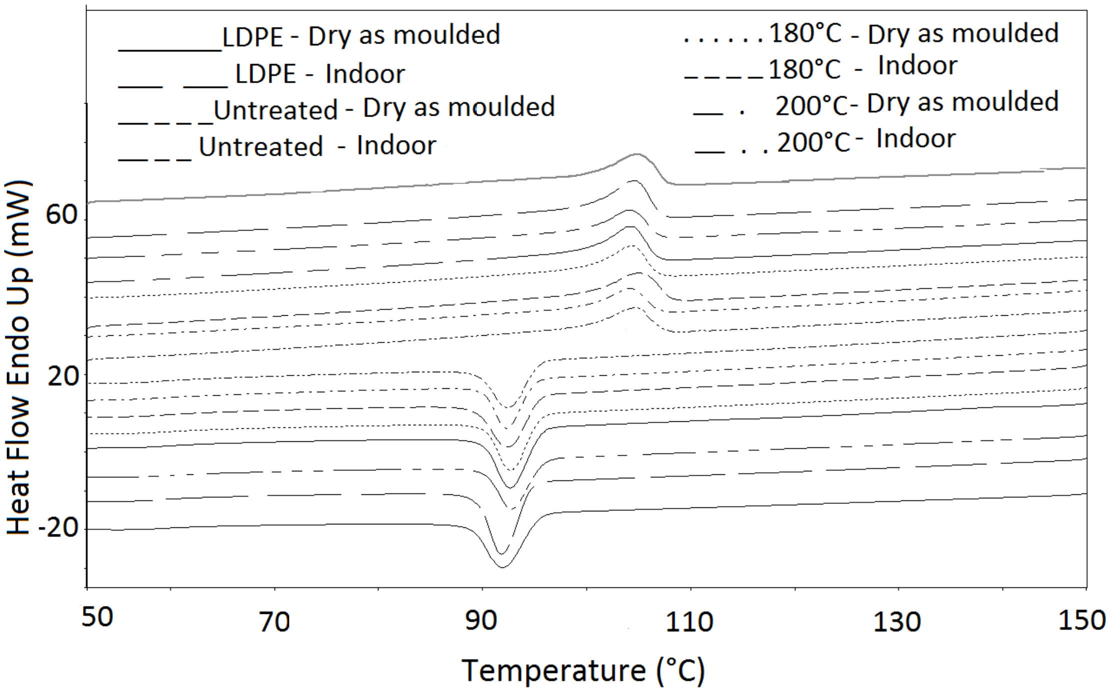
Table 4.15: TGA/DTG data of indoor exposed samples

Sample	Treatment temperature (°C)	T_p (°C)	Onset temperature, T_{onset} (°C)	$T_{50\%}$ (°C)	Degradation temperature (°C)
LDPE	-	442.7	401.5	433.6	352.9-482.4
LDPE/W$_{UN/20/0}$	-	468.1	390.2	456.6	270.2-502.0
LDPE/W$_{180/20/0}$	180.0	464.1	398.5	453.4	255.0-509.0
LDPE/W$_{200/20/0}$	200.0	469.7	413.6	458.1	259.2-501.3
LDPE/W$_{UN/37/0}$	-	463.0	401.7	446.4	245.2-502.2
LDPE/W$_{180/37/0}$	180.0	463.1	397.1	445.7	234.5-501.2
LDPE/W$_{200/37/0}$	200.0	467.1	390.3	388.3	231.5-502.7
LDPE/W$_{UN/20/2}$	-	460.8	399.2	446.9	236.9-491.0
LDPE/W$_{180/20/2}$	180.0	460.0	392.1	440.2	236.5-502.0
LDPE/W$_{200/20/2}$	200.0	457.4	385.0	435.7	235.1-500.0
LDPE/W$_{UN/37/2}$	-	452.8	399.4	446.5	250.8-506.6
LDPE/W$_{180/37/2}$	180.0	465.6	399.0	446.7	218.5-514.3
LDPE/W$_{200/37/2}$	200.0	468.2	333.7	441.1	237.8-506.5
LDPE/W$_{UN/20/6}$	-	461.9	378.9	439.6	262.7-505.6
LDPE/W$_{180/20/6}$	180.0	467.4	424.9	454.7	351.6-500.1
LDPE/W$_{200/20/6}$	200.0	465.9	419.9	452.5	347.4-501.5
LDPE/W$_{UN/37/6}$	-	470.4	416.5	449.7	230.9-502.4
LDPE/W$_{180/37/6}$	180.0	468.2	422.6	450.4	235.7-499.4
LDPE/W$_{200/37/6}$	200.0	462.1	412.0	457.3	224.8-501.1
LDPE/W$_{UN/20/10}$	-	457.2	375.4	423.8	243.7-501.1
LDPE/W$_{180/20/10}$	180.0	467.4	425.5	456.0	231.8-500.7
LDPE/W$_{200/20/10}$	200.0	468.0	405.9	454.1	249.2-499.4
LDPE/W$_{UN/37/10}$	-	466.1	395.4	439.0	235.3-512.4
LDPE/W$_{180/37/10}$	180.0	468.5	404.3	445.1	240.4-501.5
LDPE/W$_{200/37/10}$	200.0	468.9	410.8	448.7	221.6-502.8

Differential scanning calorimetry, DSC

The cooling and second heating thermograms of 37 wt% composites exposed indoors are presented in Figure 4.141. A summary of the data from these thermograms and those of 20 wt% are given in Table 4.16. Again, T_m and T_c are not significantly changed in indoor exposed samples when compared with the dry as-moulded ones. The same trend applies to ΔH_m, where the values in the dry as-moulded are relatively the same as those in the indoor exposed samples. Also, $-\Delta H_c$ showed no identifiable trend either with heat treatment or addition of MAPE (Figure 4.141b). Once more, the values of X_c in the exposed samples are almost the same as their dry as-moulded counterparts.

a)



b)

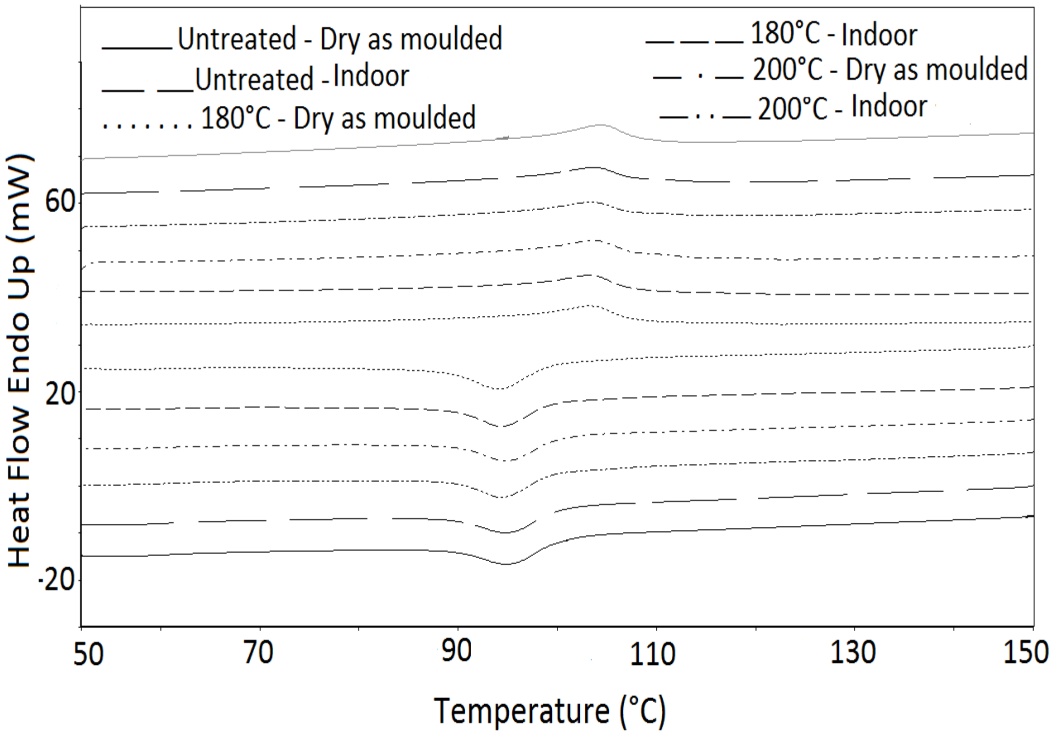


Figure 4.141: DSC thermograms of dry as-moulded and indoor exposed LDPE and 37 wt% untreated and heat-treated WTC containing: a) 0% and b) 6% MAPE

Table 4.16: DSC data of samples exposed indoors

Sample	Treatment temperature (°C)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	$-\Delta H_c$ (J/g)	X_c (%)
LDPE	-	104.6	91.8	45.8	57.1	15.6
LDPE/$W_{UN/20/0}$	-	104.7	92.6	49.0	48.6	20.9
LDPE/$W_{180/20/0}$	180.0	104.9	92.5	40.9	45.7	17.4
LDPE/$W_{200/20/0}$	200.0	105.2	92.6	28.7	46.2	12.2
LDPE/$W_{UN/37/0}$	-	104.2	92.6	52.9	41.6	28.7
LDPE/$W_{180/37/0}$	180.0	105.0	92.5	33.7	37.3	18.3
LDPE/$W_{200/37/0}$	200.0	104.7	92.4	16.2	40.8	8.8
LDPE/$W_{UN/20/2}$	-	105.2	93.5	48.9	44.2	20.9
LDPE/$W_{180/20/2}$	180.0	104.4	93.7	32.9	47.5	14.0
LDPE/$W_{200/20/2}$	200.0	104.4	93.7	34.0	44.5	14.5
LDPE/$W_{UN/37/2}$	-	104.4	93.7	30.2	36.1	16.4
LDPE/$W_{180/37/2}$	180.0	104.7	93.6	24.3	33.0	13.2
LDPE/$W_{200/37/2}$	200.0	104.1	94.1	26.4	32.0	14.3
LDPE/$W_{UN/20/6}$	-	103.4	94.9	25.5	38.8	10.9
LDPE/$W_{180/20/6}$	180.0	103.7	94.4	29.4	42.1	12.5
LDPE/$W_{200/20/6}$	200.0	103.7	95.0	21.8	43.5	9.3
LDPE/$W_{UN/37/6}$	-	103.1	94.3	15.8	29.0	8.6
LDPE/$W_{180/37/6}$	180.0	103.6	95.0	21.9	32.1	11.9
LDPE/$W_{200/37/6}$	200.0	103.4	94.5	22.1	32.7	12.0
LDPE/$W_{UN/20/10}$	-	102.8	94.7	20.5	40.2	8.7
LDPE/$W_{180/20/10}$	180.0	103.1	94.4	20.5	42.7	8.7
LDPE/$W_{200/20/10}$	200.0	103.0	94.4	24.9	33.1	10.6
LDPE/$W_{UN/37/10}$	-	103.1	94.3	16.6	28.3	9.0
LDPE/$W_{180/37/10}$	180.0	102.9	94.5	16.7	33.0	9.0
LDPE/$W_{200/37/10}$	200.0	102.9	94.5	16.7	30.2	9.0

4.3.4.3 Dynamic mechanical analysis, DMA

Storage modulus

The storage modulus curves of dry as-moulded and indoor exposed LDPE and 37 wt% treated and untreated composites are given in Figure 4.142. A summary of the data extracted from these curves and those of 20 wt% are given in Table 4.17. The storage modulus of the neat LDPE decreased on exposure to ambient conditions. The $E'_{25°\mathrm{C}}$ and $E'_{-100°\mathrm{C}}$ reduced by over 30% in both cases. Also, the magnitude of $E'_{25°\mathrm{C}}$ decreased in composites containing no compatibiliser, while the compatibilised composites showed a slight increase in $E'_{25°\mathrm{C}}$ with indoor exposure (Figure 4.142b). However, no identifiable trend could be established in the $E'_{-100°\mathrm{C}}$ values of the composites studied. This is unexpected because LDPE and the composites did not show any sign of aging while indoors (Figures 4.138 and 4.139). Again, no scientific explanation could be adduced for this behaviour and no exact trend could be observed with regards to heat treatment temperature.

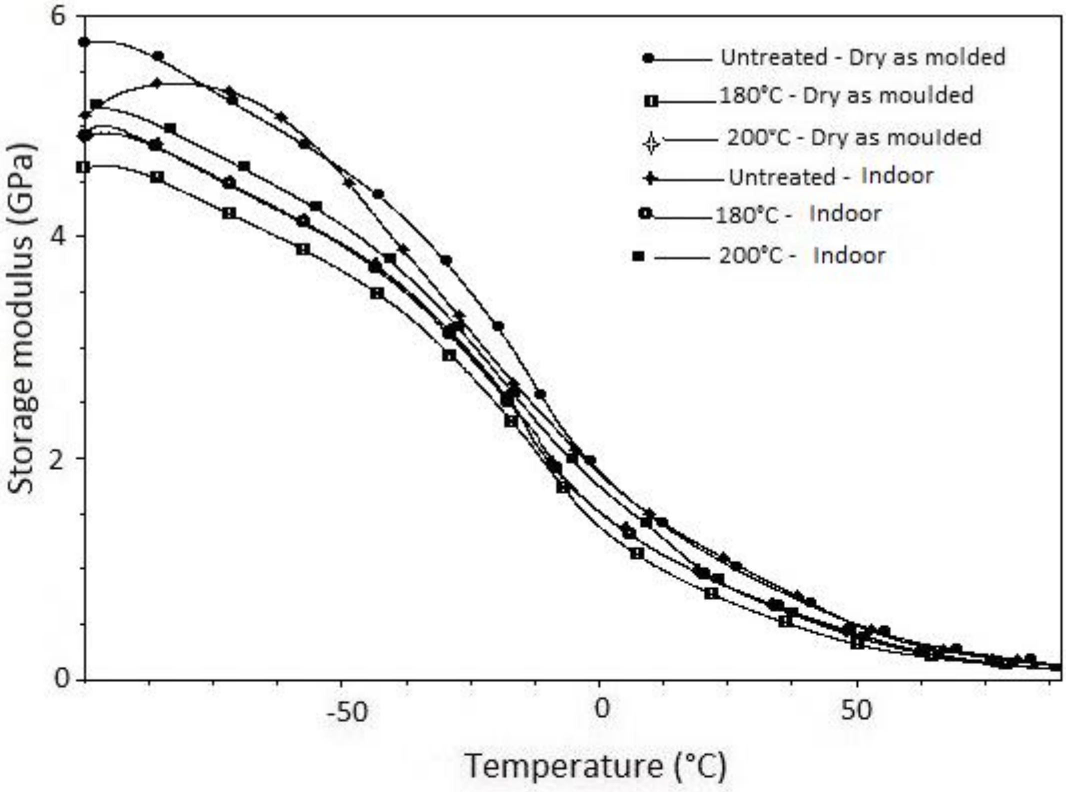
Loss modulus

Figure 4.143 presents the variation of loss modulus with temperature in dry as-moulded and indoor exposed LDPE and composites made from 37 wt% treated and untreated wood flours. The $E''_{25°\mathrm{C}}$ and $E''_{\max}$ of the dry as-moulded LDPE is higher than the indoor exposed one. Values of $E''_{25°\mathrm{C}}$ dropped from 40 MPa in the dry as-moulded to 31 MPa in the indoor exposed samples, while $E''_{\max}$ decreased from 140 MPa in the unexposed to 110 MPa in samples exposed to the ambient conditions. Also, $T_{\beta}^{E''}$ shifted to lower temperatures in the exposed LDPE. Furthermore, the loss modulus decreased generally with indoor exposure in the composites. The values of $E''_{25°\mathrm{C}}$ decreased in the uncompatibilised samples and those containing 2% MAPE. However, at higher MAPE level, an increment in $E''_{25°\mathrm{C}}$ is observed. Meanwhile, the magnitude of $E''_{\max}$ decreased significantly in the untreated samples without MAPE (Figure 4.143b). Afterwards, a clear trend could not be established in terms of heat treatment temperature and MAPE content. Once more, these results were unanticipated because the indoor exposed samples were not supposed to age as to have resulted in the change in the loss modulus properties. The $T_{\beta}^{E''}$ values are almost the same in all the composites studied except at 10% MAPE level, where a slight decrease is observed (Table 4.17).

Tan delta

The change in the tan delta of LDPE and 37 wt% composites after indoor exposure is presented in Figure 4.144. Summary of data extracted from these curves and those of 20 wt% are presented in Table 4.17. Although the temperature at $\tan\delta_{\max}$ and the $W_{\sqrt{2}}$ decreased in the LDPE samples exposed to the indoor environment, the values of $\tan\delta_{25°\mathrm{C}}$ and the magnitude of $\tan\delta_{\max}$ are higher in the sample exposed to ambient conditions relative to the dry as-moulded one. Once more, no precise explanation could be given for this trend since there is no sign of aging in the exposed LDPE. The $\tan\delta$ behaviour of the composites also displayed an inconsistent pattern. $Tan\ \delta_{\max}$ changed slightly with indoor exposure, but in an irregular manner, with no specific direction with regards to either heat treatment temperature or MAPE level (Figure 4.144b). $Tan\ \delta_{\max}$ values in exposed composites were either slightly higher, a little lower or the same with the dry as-moulded samples. $Tan\delta_{25°\mathrm{C}}$ also exhibited no particular trend in the uncompatibilised composites and samples containing MAPE generally showed a decreasing trend. The temperature at $\tan\delta_{\max}$ also changed in an inconsistent manner in the uncompatibilised composites. However, composites containing different levels of MAPE showed no change in temperature at $\tan\delta_{\max}$ with indoor exposure. Furthermore, the values of $W_{\sqrt{2}}$ in all the composites studied are similar, except at 10% MAPE level, where a decrease in $W_{\sqrt{2}}$ values is observed, with the heat-treated composites showing a rather profound decrement.

a)



b)

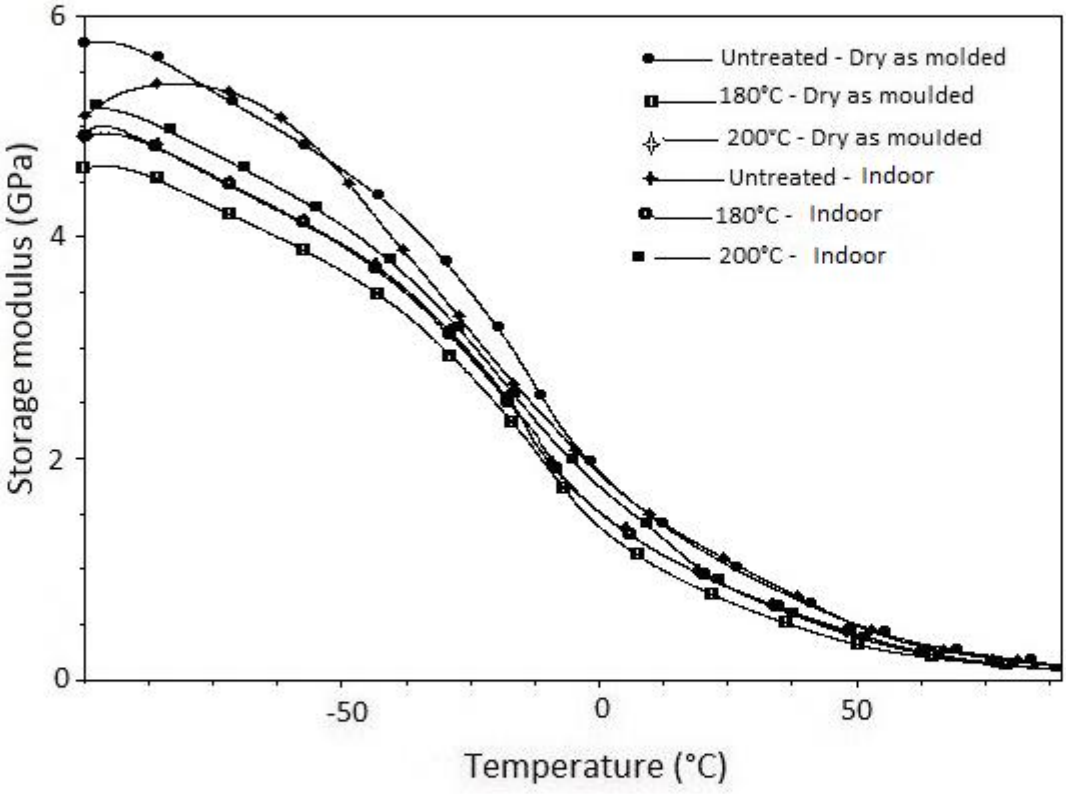


Figure 4.142: Storage modulus curves of dry as-moulded and indoor exposed LDPE and 37 wt% untreated and heat-treated WTC containing: a) 0% and b) 6% MAPE

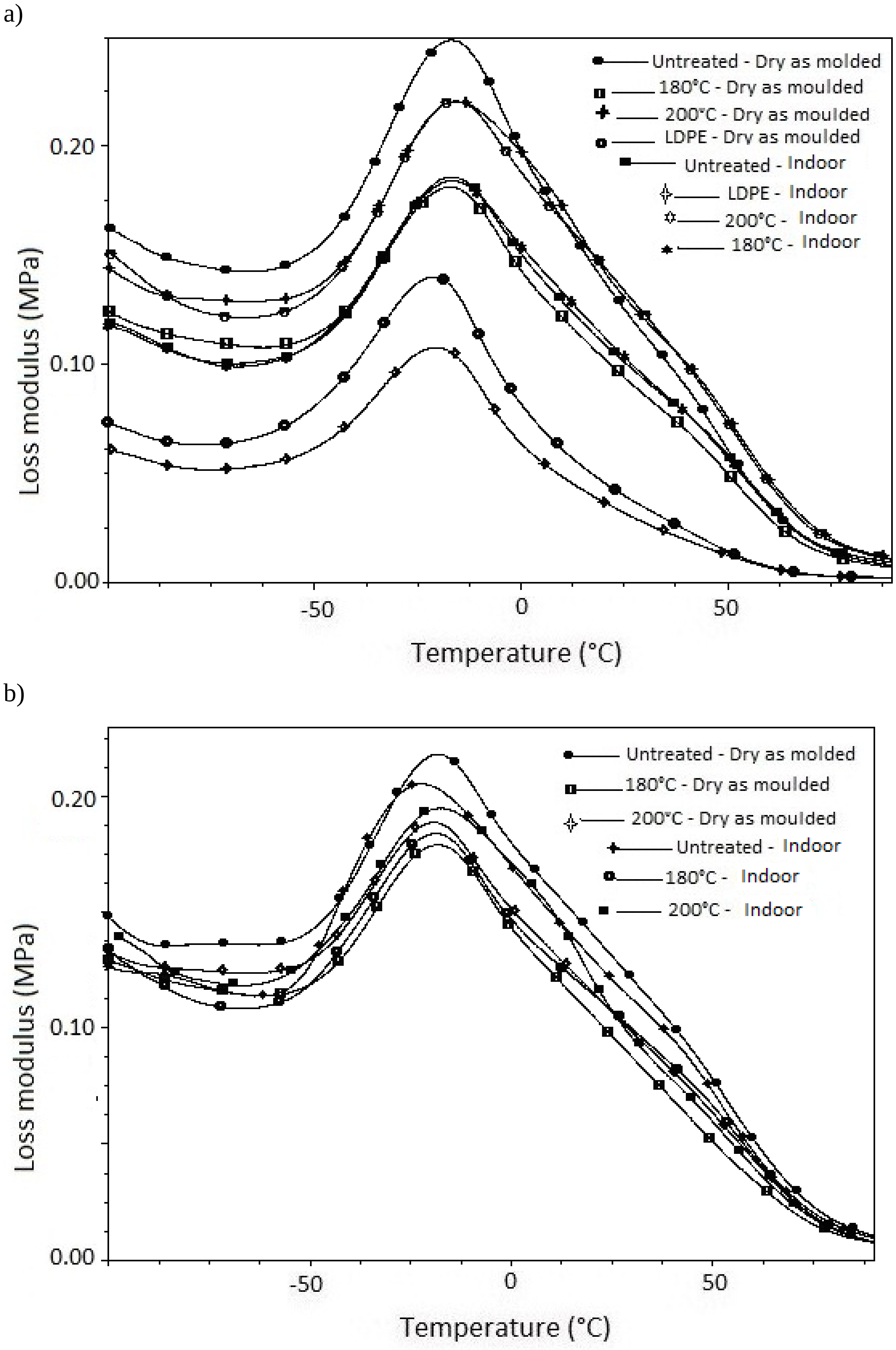


Figure 4.143: Loss modulus curves of dry as-moulded and indoor exposed LDPE and 37 wt% untreated and heat-treated WTC containing: a) 0% and b) 6% MAPE

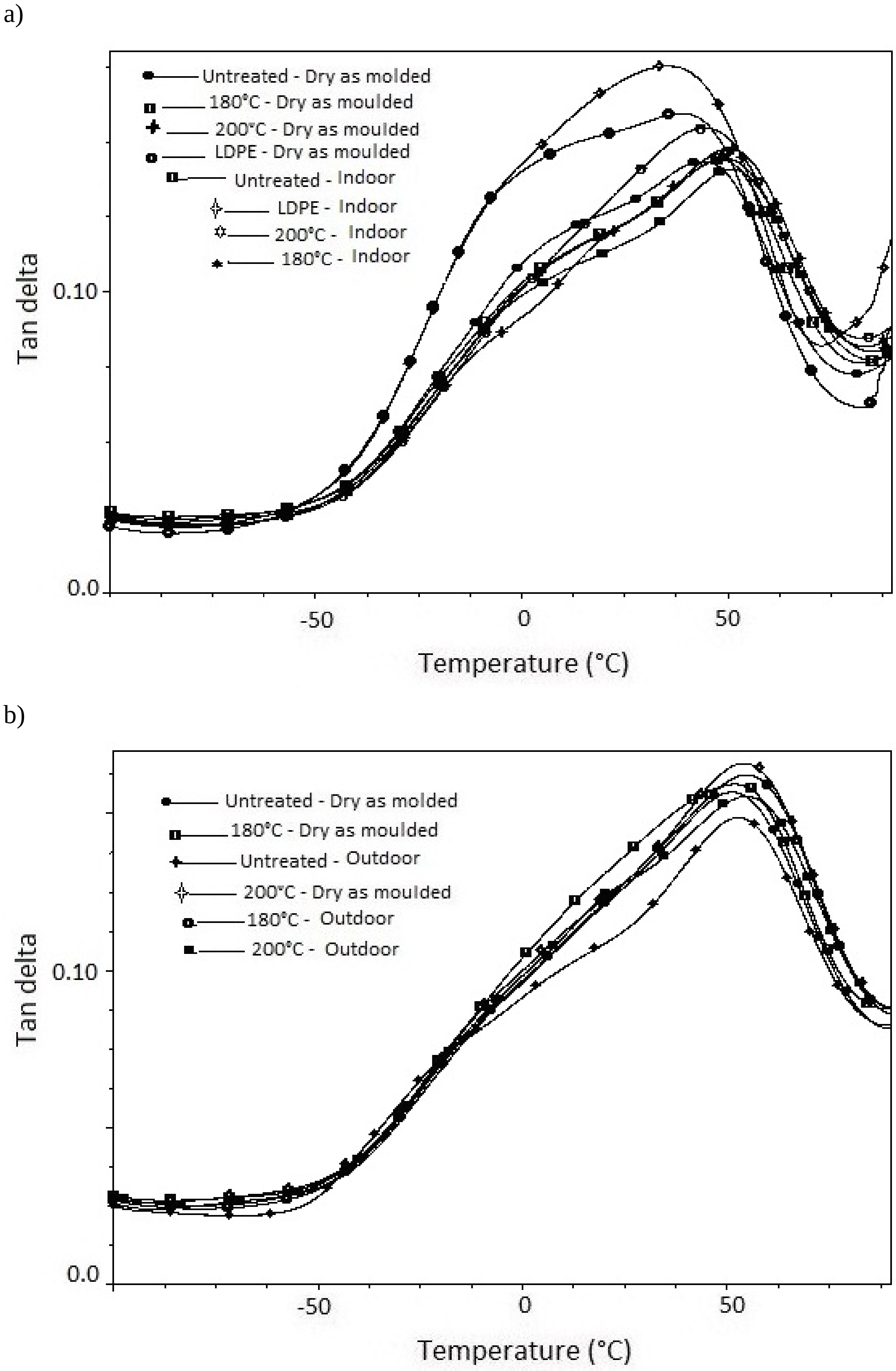


Figure 4.144: Tan delta curves of dry as-moulded and indoor exposed LDPE and 37 wt% untreated and heat-treated WTC containing: a) 0% and b) 6% MAPE

Table 4.17: DMA data of indoor exposed samples

Sample	Treatment temperature (°C)	$Tan\delta$				Storage modulus E'		Loss modulus E"		
		$Tan\ \delta_{max}$	Temperature at tan δ_{max} (℃)	$W_{\sqrt{2}}$	$Tan\delta_{25°C}$	$E'_{25°C}$ (GPa)	$E'_{-100°C}$ (GPa)	$E''_{25°C}$ (MPa)	$T_{\beta}^{E''}$ (℃)	E''_{max} (MPa)
LDPE	-	0.18	35.4	69.0	0.17	0.18	2.5	31.1	-20.3	110.0
LDPE/$W_{UN/20/0}$	-	0.15	44.3	69.9	0.14	0.46	3.6	65.0	-19.3	150.0
LDPE/$W_{180/20/0}$	180.0	0.15	43.7	67.4	0.14	0.43	3.6	60.1	-18.9	140.0
LDPE/$W_{200/20/0}$	200.0	0.16	48.5	65.1	0.13	0.55	4.0	71.0	-17.8	160.0
LDPE/$W_{UN/37/0}$	-	0.14	51.2	68.2	0.12	0.87	4.9	101.0	-17.3	190.0
LDPE/$W_{180/37/0}$	180.0	0.15	49.0	66.8	0.12	0.83	4.8	103.0	-16.6	180.0
LDPE/$W_{200/37/0}$	200.0	0.16	44.3	59.7	0.14	0.98	5.9	134.0	-15.4	220.0
LDPE/$W_{UN/20/2}$	-	0.16	49.7	69.4	0.13	0.48	3.6	64.0	-18.3	140.0
LDPE/$W_{180/20/2}$	180.0	0.16	50.0	65.8	0.14	0.56	4.0	76.0	-18.8	160.0
LDPE/$W_{200/20/2}$	200.0	0.16	48.5	63.5	0.14	0.58	4.2	79.0	-17.7	160.0
LDPE/$W_{UN/37/2}$	-	0.15	51.0	66.8	0.12	0.88	4.9	101.0	-18.2	180.0
LDPE/$W_{180/37/2}$	180.0	0.15	52.8	54.3	0.12	1.13	5.7	127.0	-16.4	210.0
LDPE/$W_{200/37/2}$	200.0	0.15	51.0	59.5	0.12	1.10	5.6	132.0	-16.4	210.0
LDPE/$W_{UN/37/6}$	-	0.15	52.3	56.8	0.12	1.07	5.1	121.0	-19.6	210.0
LDPE/$W_{180/37/6}$	180.0	0.16	53.6	65.4	0.14	0.83	4.9	107.0	-18.9	180.0
LDPE/$W_{200/37/6}$	200.0	0.16	54.6	62.0	0.13	0.83	5.2	107.0	-17.7	200.0
LDPE/$W_{UN/37/10}$	-	0.16	52.3	56.1	0.12	1.11	5.1	132.0	-23.1	210.0
LDPE/$W_{180/37/10}$	180.0	0.16	52.4	51.9	0.12	0.97	4.9	111.0	-23.3	190.0
LDPE/$W_{200/37/10}$	200.0	0.17	56.4	52.0	0.13	0.89	4.4	101.0	-23.1	170.0

4.3.4.4 Mechanical properties

The mechanical properties of the composites exposed to the indoor environment were tested in order to ascertain their response, if any, to ambient conditions.

Tensile properties

Tensile modulus

The tensile modulus of the dry as-moulded LDPE (0.231 GPa) is similar to the exposed samples (0.229 GPa). Also, there appears to be no noticeable difference in the tensile modulus of exposed composites in comparison with the dry as-moulded samples (Figure 4.145). This is an indication that indoor exposure has no detrimental effect on the tensile modulus of the composites. This trend is also seen in the compatibilised composites made from heat-treated wood flour. However, in composites containing untreated wood flour, a 20% decrease in modulus is observed (Figure 4.146).

Tensile strength

In Figure 4.147, the tensile strength of dry as-moulded and indoor exposed composites are shown. The neat LDPE showed no change in the tensile strength on indoor exposure. Values of 9.14 MPa and 9.12 MPa are obtained for the dry as-moulded and indoor exposed composites respectively. In addition, the composites showed no significant decrease on exposure to the ambient conditions, a sign that the indoor environment is not destructive to the composites. This observation is also true in the compatibilised composites (Figure 4.148).

Tensile strain

Figure 4.149 presents the tensile strain of the dry as-moulded and indoor exposed composites. The dry as-moulded LDPE has a tensile strain of 91.41% while the values reduced to 87.18% in the indoor exposed sample. Also, looking at Figure 4.149, at 20 wt% wood flour loading, the tensile strain of the indoor exposed samples reduced relative to the dry as-moulded samples. Figure 4.150 displays the same trend. Again, no scientific explanations could be given for this behaviour. However, no appreciable change is seen in the indoor exposed samples containing 37 wt% wood flour.

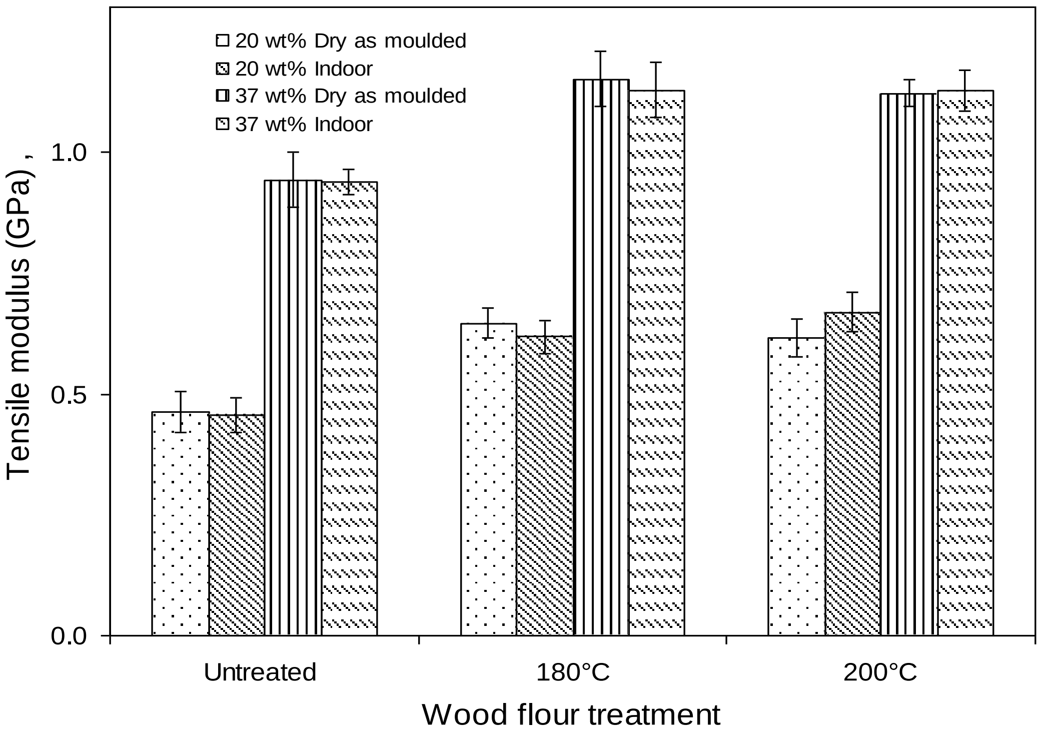


Figure 4.145: Tensile modulus of dry as-moulded and indoor exposed composites as a function of wood content and treatment temperature

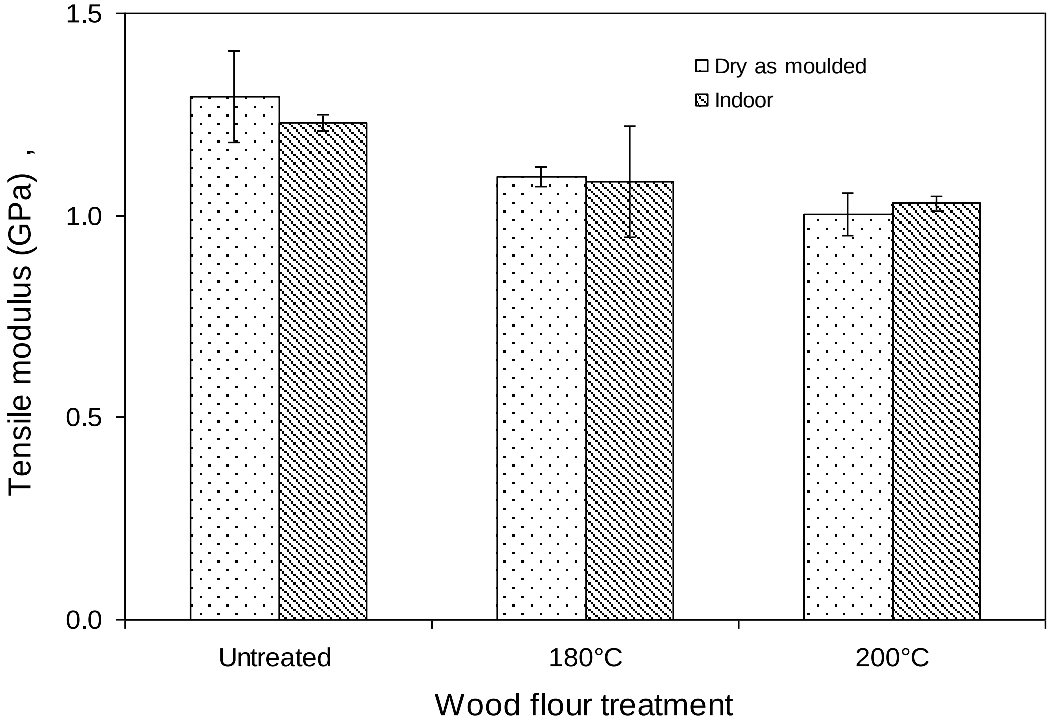


Figure 4.146: Tensile modulus of 37 wt% dry as-moulded and indoor exposed composites containing 6% MAPE

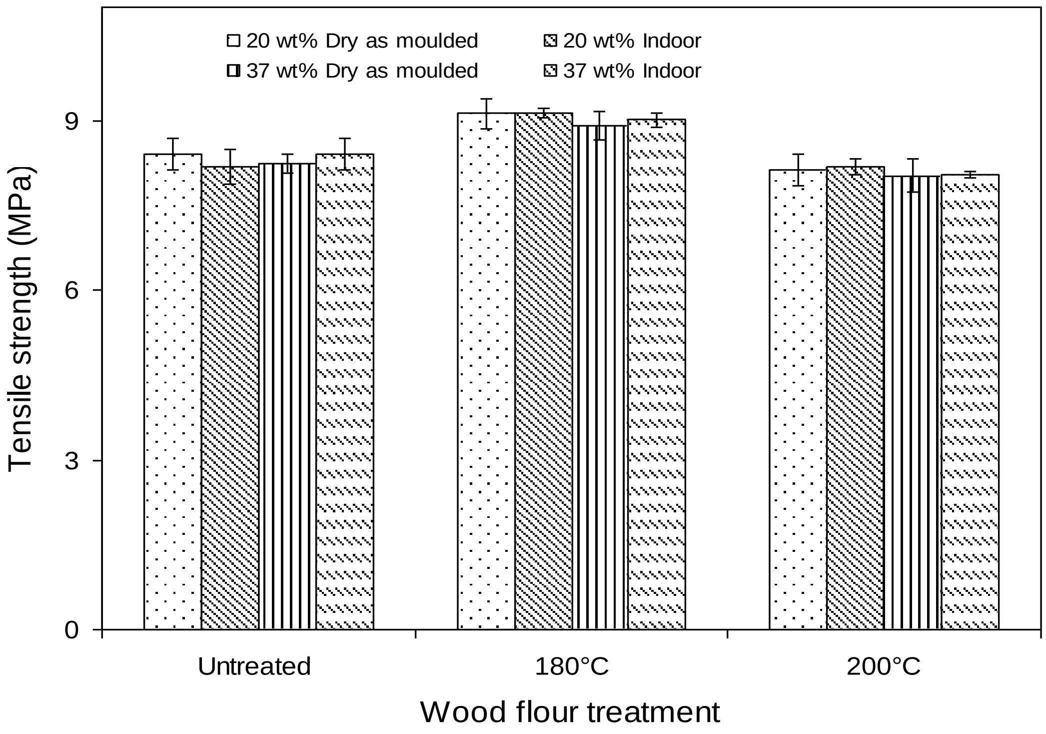


Figure 4.147: Tensile strength of indoor and dry as-moulded composites as a function of wood content and treatment temperature

Figure 4.148: Tensile strength of 37 wt% dry as-moulded and indoor exposed composites containing 6% MAPE

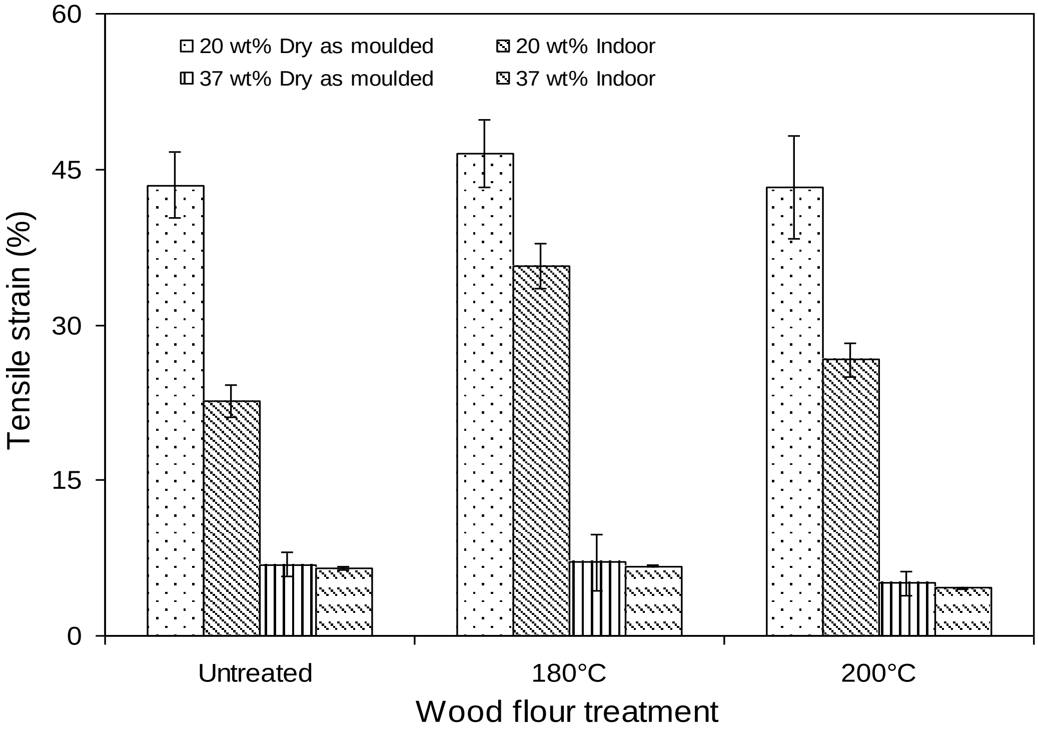


Figure 4.149: Tensile strain of dry as-moulded and indoor exposed composites as a function of wood content and treatment temperature

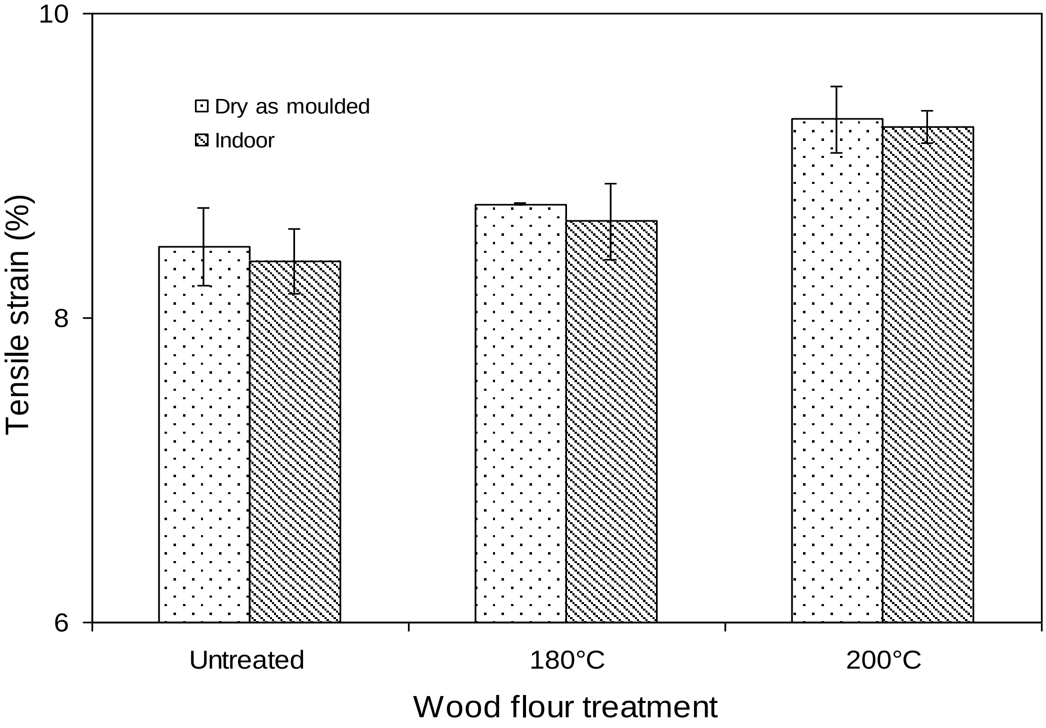


Figure 4.150: Tensile strain of 37 wt% dry as-moulded and indoor exposed composites containing 6% MAPE

Flexural properties

In the neat LDPE, the flexural modulus of the dry as-moulded sample (0.121 GPa) remained, more or less, the same with exposure to ambient conditions (0.123 GPa). The flexural modulus of the dry as-moulded and composites exposed to the indoor environment are presented in Figures 4.151 and 4.152. From these figures, there is no obvious difference in the flexural modulus of the exposed and unexposed samples. Again, this may mean that the indoor environment did not change the flexural modulus of the composites in any noticeable way. Values of the flexural strength of the dry as-moulded LDPE (7.13 MPa) is similar with the indoor exposed ones (7.16 MPa). Likewise, the flexural strength of the composites varied slightly with indoor exposure (Figures 4.153 and 4.154), but in no particular trend. Similarly, the flexural displacement of the dry as-moulded and indoor exposed composites is almost the same (Figures 4.155 and 4.156). Again, demonstrating that ambient condition is favourable to the flexural properties of the composites.

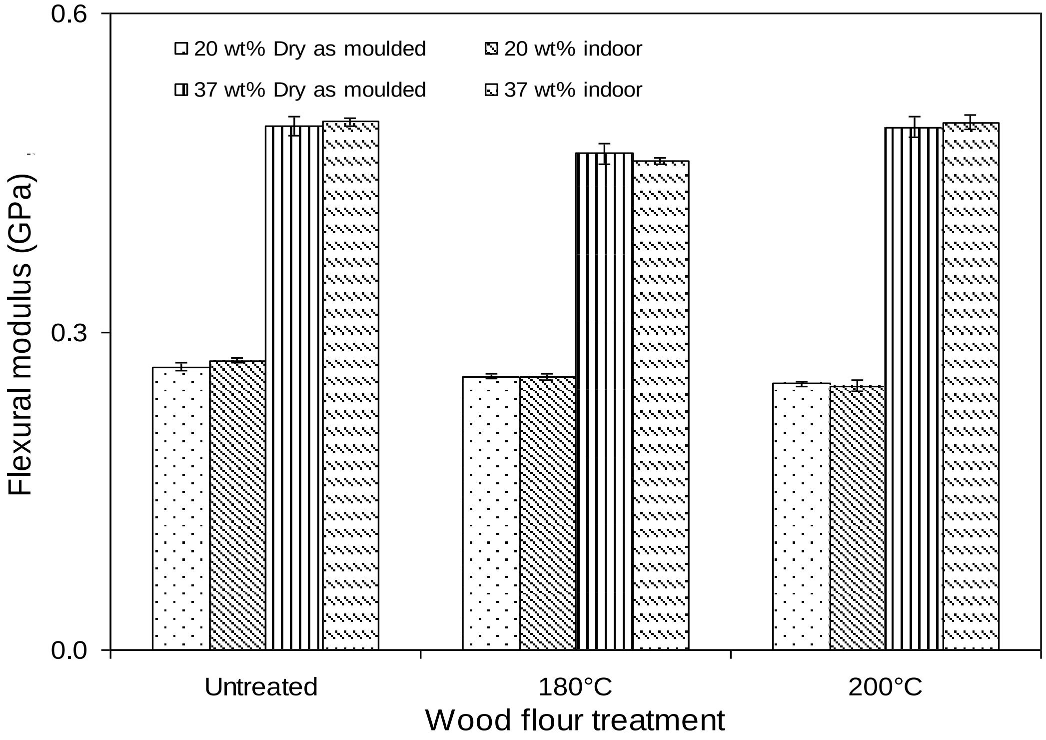


Figure 5.151: Flexural modulus of dry as-moulded and indoor exposed samples as a function of wood content and treatment temperature

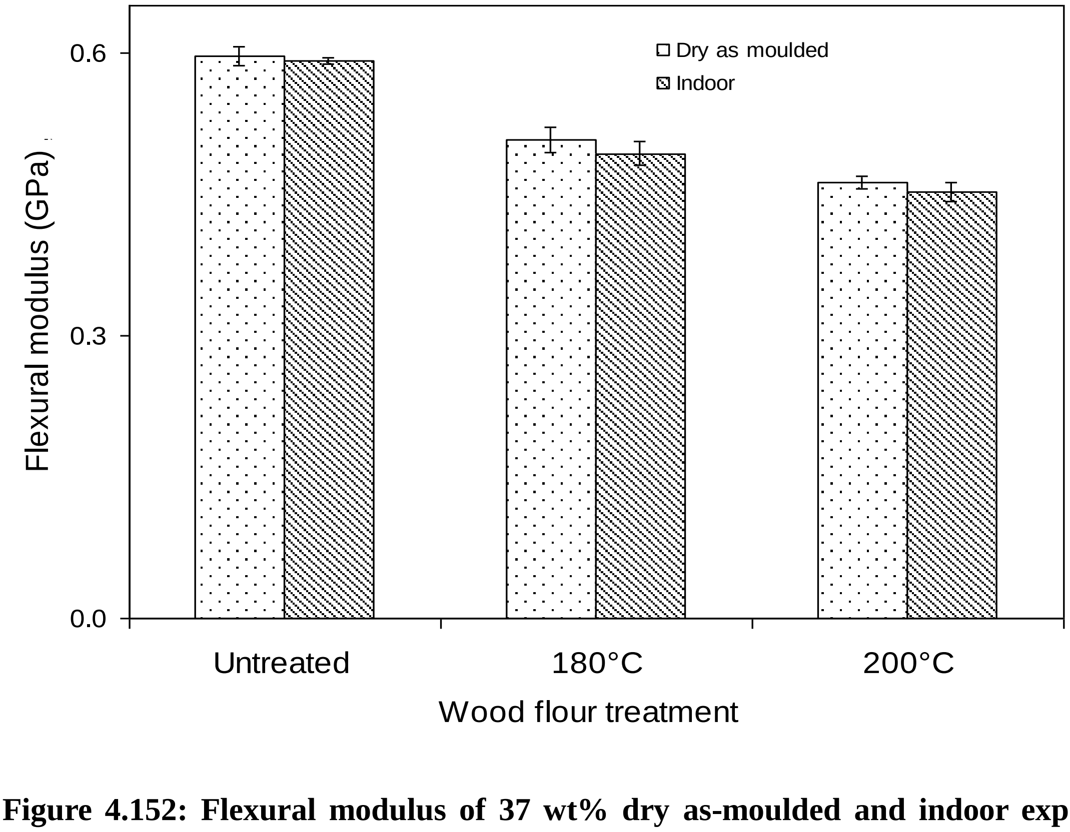


Figure 4.152: Flexural modulus of 37 wt% dry as-moulded and indoor exposed samples containing 6% MAPE

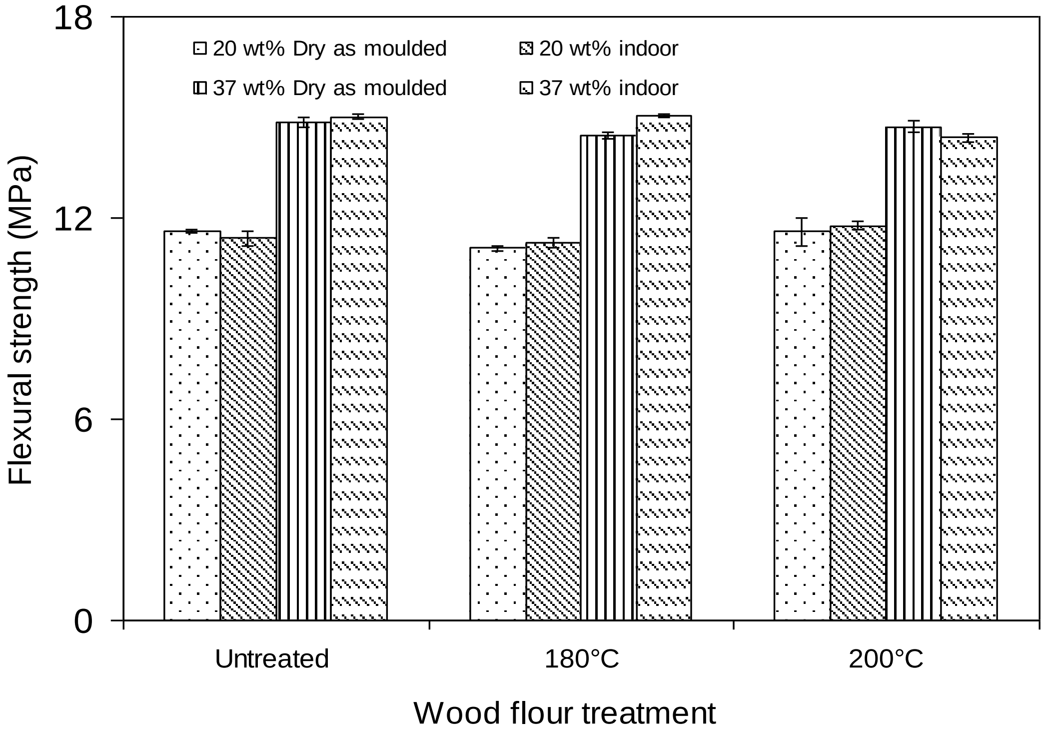


Figure 4.153: Flexural strength of dry as-moulded and indoor exposed samples as a function of wood content and treatment temperature

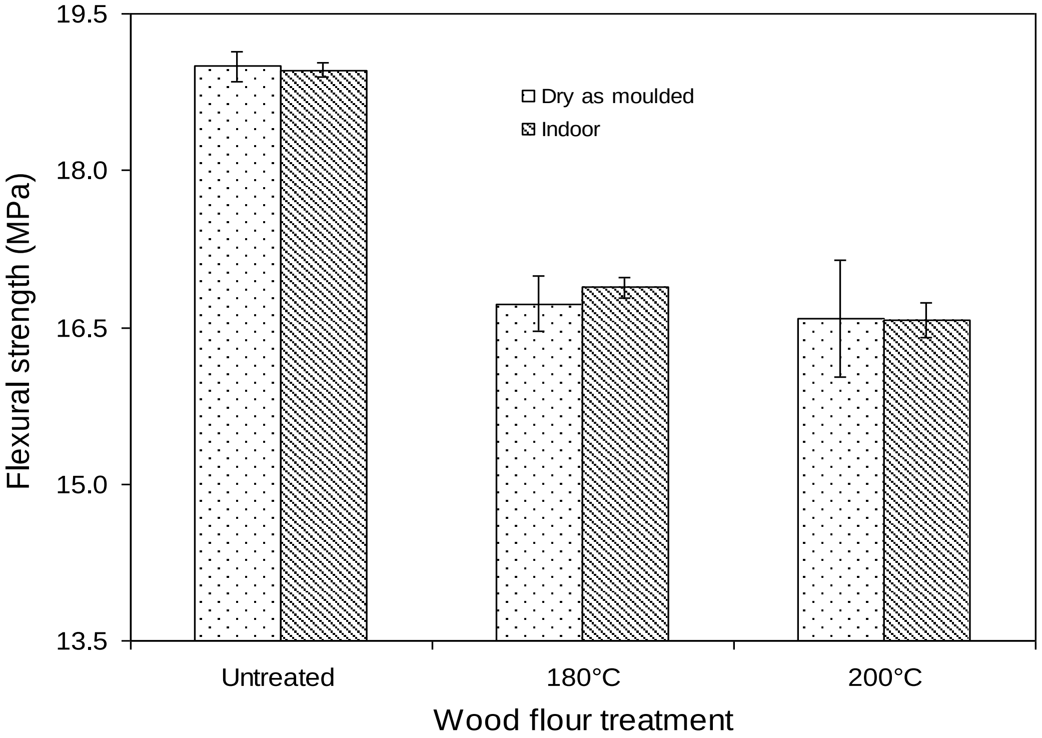


Figure 4.154: Flexural strength of 37 wt% dry as-moulded and indoor exposed samples containing 6% MAPE

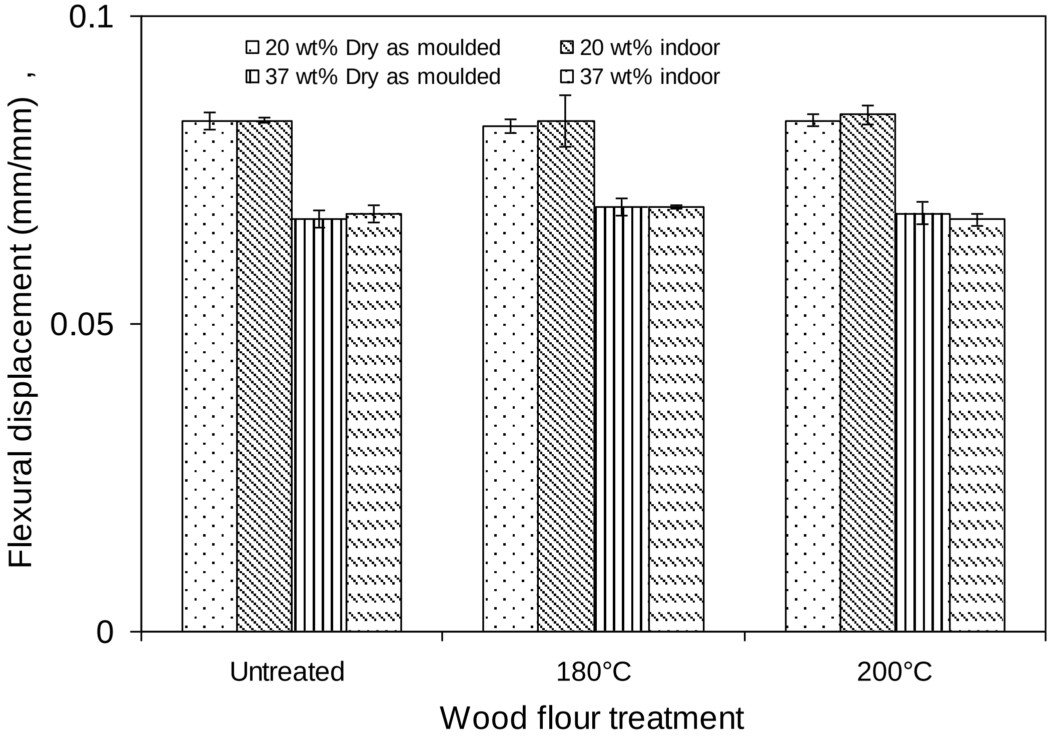


Figure 4.155: Flexural displacement of dry as-moulded and indoor exposed samples as a function of wood content and treatment temperature

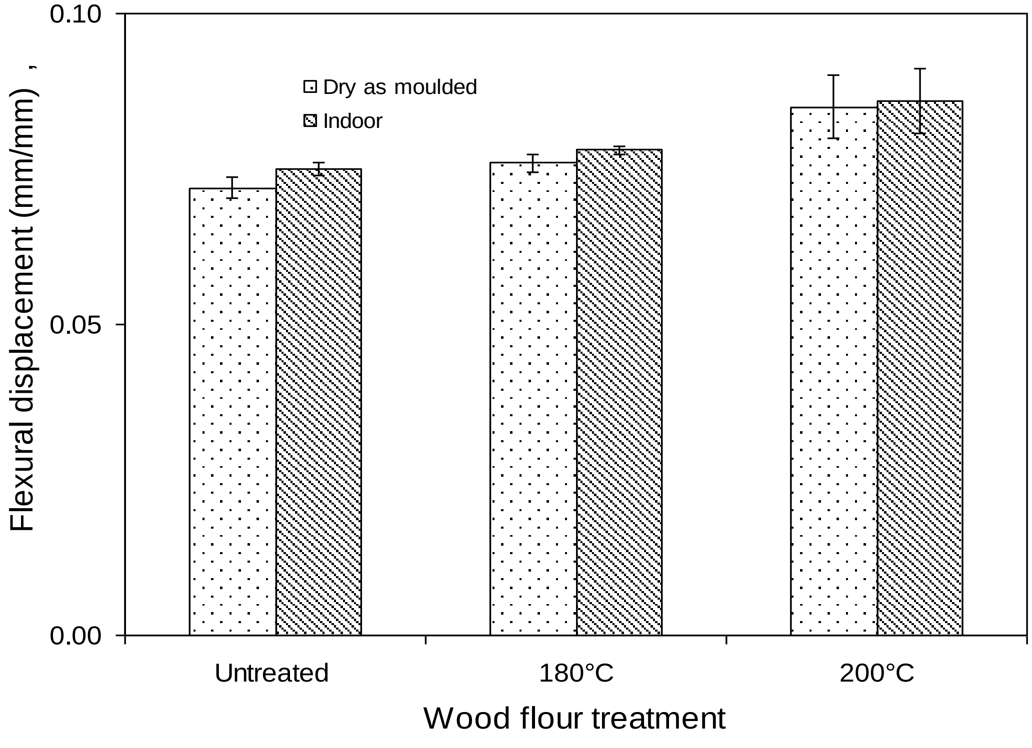


Figure 4.156: Flexural displacement of 37 wt% dry as-moulded and indoor exposed composites containing 6% MAPE

Impact properties

Peak load, *P* and critical stress intensity factor, K_c

The dry as-moulded and indoor exposed LDPE present peak load values of 266.6 N, 225.26 N, 184.53 N, 137.36 N and 284.73 N, 245.27 N, 204.06 N, 155.63 N for a/D ratios 0.1, 0.2, 0.3 and 0.4 respectively. This result showed a slight increase in *P* of the indoor exposed sample, relative to the dry as-moulded samples. It is not clear what is responsible for this trend because the indoor exposed samples showed no visible signs of aging. Figure 4.157 presents the peak load of the composites as a function of heat treatment and wood content. A clear difference could not be seen in the values of *P* of the dry as-moulded when compared to the indoor exposed composites. In addition, no variation is observed with regard to heat treatment and MAPE content (Figure 4.158). The K_c of the dry as-moulded LDPE (96.58 MPa.m$^{0.5}$) is almost the same with that exposed to ambient conditions (94.59 MPa.m$^{0.5}$). The variation of K_c of the dry as-moulded and indoor exposed composites with wood content and heat treatment is given in Figure 4.159. There is no observable difference between the K_c of the composites on exposure to ambient conditions. This trend is also seen in the compatibilised samples (Figure 4.160).

Energy to failure, *W* and critical energy release rate, G_c

The neat LDPE presents similar *W* values of 4.62 J, 3.48 J, 3.17 J and 2.12 J while the indoor exposed samples have values of 4.25 J, 3.83 J, 3.02 J and 2.31 J for a/D ratios 0.1, 0.2, 0.3 and 0.4 respectively. Also, in Figures 4.161 and 4.162, the values of *W* of the composites are almost the same. This is a sign that the indoor environment has no adverse effect on *W* of the samples. The G_c of the dry as-moulded composites are also not significantly different from the indoor exposed samples (Figure 4.163). However, an inconsistent trend is seen with composites containing 6% MAPE (Figure 4.164).

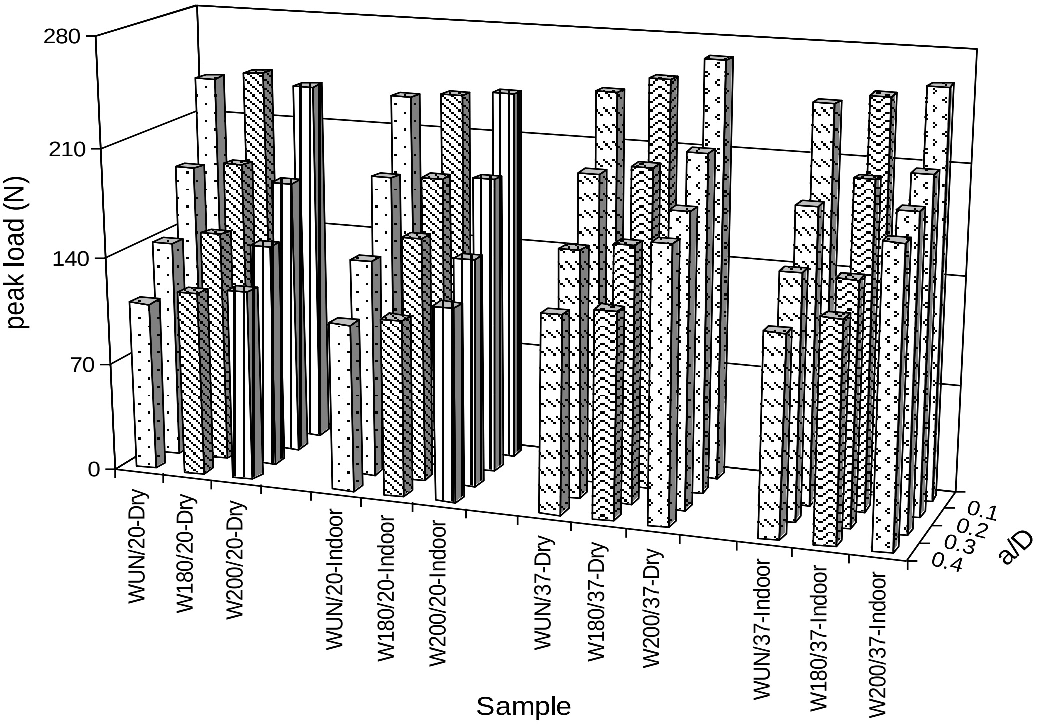


Figure 4.157: Peak load of dry as-moulded and indoor exposed samples as a function of wood content and heat treatment

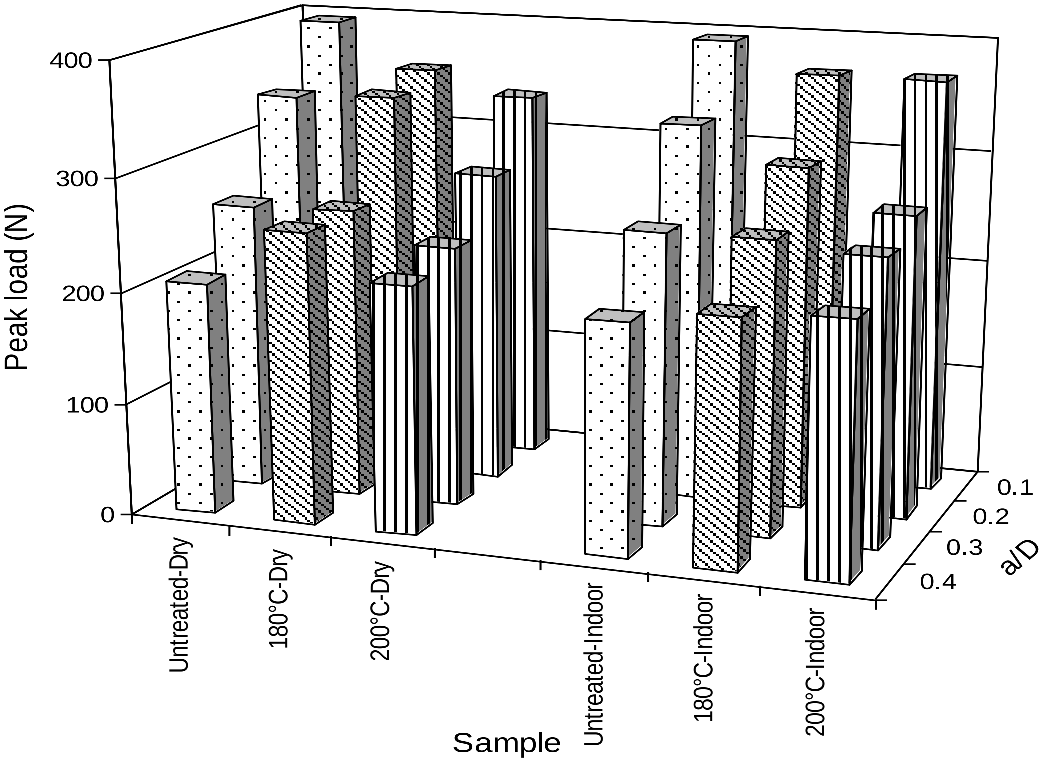


Figure 4.158: Peak load of 37 wt% dry as-moulded and indoor exposed samples containing 6% MAPE

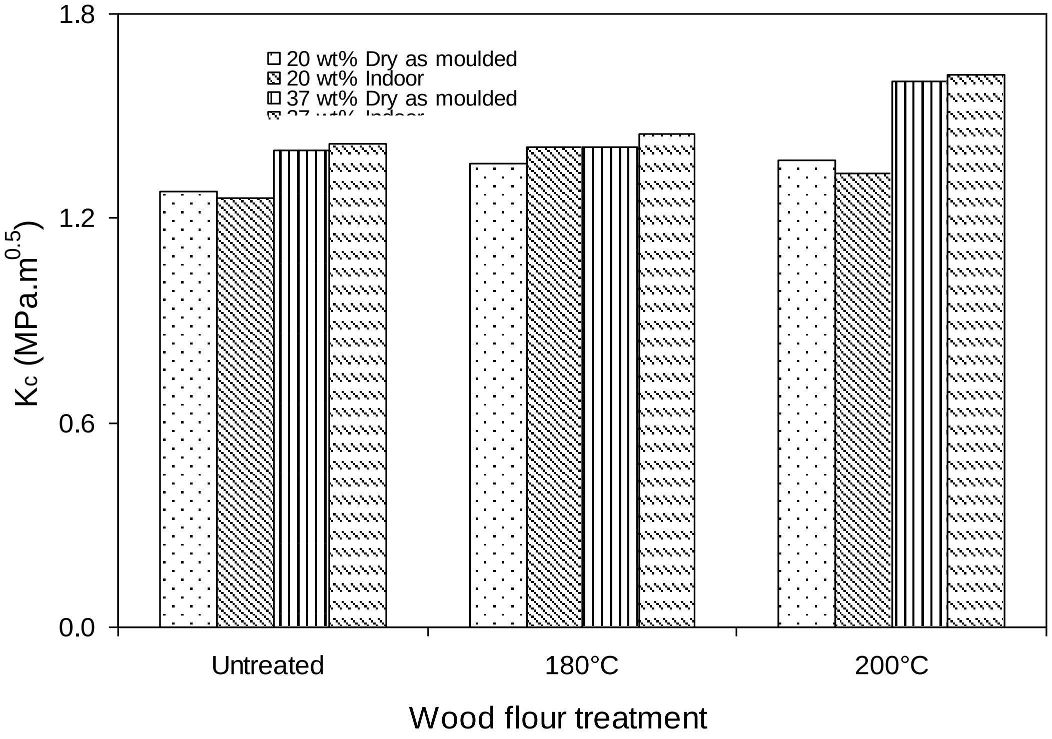


Figure 4.159: K_c of dry as-moulded and indoor exposed samples as a function of wood content and heat treatment

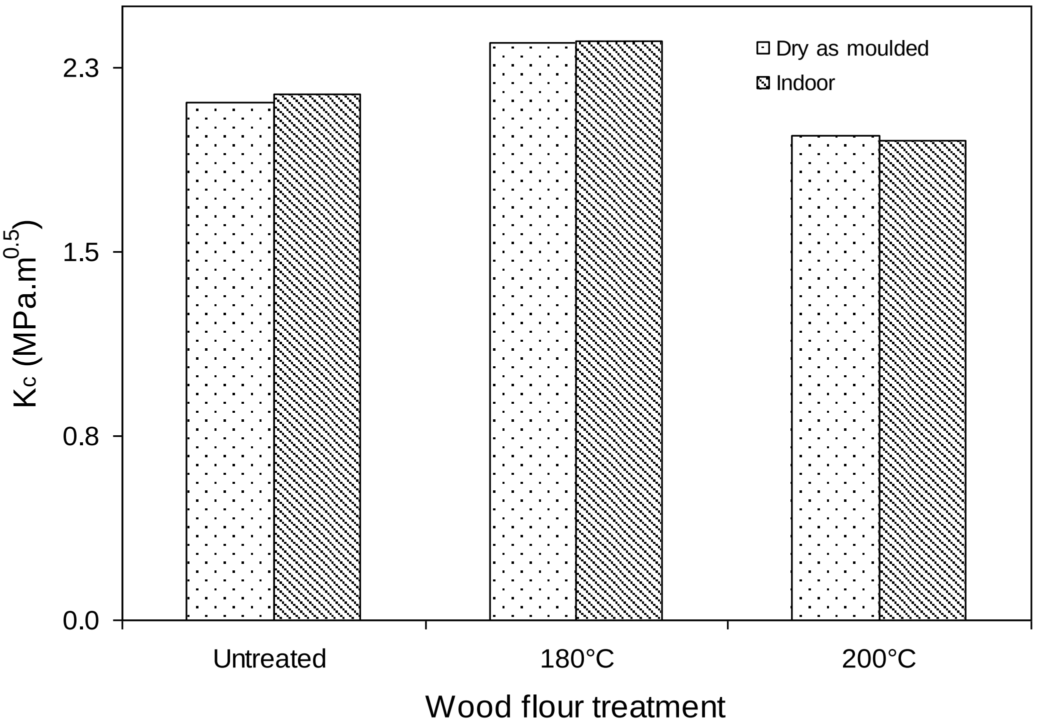


Figure 4.160: K_c of 37 wt% dry as-moulded and indoor exposed samples containing 6% MAPE

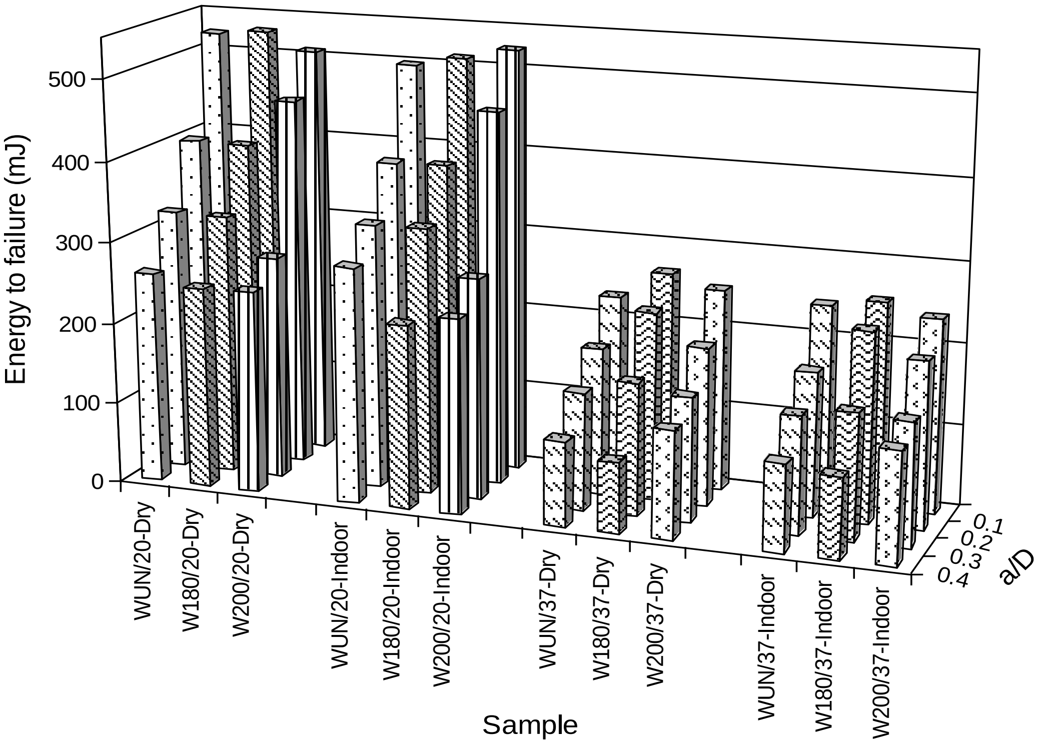


Figure 4.161: Energy to failure of dry as-moulded and indoor exposed samples as a function of wood content and heat treatment

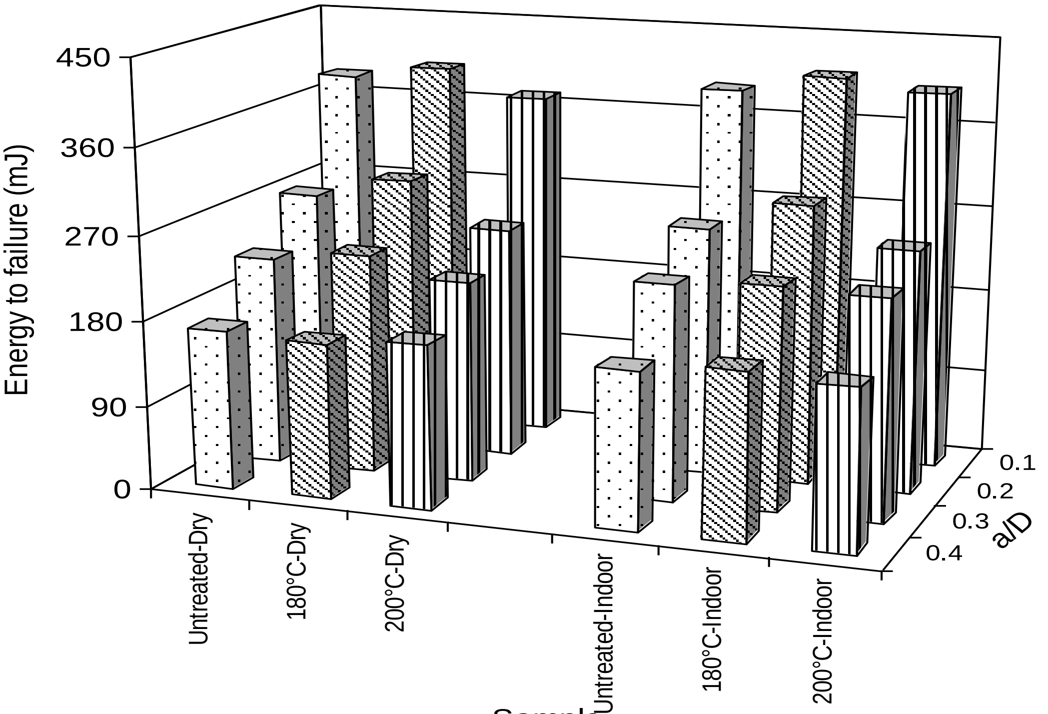


Figure 4.162: Energy to failure of 37 wt% dry as-moulded and indoor exposed samples with 6% MAPE

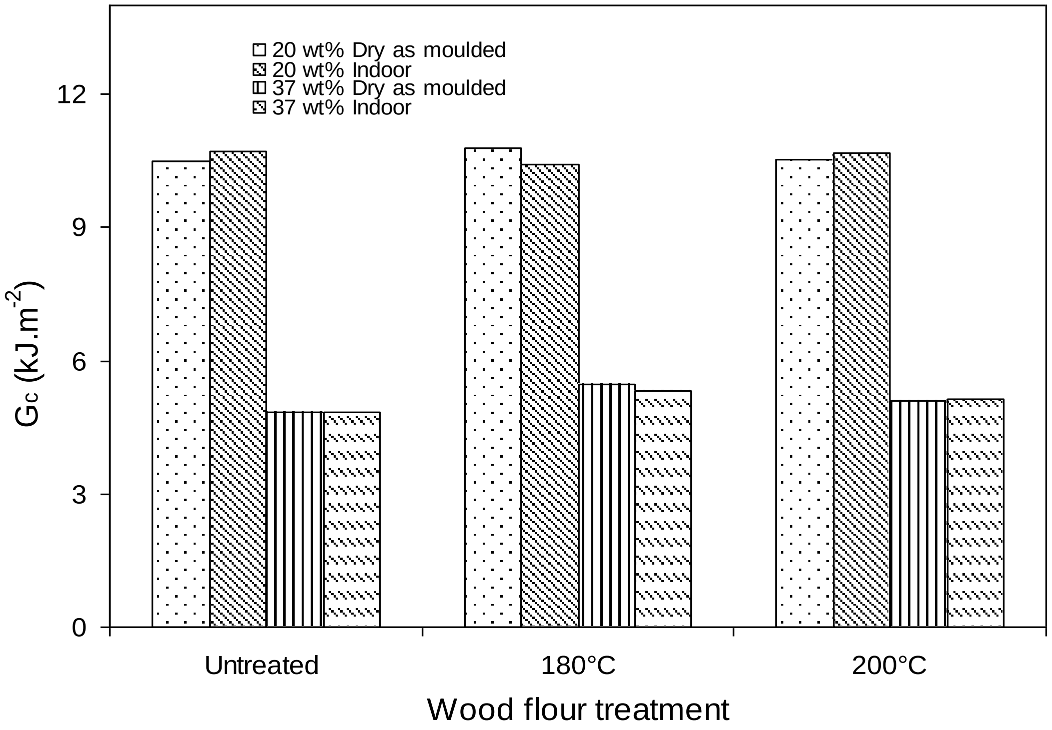


Figure 4.163: ***G*** **of dry as-moulded and indoor exposed samples as a function of wood content and heat treatment**

Figure 4.164: **G_c of 37 wt% dry as-moulded and indoor exposed samples with 6% MAPE**

CHAPTER FIVE

5.1 Conclusion

This research serves as a step towards the development of a wood thermoplastic composite by using renewable raw materials and reducing the amount of petroleum-based plastic in the composition. In addition, the thermal modification of wood flour employed in this study is considered as an environmentally benign method of surface treatment, as no chemicals are used and no effluents are generated.

From this research, it can be concluded that heat treatment of wood flour at a higher temperature (than normal drying) changed the chemistry of the wood, reduced its polarity, decreased its hygroscopicity and rendered it more compatible with a non-polar matrix, resulting in better interfacial adhesion between the wood particles and the polymer matrix, thereby leading to improved mechanical properties.

Thermogravimetric investigations revealed that heat treatment improved the thermal properties of wood because of the degradation of hemicellulose and modification of the lignin component in wood. Also, the thermal stability of the composites was enhanced relative to the neat matrix, with composites made from heat-treated wood giving higher thermal stability when compared to those from untreated wood flour. Differential scanning calorimetric study showed that incorporating wood into LDPE had no significant effect on the melting behaviour of the composites. However, the degree of crystallinity of the composites containing untreated wood flour increased with wood content because of the nucleating ability of the untreated wood flour. For the composites made from heat-treated wood flour, a decreasing trend in the degree of crystallinity was observed as the wood content increased.

The dynamic mechanical analysis revealed that composites made from the heat-treated wood flour exhibited higher storage modulus and loss modulus than those containing untreated wood flour. Furthermore, lower tan delta values were observed in heat-treated composites, relative to the untreated materials as a result of decreased damping, resulting from improved interaction between the heat-treated wood particle and the LDPE matrix.

Heat-treated wood flour increased the tensile modulus of the neat LDPE to the tune of 400% more than the untreated samples (309%) as a result of improved wetting of the heat-treated wood particles by the matrix, leading to better interfacial adhesion. Although the tensile strength of the neat matrix decreased with filler loading and treatment temperature, composites containing wood treated at 180°C showed higher tensile strength value in all the compositions studied. In addition, flexural properties were found to have increased with filler loading in untreated wood composites relative to composites containing heat-treated wood.

Peak load and critical stress intensity factor increased with both wood content and treatment temperature. While the energy to failure and the critical strain energy release rate decreased with wood content, the values were highest in composites made from wood flour treated at 180°C and reduced in 200°C heat-treated wood composites. This behaviour revealed that heat treatment of wood flour at the 200°C resulted in poorer impact properties of the composites.

By introducing maleic anhydride grafted polyethylene (MAPE) into the composite, the C=O group of MAPE reacted with the O-H group of the cellulose in wood and formed an ester bond at the interface leading to increased interfacial adhesion. This led to the improvement in the thermal and mechanical properties to various extents. In the composites containing untreated wood flour, incorporation of 8% MAPE provided the highest tensile strength and modulus values, indicating that this MAPE content is appropriate for imparting the needed interfacial adhesion for better stress transfer between the filler and the matrix, whereas 6% MAPE content was observed to be appropriate to attain maximum enhancement of flexural modulus. In view of these results, it can be seen that tensile properties required higher MAPE content relative to flexural properties. Meanwhile, only a marginal improvement in thermal and mechanical properties were seen when MAPE was applied to composites made from heat-treated wood flour. This showed that coupling is not as effective in heat-treated wood as it is in the untreated materials because of the possibility of reduced O-H groups on the surface of heat-treated wood flour. In general, heat treatment of wood flour at appropriate temperature produced composites with better compatibility and improved mechanical performance. Moreover, this research has demonstrated that the mechanical properties of LDPE can be significantly improved by addition of red balau sawdust as fillers with adequate level of MAPE content. Therefore, this presents a way of extending the applications of LDPE beyond its traditional uses.

All the composites were found to absorb moisture to various extents due to the hydrophilic nature of wood. However, composites made from heat-treated wood flour showed a reduction in water absorption up to 90% because of the reduced hydrophilicity imparted to the wood flour by heat treatment. Accordingly, the decrease in the water absorption capacity of wood used in this study has beneficial effect on the lifetime of the product and its applications. Also, the inclusion of MAPE reduced the water absorption of the composites to various degrees. However, it was observed that a 2% MAPE content achieved almost the same extent of moisture reduction as the 6% or the 10% MAPE level in untreated wood composites. The effect of MAPE on the water absorption of heat-treated wood composites was negligible as this category of composites showed minimal decrease in equilibrium moisture with the addition of MAPE. Wood flour modification by heat treatment has therefore invalidated the use of MAPE in this group of composites. Therefore, heat treatment of wood flour can reduce the moisture absorption of wood thermoplastic composites without the use of MAPE.

Reductions in thickness swelling were observed with composites made from heat-treated wood flour, relative to those containing untreated wood flour. The thickness swelling of composites made from 200°C treated wood flour was lowest even without the addition of MAPE. This was achieved by the decrease in the hygroscopic character of the wood flour and the resultant improvement in the interfacial adhesion. These results demonstrated that treating wood flour at 200°C is more efficient in checking the thickness swelling of wood thermoplastic composites than the incorporation of coupling agents.

Studying the kinetics of water absorption revealed that the composites exhibited a deviation from the Fickian mode of water absorption with n values greater or less than 0.5. At higher filler loading, k values were higher in untreated wood composites than in the heat-treated materials, showing higher wood-water interaction in the former than the latter. The true diffusion coefficient was lower in untreated wood composites due to delayed transport as a result of hydrogen bonding. The values were higher in heat-treated wood composites relative to untreated materials indicating, higher diffusion rate.

The mechanical properties deteriorated generally with water absorption in all composites studied but the extent of decline was more pronounced in the untreated wood composites when compared to the heat-treated composites. Therefore, heat treatment can reduce the moisture absorbing tendency in wood fillers leading to better water resistant composites with the ability to retain its mechanical properties after long time exposure to moisture. It is, therefore, a good method of improving wood thermoplastic composites properties in applications that pose moisture-related challenges.

The surfaces of the composites containing untreated wood flour showed a level of fungal colonisation on soil burial, with the attendant decline in mechanical properties. However, composites made from heat-treated wood flour exhibited less fungal growth on the surface and better resistance to mechanical properties deterioration. Due to its inability to be used in structural applications, the LDPE composites prepared in this study may be used as flower pots. Thus, the tendency for it to retain its mechanical properties after soil burial is very pertinent.

All the composites studied showed a change in colour, fading from dark brown to light grey on exposure to the outdoor environment; this is an indication of the degradation of wood components by UV radiation. Thermal and mechanical properties declined with outdoor exposure as a result of the deteriorating effect of the outdoor environment on the composite's properties by photodegradation. However, composites made from heat-treated wood flour showed better resistance to the elements of the outdoor environment than their untreated counterparts. From these findings, it can be concluded that heat treatment of wood flour enhanced the properties of wood thermoplastic composites with the ability to retain mechanical properties after exposure to harsh outdoor environment. In general, the properties of the composites were not adversely affected on exposure to the indoor environment. Thus, using this product in domestic applications will be worthwhile.

5.2 Recommendations for further work

- Proper characterisation of the surface of untreated and heat-treated wood flour by X-ray photoelectron spectroscopy, XPS and wettability by contact angle measurement will enhance the understanding of the degree of modification by heat treatment.
- Flammability tests will improve on the knowledge of the thermal stability of the wood flour and composites.
- Longer exposure of the composites to different environmental conditions will allow better interaction between the material and the elements of the different

environments. This will enable an enhanced understanding of the degree of the material’s response to environmental degradation.

- Determination of the molecular weight and molecular weight distribution in order to establish extent of environmental degradation in the material .
- Conduct of biodegradability tests on the samples in order to ascertain the environmental friendliness of the material and to find out the effect of heat treatment of wood flour, if any, on the biodegradability of the composites.

REFERENCES

1. ASTM standared D-3878. *Standard terminology for composite materials. ASTM International, West Conshoshocken, PA, DOI: 10.1520/D3878-07. www.astm.org.* 2007.

2. Mazumdar S. K. *Composites manufacturing materials, product, and process engineering*. Boca Raton: CRC Press, 2001. 392.

3. Bledzki A. K., Sperber V. E and Faruk O. *Natural and wood fibre reinforcement in polymers*. Shrewsbury GBR: Smithers Rapra, Smart Publications, 13. 2002. 147.

4. Pritchard G. Two technologies merge: Wood plastic composites. *Reinforced Plastics* 2004. 48(6): 26-29.

5. Bledzki A. K., Mamun A. A and Volk J. Physical, chemical and surface properties of wheat husk, rye husk and soft wood and their polypropylene composites. *Composites Part A: Applied Science and Manufacturing* 2010. 41(4): 480-488.

6. Stark N. M. Influence of moisture absorption on mechanical properties of wood flour-polypropylene composites. *Journal of Thermoplastic Composite Materials* 2001. 14(5): 421-432.

7. Sanadi A. R., Caulfield D. F and Jacobson R. E. *Agro-fibre thermoplastic composites*. In: R. M. Rowell., R. A. Young and J. K. Rowell, editor. Paper and composites from agro-based resources. Boca Raton: CRC Press, 1997. 377-401.

8. Rowell R. M. The state of art and future development of bio-based composite science and technology towards the 21st century. In: *Fourth Pacific Rim bio-based composites symposium*. Indonesia,1998. 1-18.

9. Devi R. R., Ali I and Maji T. K. Chemical modification of rubber wood with styrene in combination with a crosslinker: effect on dimensional stability and strength property. *Bioresource Technology* 2003. 88(3): 185-188.

10. Akyildiz M. H., Ates S and Özdemir H. Technological and chemical properties of heat-treated Anatolian black pine wood. *African Journal of Biotechnology* 2010. 8(11): 2565-2572.

11. Kokaefe D., Poncsak S and Boluk Y. Effect of thermal treatment on the chemical composition and mechanical properties of birch and aspen. *BioResources* 2008. 3(2): 517-537.

12. Wiemann M. C. *Characteristics and availability of commercially important woods*. In: R. J. Ross, editor. Wood Handbook. General Technical Report FPL-GTR-190. Madison. WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, 2010. 2-1 - 2-45.

13. Yang H. S., Wolcott M. P., Kim H. S., Kim S and Kim H. J. Effect of different compatibilizing agents on the mechanical properties of lignocellulosic material filled polyethylene bio-composites. *Composite Structures* 2007. 79(3): 369-375.

14. Nachtigall S., Cerveira G. S and Rosa S. M. L. New polymeric-coupling agent for polypropylene/wood-flour composites. *Polymer Testing* 2007. 26(5): 619-628.

15. Clemons C. Wood-plastic composites in the United States: The interfacing of two industries. *Forest Products Journal* 2002. 52(6): 10-18.

16. Ashori A. Wood–plastic composites as promising green-composites for automotive industries! *Bioresource Technology* 2008. 99(11): 4661-4667.

17. Gupta B. S., Reiniati I and Laborie M-P. G. Surface properties and adhesion of wood fibre reinforced thermoplastic composites. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2007. 302(1–3): 388-395.

18. Lafia-Araga R. A., Hassan A., Yahya R., Rahman N. A., Hornsby P. R and Heidarian J. Thermal and mechanical properties of treated and untreated Red Balau (Shorea dipterocarpaceae)/LDPE composites. *Journal of Reinforced Plastics and Composites* 2012. 31(4): 215-224.

19. Stark N. M., Cal Z and Carll C. *Wood-based composite materials panel products, glued-laminated timber, structural composite lumber, and wood–nonwood composite materials*. In: R. J. Ross, editor. Wood Handbook: Wood as an engineering material. General Technical Report FPL-GTR-190. Madison WI.: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory., 2010. 11-1 – 11-28.

20. Shenoy A. V. *Rheology of filled polymer systems*. Springer, 1999. 477.

21. Eight selected species for forest plantation programme in Malaysia, Malaysian Timber Industry Board, 2008: Malaysia.

22. Lee Y and Chu Y. P., *Commercial timbers of Peninsular Malaysia*, Peninsular Malaysia and the Malaysian Timber Industry Board. Department of Forestry, Editor 1979: Malaysia.

23. Malaysian Forum for Environmental Journalists, *Reporting on the environment: A Handbook for Malaysian Environmental Journalists,*, 1989.

24. Krässig H. A. and Chemist G. Cellulose: structure, accessibility and reactivity. *Polymer Monograph* 1993. 11: 1-3.

25. Peacock A. *Handbook of polyethylene: Structures: properties, and applications*. CRC, Vol. 57. 2000. 537.

26. Mohanty A. K., Misra M and Drzal L. T. Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. *Journal of Polymers and the Environment* 2002. 10(1): 19-26.

27. Lim S. C., Samsudin M and Gan K. S. A Second growth forest as a future source of Wood from the natural forest-their availability, utilization and identification In: *International symposium on development of improved methods to identify Shorea species wood and its origin*. Japan,2007. 3-9.

28. Commercial timbers of Malaysia, Malaysian Timber Council, Editor 2010: Malaysia.

29. Sever K., Erden S., Gülec H. A., Seki Y and Sarikanat M. Oxygen plasma treatments of jute fibres in improving the mechanical properties of jute/HDPE composites. *Materials Chemistry and Physics* 2011. 129(1): 275-280.

30. Tjeerdsma B. F., Boonstra M., Pizzi A., Tekely P and Militz H. Characterization of thermally modified wood: molecular reasons for wood performance improvement. *European Journal of Wood and Wood Products* 1998. 56: 149-153.

31. Rowell R. M., Pettersen R., Han J. S., Rowell J. S and A. Tshabalala M. *Cell wall chemistry*. In: R. M. Rowell, editor. Handbook of wood chemistry and wood composites. Boca Raton: CRC Press, 2005. 473.

32. Risbrudt C. D. *Wood and society*. In: R. M. Rowell, editor. Handbook of wood chemistry and wood composites. Boca Raton CRC Press, 2005. 473.

33. Minor J. L., Pettersen R. C., Rowell R. M., Simpson W. T., Youngquist J. A and Zinkel D. F. *Wood*: In: H. F. Mark., N. Bikales., C. G. Overberger., G. Menges and J. I. Kroschwtz, editors. *Encyclopedia of polymer science and engineering*. 1989, John Wiley and Sons: USA. 843–887.

34. Olesen P. O and Plackett D. V. Perspectives on the performance of natural plant fibres. In: *Natural fibres performance forum*. Copenhagen Denmark.,1999. 1-7.

35. Petersen R. C. *The chemical composition of wood*. In: R. M. Rowell, editor. The chemistry of solid wood. 1984, American Chemical Society publications: U S A, 57-126.

36. Sjöström E. *Wood chemistry: Fundamentals and applications*. USA: Academic Press, 1993. 293.

37. Wellenberger F. T and Weston E. N. *Science and Technology*. In: F. T. Wellenberger and E. N. Weston, editors. Natural fibres plastics and composites. Kluwer Academic Publishers: New York, 2004. 1-8.

38. Bismarck A., Mishra S and Lampke T. *Plant fibres as reinforcement for green composites*. In: A. K Mohanty., M Misra and L. T Drzal, editors. Natural fibres, biopolymers, and biocomposites. Boca Raton: CRC Press, 2005. 37-109.

39. Homan W. J and Jorissen A. J. M. Wood modification developments. *Heron* 2004. 49(4): 360-369.

40. Hill C. A. S. *Wood modification: Chemical, thermal and other processes*. England: John Wiley and Sons, Wiley series in renewable resources, ed. C. V. Stevens 2006. 262.

41. Li X., Tabil L. G and Panigrahi S. Chemical treatment of natural fibre for use in natural fibre-reinforced composites - A review. *Journal of Polymers and the Environment.* 2007. 15: 25-33.

42. Kalia S., Kaith B. S and Kaur I. Pretreatments of natural fibres and their application as reinforcing material in polymer composites - A review. *Polymer Engineering & Science* 2009. 49(7): 1253-1272.

43. Gassan J and Bledzki A. K. Alkali treatment of jute fibres: Relationship between structure and mechanical properties. *Journal of Applied Polymer Science* 1999. 71(4): 623-629.

44. John M. J and Anandjiwala R. D. Recent developments in chemical modification and characterization of natural fibre reinforced composites. *Polymer Composites* 2007. 29(2): 187-207.

45. Farsi M. Wood-plastic composites: Influence of wood flour chemical modification on the mechanical performance. *Journal of Reinforced Plastics and Composites* 2010. 29(24): 3587-3592.

46. Liu W., Mohanty A. K., Drzal L. T., Askel P and Misra M. Effects of alkali treatment on the structure, morphology and thermal properties of native grass fibres as reinforcements for polymer matrix composites. *Journal of Materials Science* 2004. 39(3): 1051-1054.

47. Jacob M., Thomas S and Varughese K. T. Mechanical properties of sisal/oil palm hybrid fibre reinforced natural rubber composites. *Composites Science and Technology* 2004. 64(7): 955-965.

48. Mishra S., Mohanty A. K., Drzal LT, Misra M., Parija S., Nayak S. K and Tripathy S. S. Studies on mechanical performance of biofibre/glass reinforced polyester hybrid composites. *Composites Science and Technology* 2003. 63(10): 1377-1385.

49. Manikandan Nair K. C., Thomas S and Groeninckx G. Thermal and dynamic mechanical analysis of polystyrene composites reinforced with short sisal fibres. *Composites Science and Technology* 2001. 61(16): 2519-2529.

50. Abdul Khalil H. P. S and Ismail H. Effect of acetylation and coupling agent treatments upon biological degradation of plant fibre reinforced polyester composites. *Polymer Testing* 2000. 20(1): 65-75.

51. Rong M. Z., Zhang M. Q., Liu Y., Yang G. C and Zeng H. M. The effect of fibre treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites. *Composites Science and Technology* 2001. 61(10): 1437-1447.

52. Agrawal R., Saxena N. S., Sharma K. B., Thomas S and Sreekala M. S. Activation energy and crystallization kinetics of untreated and treated oil palm fibre reinforced phenol formaldehyde composites. *Materials Science and Engineering: A* 2000. 277(1): 77-82.

53. Kim J. K., Sham M. L and Wu J. Nanoscale characterisation of interphase in silane treated glass fibre composites. *Composites Part A: Applied Science and Manufacturing* 2001. 32(5): 607-618.

54. Valadez-Gonzalez A., Cervantes-Uc J. M., Olayo R and Herrera-Franco P. J. Chemical modification of henequen fibres with an organosilane coupling agent. *Composites Part B: Engineering* 1999. 30(3): 321-331.

55. Grubbström G., Holmgren A and Oksman K. Silane-crosslinking of recycled low-density polyethylene/wood composites. *Composites Part A: Applied Science and Manufacturing* 2010. 41(5): 678-683.

56. Sreekala M. S., Kumaran M. G., Joseph S., Jacob M and Thomas S. Oil palm fibre reinforced phenol formaldehyde composites: Influence of fibre surface modifications on the mechanical performance. *Applied Composite Materials* 2000. 7(5): 295-329.

57. Paul A., Joseph K and Thomas S. Effect of surface treatments on the electrical properties of low-density polyethylene composites reinforced with short sisal fibres. *Composites Science and Technology* 1997. 57(1): 67-79.

58. Sapieha S., Allard P and Zang Y. H. Dicumyl peroxide modified cellulose/LLDPE composites. *Journal of Applied Polymer Science* 2003. 41(9-10): 2039-2048.

59. Keener T. J., Stuart R. K and Brown T. K. Maleated coupling agents for natural fibre composites. *Composites Part A: Applied Science and Manufacturing* 2004. 35(3): 357-362.

60. Van de Velde K and Kiekens P. Effect of material and process parameters on the mechanical properties of unidirectional and multidirectional flax/polypropylene composites. *Composite Structures* 2003. 62(3): 443-448.

61. Cantero G., Arbelaiz A., Llano-Ponte R and Mondragon I. Effects of fibre treatment on wettability and mechanical behaviour of flax/polypropylene composites. *Composites Science and Technology* 2003. 63(9): 1247-1254.

62. Gassan J and Bledzki A. K. The influence of fibre-surface treatment on the mechanical properties of jute-polypropylene composites. *Composites Part A: Applied Science and Manufacturing* 1997. 28(12): 1001-1005.

63. Van den Oever M and Peijs T. Continuous-glass-fibre-reinforced polypropylene composites II. Influence of maleic-anhydride modified polypropylene on fatigue behaviour. *Composites Part A: Applied Science and Manufacturing* 1998. 29(3): 227-239.

64. Joseph P. V., Joseph K., Thomas S., Pillai C.K. S., Prasad V. S., Groeninckx G and Sarkissova M. The thermal and crystallisation studies of short sisal fibre reinforced polypropylene composites. *Composites Part A: Applied Science and Manufacturing* 2003. 34(3): 253-266.

65. Bledzki A. K., Reihmane S and Gassan J. Properties and modification methods for vegetable fibres for natural fibre composites. *Journal of Applied Polymer Science* 1996. 59(8): 1329-1336.

66. Mishra S., Naik J. B and Patil Y. P. The compatibilising effect of maleic anhydride on swelling and mechanical properties of plant-fibre-reinforced novolac composites. *Composites Science and Technology* 2000. 60(9): 1729-1735.

67. Mohanty S., Nayak S. K., Verma S. K and Tripathy S. S. Effect of MAPP as a coupling agent on the performance of jute - PP composites. *Journal of Reinforced Plastics and Composites* 2004. 23(6): 625-637.

68. Höcker H. Plasma treatment of textile fibres. *Pure and Applied Chemistry* 2002. 74(3): 423-427.

69. Martin A. R., Manolache S., Mattoso L. H. C., Rowell R. M and Denes F. Plasma modification of sisal on high density polyethylene composites: Effect on mechanical properties. In: *Third international symposium on natural polymers and composites–ISNaPol/2000 and the workshop on progress in production and processing of cellulosic fibres and natural polymer*. Sao Pedro. Brazil,2000. 431-436.

70. Rowell R., Lange S., McSweeny J and Davis M. Modification of wood fibre using steam. In: *6th Pacific rim bio-based composites symposium and workshop on the chemical modification of cellulosics.* Portland Oregon, USA, 2002. 606-615.

71. Okamoto T., Takatani M and Kitayama T. Wood-plastic composites with steam-exploded wood flour. In: *Third international wood and natural fibre composites symposium*. Kassel, Germany.,2000. 9-1 – 9-5.

72. Kaboorani A. Thermal properties of composites made of heat-treated wood and polypropylene. *Journal of Composite Materials* 2009. 43(22): 2599-2607.

73. Robin J. J and Breton Y. Reinforcement of recycled polyethylene with wood fibres heat-treated. *Journal of Reinforced Plastics and Composites* 2001. 20(14-15): 1253-1262.

74. Kaboorani A., Faezipour M and Ebrahimi G. . Feasibility of using heat-treated wood in wood/thermoplastic composites. *Journal of Reinforced Plastics and Composites* 2008. 27(16): 1689-1699.

75. Hassan A., Rahman N. A and Yahya R. Extrusion and injection-moulding of glass fibre/MAPP/polypropylene: Effect of coupling agent on DSC, DMA, and mechanical properties. *Journal of Reinforced Plastics and Composites* 2011. 30(14): 1223-1232.

76. Gwon J. G., Lee S. Y., Chun S. J., Doh G. H and Kim J. H. Physical and mechanical properties of wood–plastic composites hybridized with inorganic fillers. *Journal of Composite Materials* 2012. 46(3): 301-309.

77. Yeh S. K and Gupta R. K. Nanoclay reinforced, polypropylene based wood–plastic composites. *Polymer Engineering and Science* 2010. 50(10): 2013-2020.

78. Panthapulakkal S and Sain M. Studies on the water absorption properties of short hemp-glass fibre hybrid polypropylene composites. *Journal of Composite Materials* 2007. 41(15): 1871-1883.

79. Tadmor Z and Gogos C. G. *Principles of polymer processing*. New Jersey: John Wiley and Sons, 2006. 332.

80. Shakouri E., Behravesh A. H., Zolfaghari A and Golzar M. Effect of die pressure on mechanical properties of wood-plastic composite in extrusion process. *Journal of Thermoplastic Composite Materials* 2009. 22(6): 605-616.

81. Bledzki A. K., Letman M., Viksne A and Rence L. A comparison of compounding processes and wood type for wood fibre—PP composites. *Composites Part A: Applied Science and Manufacturing* 2005. 36(6): 789-797.

82. Berlin A., Volfson S. A., Enikolopian N. S and Negmatov S. S. *Principles of polymer composites*. Springer-Verlag, 1986. 124.

83. Takase S and Shiraishi N. Studies on composites from wood and polypropylenes. II. *Journal of Applied Polymer Science* 2003. 37(3): 645-659.

84. Lu J. Z, Wu Q and Negulescu I. I. Wood-fibre/high density polyethylene composites: Compounding process. *Journal of Aplied Polymer Science* 2004. 93(6): 2570-2578.

85. Rozman H. D and Peng G. B. The effect of compounding techniques on the mechanical properties of oil palm empty fruit bunch–polypropylene composites. *Journal of Applied Polymer Science* 1998. 70(13): 2647-2655.

86. Rauwendaal C. *Mixing in polymer processing*. New York: Marcel Dekker, 1991. 475.

87. Zhang J., Park C. B., Rizvi G. M., Huang H and Guo Q. Investigation on the uniformity of high density polyethylene/wood fibre composites in a twin screw extruder. *Journal of Applied Polymer Science* 2009. 113(4): 2081-2089.

88. Yeh S. K and Gupta R. K. Improved wood–plastic composites through better processing. *Composites Part A: Applied Science and Manufacturing* 2008. 39(11): 1694-1699.

89. Caulfield D. F., Clemons C., Jacobson R. E and Rowell R. M. , *Wood-thermoplastic composites*. In: *Handbook of wood chemistry and wood composites*. R. M. Rowell, editor. 2005, CRC press: Boca Raton. 365–380.

90. Chanda M and Roy S. K. *Plastics technology handbook*. Boca Raton: CRC Press, Vol. 72. 2006. 866.

91. Dixit N., Kortschot M. T., Sain M and Gulati D. Effect of interactions between interface modifiers and viscosity modifiers on the performance and processibility of the rice hulls-HDPE composites. *Journal of Reinforced Plastics and Composites* 2006. 25(16): 1691-1699.

92. Bengtsson M., Baillif M. L and Oksman K. Extrusion and mechanical properties of highly filled cellulose fibre–polypropylene composites. *Composites Part A: Applied Science and Manufacturing* 2007. 38(8): 1922-1931.

93. Tungjitpornkull S and Sombatsompop N. Processing technique and fibre orientation angle affecting the mechanical properties of E-glass fibre reinforced wood/PVC composites. *Journal of Materials Processing Technology* 2009. 209(6): 3079-3088.

94. Kissel W. J., Han J. H and Meyer J. *Polypropylene: Structure, properties, manufacturing processes, and applications*. In: H. G. Karian, editor. Handbook of polypropylene and polypropylene composites. New York: Marcel Dekker, 2003. 11-34.

95. Šercer M., Raos P and Rujnić-Sokele M. Processing of wood-thermoplastic composites. *International Journal of Material Forming* 2009. 2(1): 721-724.

96. Gosselin R., Rodrigue D and Riedl B. Injection moulding of postconsumer wood–plastic composites I: Morphology. *Journal of Thermoplastic Composite Materials* 2006. 19(6): 639-657.

97. Gosselin R., Rodrigue D and Riedl B. J. Injection moulding of postconsumer wood-plastic composites I: Mechanical properties. *Thermoplastic Composite Materials* 2006. 19(6): 659-669.

98. Jam N. J and Behravesh A. H. Challenge to the production of fine wood-plastic injection moulded composites. *Journal of Reinforced Plastics and Composites* 2009. 28(1): 73-82.

99. ASTM standard D-1106. *Standard test method for acid-insoluble lignin in wood, ASTM International, West Conshoshocken, PA, 1996, DOI: 10.1520/D1106-96R07, www.astm.org*. 1996.

100. ASTM standard D-1105. *Standard test method for preparation of extractive-free wood. ASTM International, West Conshoshocken, PA, 1996, DOI: 10.1520/D1105-96R07, www.astm.org.* 2007.

101. ASTM standard E-1755. *Standard test method for ash in biomass. ASTM International West Conshoshocken, PA, 1996, DOI: 10.1520/E1755-01R07, www.astm.org.* 2007.

102. ASTM Standard B-212. Apparent density of free-flowing metal powders using the hall flowmeter funnel, ASTM International, West Conshoshocken, PA, 1999. www.astm.org. 1999.

103. ASTM standard D-638. *Standard test method for tensile properties of plastics. ASTM International, West Conshoshocken, PA, 2008, DOI: 10.1520/D0638-08, www.astm.org* 2008.

104. ASTM Standard D-570. *Standard test method for water absorption of plastics. ASTM International, West Conshoshocken, PA, 2010, DOI: 10.1520/D0570-98R10E01, www.astm.org.* 2010.

105. ASTM Standard D-1435. *Standard practice for outdoor weathering of plastics. ASTM International, West Conshoshocken, PA, 1999, DOI: 10.1520/D1435-99. www.astm.org.* 1999.

106. Malaysian Meteorological agency, 2012. Malaysia.

107. ASTM Standard D-790. *Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials, ASTM International, West Conshoshocken, PA, 2010, DOI 10.1520/D0790-10, www.astm.org.* 2010.

108. ASTM standard E-23. *Standard test method for notched bar impact testing of metallic materials, ASTM International, West Conshohocken, PA. 2009, DOI: 10.1520/E0023-07AE01, www.astm.org.* 2007.

109. Zaman A., Alén R. and Kotilainen R. Thermal behaviour of scots pine (Pinus Sylvestris) and silver birch (*Betula pendula*) at 200-230°C. *Wood and Fibre Science* 2000. 32(2): 138-143.

110. Alén R., Kotilainen R and Zaman A. Thermochemical behaviour of Norway spruce (Picea abies) at 180–225°C. *Wood Science and Technology* 2002. 36(2): 163-171.

111. Kotilainen R., Alen R and Arpiainen V. Changes in the chemical composition of Norway spruce (Picea abies) at 160-260°C under nitrogen and air atmospheres. *Paper and Pulp* 1999. 81(5): 384-388.

112. Baeza J and Freer J. *Chemical characterization of wood and its components*. In: D. N. S. Hon and N. Shirashi, editors. Wood and Cellulosic Chemistry. New York: Marcel Dekker 2001. 275-384.

113. Tjeerdsma B. F and Militz H. Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat-treated wood. *European Journal of Wood and Wood Products* 2005. 63(2): 102-111.

114. Aydemir D., Gunduz G., Altuntas E., Ertas M., Sahin H. T and Alma H. Investigating changes in the chemical constituents and dimensional stability of heat-treated hornbeam and uludag fir wood. *BioResources* 2011. 6(2): 1308-1321.

115. Poncsák S., Kocaefe D., Bouazara M and Pichette A. Effect of high temperature treatment on the mechanical properties of birch (*Betula papyrifera*). *Wood Science and Technology* 2006. 40(8): 647-663.

116. Byrne C. E and Nagle D. C. Carbonization of wood for advanced materials applications. *Carbon* 1997. 35(2): 259-266.

117. Yang H. S., Wolcott M. P., Kim H. S and Kim H. J. Thermal properties of lignocellulosic filler-thermoplastic polymer bio-composites. *Journal of Thermal Analysis and Calorimetry* 2005. 82(1): 157-160.

118. Korošec R. C., Lavrič B., Rep G., Pohleven F and Bukovec P. Thermogravimetry as a possible tool for determining modification degree of thermally treated Norway spruce wood. *Journal of Thermal Analysis and Calorimetry* 2009. 98(1): 189-195.

119. Esteves B and Pereira H. M. Wood modification by heat treatment: A review. *BioResources* 2009. 4(1): 370-404.

120. Chartoff R. P and Sircar A. K. *Thermal analysis of polymers*. In: *Encyclopedia of polymer science and technology* 2008. John Wiley and Sons: New York. 1-86.

121. Hatakeyama T and Quinn F. X. *Thermal analysis: Fundamentals and applications to polymer science*. New York: John Wiley and Sons, 1999. 189.

122. Xie L., Grueneberg T., Steuernagel L., Ziegmann G and Militz H. Influence of particle concentration and type on flow, thermal, and mechanical poperties of wod-plypropylene cmposites. *Journal of Reinforced Plastics and Composites* 2010. 29(13): 1940-1951.

123. Doufnoune R., Haddaoui N and Riahi F. The effects of coupling agents on the mechanical, rheological and thermal properties of calcium carbonate-filled LDPE compatibilized with maleic anhydride-g-LDPE (Part II). *International Journal of Polymeric Materials* 2008. 57(7): 690-708.

124. Pouteau C., Dole P., Cathala B., Averous L and Boquillon N. Antioxidant properties of lignin in polypropylene. *Polymer Degradation and Stability* 2003. 81(1): 9-18.

125. Gabbott P. *A practical introduction to differential scanning calorimetry*. In: P. Gabbott, editor. Principles and applications of thermal analysis. Oxford: Blackwell, 2008. 1-50.

126. Jespersen N. *Evaluation of basic physical properties*. In: S. Ahuja and N. Jespersen, editors. Modern instrumental analysis. United Kingdom: Elsevier Science, 2006. 41-62.

127. Cui Y. H., Tao J., Noruziaan B., Cheung M and Lee S. DSC analysis and mechanical properties of wood-plastic composites. *Journal of Reinforced Plastics and Composites* 2010. 29(2): 278-289.

128. Riande E., Diaz-Calleja R., Prolongo M., Masegosa R and Salom C. *Polymer viscoelasticity: stress and strain in practice*. New York: Mercel Dekker, Vol. 55. 2000. 895.

129. Blain R. L. *Polymer heats of fusion.*, T.A Instruments: New Castle, DE.

130. Amash A and Zugenmaier P. Morphology and properties of isotropic and oriented samples of cellulose fibre–polypropylene composites. *Polymer* 2000. 41(4): 1589-1596.

131. Arbelaiz A., Fernandez B., Ramos J. A and Mondragon I. Thermal and crystallization studies of short fFlax fibre reinforced polypropylene matrix composites: Effects of treatments. *Thermochimica Acta* 2006. 440: 111-121.

132. Borysiak S and Doczekalska B. Influence of chemical modification of wood on the crystallisation of polypropylene. *European Journal of Wood and Wood Products* 2006. 64(6): 451-454.

133. Pan M., Zhang S. Y and Zhou D. Preparation and properties of wheat straw fibre-polypropylene composites. Part II. Investigation of surface treatments on the thermo-mechanical and rheological properties of the composites. *Journal of Composite Materials* 2010. 44(9): 1061-1073.

134. Chartoff R. P., Menczel J. D and Dillman S. H., *Dynamic mechanical analysis (DMA)*. In: J. D. Menczel and R. B. Prime, editors. Thermal analysis of polymers: Fundamentals and applications. New York: John Wiley and Sons, 2009. 387-495.

135. Yang H. S., Gardner D. J and Kim H. J. Viscoelastic and thermal analysis of lignocellulosic material filled polypropylene bio-composites. *Journal of Thermal Analysis and Calorimetry* 2009. 98(2): 553-558.

136. Joseph P. V., Mathew G., Joseph K., Groeninckx G and Thomas S. Dynamic mechanical properties of short sisal fibre reinforced polypropylene composites. *Composites Part A: Applied Science and Manufacturing* 2003. 34(3): 275-290.

137. Nayak S. K and Mohanty S. Sisal glass fibre reinforced PP hybrid composites: Effect of MAPP on the dynamic mechanical and thermal properties. *Journal of Reinforced Plastics and Composites* 2010. 29(10): 1551-1568.

138. Hristov V. N., Krumova M., Vasileva S and Michler G. H. Modified polypropylene wood flour composites. II. Fracture, deformation, and mechanical properties. *Journal of Applied Polymer Science* 2004. 92(2): 1286-1292.

139. Behzad M., Tajvidi M., Ehrahimi G and Falk R. H. Dynamic mechanical analysis of compatibiliser effect on the mechanical properties of wood flour/high-density polyethylene composites. *IJE Transactions. B: Applications* 2004. 17(1): 95-104.

140. López-Manchado M. A., Biagitti J and Kenny J. M. Comparative study of the effects of different fibres on the processing and properties of ternary composites based on PP-EPDM blends. *Polymer Composites* 2002. 23(5): 779-789.

141. Mohanty S., Verma S. K and Nayak S. K. Dynamic mechanical and thermal properties of MAPE treated jute/HDPE composites. *Composites Science and Technology* 2006. 66(3): 538-547.

142. Kalaprasad G., Mathew G., Pavithran C and Thomas S. Melt rheological behaviour of intimately mixed short sisal–glass hybrid fibre-reinforced low-density polyethylene composites. I. Untreated fibres. *Journal of Applied Polymer Science* 2003. 89(2): 432-442.

143. John B., Varughese K. T., Oommen Z., Pötschke P and Thomas S. Dynamic mechanical behaviour of high density polyethylene/ethylene vinyl acetate copolymer blends: The effects of the blend ratio, reactive compatibilisation, and dynamic vulcanisation. *Journal of Applied Polymer Science* 2003. 87(13): 2083-2099.

144. Rana A. K., Mandal A., Mitra B. C., Jacobson R., Rowell R and Banerjee A. N. Short jute fibre-reinforced polypropylene composites: Effect of compatibiliser. *Journal of Applied Polymer Science* 1998. 69(2): 329-338.

145. Nielsen L. E and Landel R. F. *Mechanical properties of polymers and composites*. New York: Mercel Dekker, Vol. 90. 1994. 545.

146. Hosford W. F. *Mechanical behaviour of materials*. New York: Cambridge University Press, 2010. 437.

147. Hakkou M., Pétrissans M., Zoulalian A and Gérardin P. Investigation of wood wettability changes during heat treatment on the basis of chemical analysis. *Polymer Degradation and Stability* 2005. 89(1): 1-5.

148. Follrich J., Müller U and Gindl W. Effects of thermal modification on the adhesion between spruce wood (Picea abies Karst.) and a thermoplastic polymer. *European Journal of Wood and Wood Products* 2006. 64(5): 373-376.

149. Kim H. S., Lee B. H., Choi S. W., Kim S and Kim H. J. The effect of types of maleic anhydride-grafted polypropylene (MAPP) on the interfacial adhesion properties of bio-flour-filled polypropylene composites. *Composites Part A: Applied Science and Manufacturing* 2007. 38(6): 1473-1482.

150. Nielsen L. E. *Polymer rheology*. New York: Mercel Dekker, 1977. 203.

151. Ismail H., Nizam J. M and Abdul Khalil H. P. S. The effect of a compatibiliser on the mechanical properties and mass swell of white rice husk ash filled natural rubber/linear low density polyethylene blends. *Polymer Testing* 2001. 20(2): 125-133.

152. Yang H. S., Kim H. J., Son J., Park H. J., Lee B. J and Hwang T. S. Rice-husk flour filled polypropylene composites; mechanical and morphological study. *Composite Structures* 2004. 63(3): 305-312.

153. Yang H. S., Kim H. J., Park H. J., Lee B. J and Hwang T. S. Effect of compatibilising agents on rice-husk flour reinforced polypropylene composites. *Composite Structures* 2007. 77(1): 45-55.

154. Ismail Y. S., Richardson M. O. W and Olley R. H. Optimising impact properties of PP composites by control of spherulitic morphology. *Journal of Applied Polymer Science* 2000. 79(9): 1704-1715.

155. Correa C. A., Razzino C. A and Hage E. Role of Maleated coupling agents on the interface adhesion of polypropylene-wood composites. *Journal of Thermoplastic Composite Materials* 2007. 20(3): 323-339.

156. Brown R. *Handbook of polymer testing:Short-term mechanical tests*, In: *Rapra polymer testing series*, Brown R, editor 2002, Rapra Technology: United Kingdom. 226.

157. Joseph P. V., Rabello M. S., Mattoso L. H. C., Joseph K and Thomas S. Environmental effects on the degradation behaviour of sisal fibre reinforced polypropylene composites. *Composites Science and Technology* 2002. 62(10): 1357-1372.

158. Hancox N. L. *An overview of the impact behaviour of fibre-reinforced composites*. In: S. R. Reid and G. Zhou, editors. Impact behaviour of fibre-reinforced composite materials and structures. Boca Raton: CRC Press, 2000. 1-32.

159. Callister W.D. Jr. *Materials science and engineering: An introduction*. New York: John Wiley and Sons, 2007. 975.

160. Hassan A., Hassan A. A and Mohd Rafiq M. I. Impact properties of moulded glass fibre/polyamide-6 composites: Effect of testing parameters. *Journal of Reinforced Plastics and Composites* 2011. 30(10): 889-898.

161. Razi P. S and Raman A. Studies on impact fracture properties of wood-polymer composites. *Journal of Composite Materials* 2000. 34(12): 980-997.

162. Crosby J. M and Drye T. R. Fracture studies of discontinuous fibre reinforced thermoplastic composites. *Journal of Reinforced Plastics and Composites* 1987. 6(2): 162-177.

163. Bhaskar J., Haq S and Yadaw S. B. Evaluation and testing of mechanical properties of wood plastic composite. *Journal of Thermoplastic Composite Materials* 2012. 25(4): 391-401.

164. Crawford R. J. *Plastics engineering*. Oxford: Butterworth-Heinemann, 1998. 530.

165. White J. R and Turnbull A. Weathering of polymers: Mechanisms of degradation and stabilization, testing strategies and modelling. *Journal of Materials Science* 1994. 29(3): 584-613.

166. Marcovich N. E., Reboredo M. M and Aranguren M. I. Moisture diffusion in polyester–woodflour composites. *Polymer* 1999. 40(26): 7313-7320.

167. Balatinecz J. J and Park B-D. The effects of temperature and moisture exposure on the properties of wood-fibre thermoplastic composites. *Journal of Thermoplastic Composite Materials* 1997. 10(5): 476-487.

168. Khalil H. P. S. A., Shahnaz S. B. S., Ratnam M. M., Ahmad F and Nik Fuaad N. A. Recycle polypropylene (RPP)-wood saw dust (WSD) composites-Part 1: The effect of different filler size and filler Loading on mechanical and water absorption properties. *Journal of Reinforced Plastics and Composites* 2006. 25(12): 1291-1303.

169. Sreekala M. S., Kumaran M. G and Thomas S. Water sorption in oil palm fibre reinforced phenol formaldehyde composites. *Composites Part A: Applied Science and Manufacturing* 2002. 33(6): 763-777.

170. Thwe M. M and Liao K. Durability of bamboo-glass fibre reinforced polymer matrix hybrid composites. *Composites Science and Technology* 2003. 63(3): 375-387.

171. Kaboorani A and Englund K. R. Water sorption and mechanical performance of preheated wood/thermoplastic composites. *Journal of Composite Materials* 2011. 45(13): 1423-1433.

172. Espert A., Vilaplana F and Karlsson S. Comparison of water absorption in natural cellulosic fibres from wood and one-year crops in polypropylene composites and its influence on their mechanical properties. *Composites Part A: Applied Science and Manufacturing* 2004. 35(11): 1267-1276.

173. Crank J. *The mathematics of diffusion*. London: Oxford University Press, 1975. 421.

174. Mat Taib R., Ishak Z. A., Rozman H. D and Glasser W. G. Effect of moisture absorption on the tensile properties of steam-exploded acacia mangium fibre–polypropylene composites. *Journal of Thermoplastic Composite Materials* 2006. 19(5): 475-489.

175. Van Krevelen D. W and Te Nijenhuis K. *Properties of polymers* London: Elsevier, 2009. 1031.

176. Rao R., Balasubramanian N and Chanda M. Factors affecting moisture absorption in polymer composites part I: Influence of internal factors. *Journal of Reinforced Plastics and Composites* 1984. 3(3): 232-245.

177. Park H. S., Sung J and Chang T. Hydrogen bonding effect on probe diffusion in semi-dilute polymer solutions: Polymer chain structure dependence. *Macromolecules* 1996. 29(9): 3216-3219.

178. Tamai Y., Tanaka H and Nakanishi K. Molecular dynamics study of polymer - water interaction in hydrogels. I. Hydrogen-bond structure. *Macromolecules* 1996. 29(21): 6750-6760.

179. Yang H. S., Kim H. J., Park H. J., Lee B. J and Hwang T. S. Water absorption behaviour and mechanical properties of lignocellulosic filler–polyolefin bio-composites. *Composite Structures* 2006. 72(4): 429-437.

180. Hassan A., Salleh N. M., Yahya R and Sheikh M. R. K. Fibre length, thermal, mechanical, and dynamic mechanical properties of injection-molded glass-fibre/polyamide 6, 6: Plasticization effect. *Journal of Reinforced Plastics and Composites* 2011. 30(6): 488-498.

181. Shaw M. T and MacKnight W. J. *Introduction to polymer viscoelasticity*. New Jersey: John Wiley and Sons, 2005. 327.

182. Mat Taib R., Ramarad S., Mohd Ishak Z. A and Rozman H. D. Effect of immersion time in water on the tensile properties of acetylated steam-exploded Acacia mangium fibres-filled polyethylene composites. *Journal of Thermoplastic Composite Materials* 2009. 22(1): 83-98.

183. Stamboulis A., Baillie C. A and Peijs T. Effects of environmental conditions on mechanical and physical properties of flax fibres. *Composites Part A: Applied Science and Manufacturing* 2001. 32(8): 1105-1115.

184. Dhakal H. N., Zhang Z. Y and Richardson M. O. W. Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites. *Composites Science and Technology* 2007. 67(7): 1674-1683.

185. Cui Y. H., Wang X. X., Xu Q and Xia Z. Z. Research on moisture absorption behaviour of recycled polypropylene matrix wood plastic composites. *Journal of Thermoplastic Composite Materials* 2011. 24(1): 65-82.

186. Bledzki A. K and Faruk O. Creep and impact properties of wood fibre–polypropylene composites: influence of temperature and moisture content. *Composites Science and Technology* 2004. 64(5): 693-700.

187. Clemons C. Exploratory microscopic investigation of impacted paper fibre-reinforced polypropylene composites. In: *Wood fibre–plastic composites—Virgin and recycled wood fibre and polymers for composites*. Madison, WI,1995. 173-179.

188. Searle N. D. *Environmental effects on polymeric materials*. In: A. L. Andrady, editor. Plastics and the environment. New Jersey: John Wiley and Sons, 2003. 313-358.

189. Colin G., Cooney J. D., Carlsson D. J and Wiles D. M. Deterioration of plastic films under soil burial conditions. *Journal of Applied Polymer Science* 2003. 26(2): 509-519.

190. Behjat T., Russly A. R., Luqman C. A., Yus A. Y and Nor Azowa I. Effect of PEG on the biodegradability studies of Kenaf cellulose-polyethylene composites. *International Food Research Journal* 2009. 16(2): 243-247.

191. lbach R. E and Clemons C. M. Biological resistance of polyethylene composites made With chemically modified fibre or flour. In: *6th Pacific Rim bio-based composites symposium & workshop on the chemical modification of cellulosics*. Portland Oregon, 2002. 574-579.

192. Schirp A., Ibach R., Pendleton D. E and Wolcott M. P. *Biological degradation of WPC and strategies for improving the resistance of WPC against biological decay*. In: T. P. Schultz., H. Militz., M. H. Freeman., B. Goodell and D. D. Nicholas, editors. Development of commercial wood preservatives: Efficacy, environmental and health issues. ACS Symposium Series USA: American Chemical Society, 2008. 480-507.

193. Khavkine M., Kazayawoko M., Law S and Balatinecz J. J. Durability of wood flour-thermoplastic composites under extreme environmental conditions and fungal exposure. *International Journal of Polymeric Materials* 2000. 46(1-2): 255-269.

194. Morancho J. M., Ramis X., Fernández X., Cadenato A., Salla J. M., Vallés A., Contat L and Ribes A. Calorimetric and thermogravimetric studies of UV-irradiated polypropylene/starch-based materials aged in soil. *Polymer Degradation and Stability* 2006. 91(1): 44-51.

195. Arutchelvi J., Sudhakar M., Arkatkar A., Doble M., Bhaduri S and Uppara P. V. Biodegradation of polyethylene and polypropylene. *Indian Journal of Biotechnology* 2008. 7(1): 9-22.

196. Bonhomme S., Cuer A., Delort A. M., Lemaire J., Sancelme M and Scott G. Environmental biodegradation of polyethylene. *Polymer Degradation and Stability* 2003. 81(3): 441-452.

197. Albertsson A. C and Karlsson S. The three stages in degradation of polymers—polyethylene as a model substance. *Journal of Applied Polymer Science* 1988. 35(5): 1289-1302.

198. Albertsson A. C and Banhidi Z. G. Microbial and oxidative effects in degradation of polyethene. *Journal of Applied Polymer Science* 1980. 25(8): 1655-1671.

199. Ołdak D., Kaczmarek H., Buffeteau T and Sourisseau C. Photo- and bio-degradation processes in polyethylene, cellulose and their blends studied by ATR-FTIR and Raman spectroscopies. *Journal of Materials Science* 2005. 40: 4189 – 4198.

200. Bikiaris D., Prinos J., Koutsopoulos K., Vouroutzis N., Pavlidou E., Frangis N. and Panayiotou C. LDPE/plasticized starch blends containing PE-g-MA copolymer as compatibiliser. *Polymer Degradation and Stability* 1998. 59(1–3): 287-291.

201. Schirp A and Wolcott M. P. Fungal degradation of wood-plastic composites and evaluation using dynamic mechanical analysis. *Journal of Applied Polymer Science* 2006. 99(6): 3138-3146.

202. Wu J., Yu D., Chan C. M., Kim J and Mai Y. W. Effect of fibre pretreatment condition on the interfacial strength and mechanical properties of wood fibre/PP composites. *Journal of Applied Polymer Science* 2000. 76(7): 1000-1010.

203. Karger-Kocsis J. *Reinforced polymer blends*. In: D. R. Paul and C. B. Bucknall, editors. Polymer blends. New York: John Wiley and Sons, 2000. 395-428.

204. Hobbs J. K. The fracture of poly (hydroxybutyrate) Part I: Fracture mechanics study during ageing. *Journal of Materials Science* 1998. 33(10): 2509-2514.

205. Feldman D. Polymer weathering: Photo-oxidation. *Journal of Polymers and the Environment* 2002. 10(4): 163-173.

206. Stark N. M and Matuana L. M. Surface chemistry changes of weathered HDPE/wood-flour composites studied by XPS and FTIR spectroscopy. *Polymer Degradation and Stability* 2004. 86: 1-9.

207. Tolinski M. *Additives for polyolefins: Getting the most out of polypropylene, polyethylene and TPO*. USA: Elsevier PDL Handbook Series 2009. 275.

208. Tidjani A. Comparison of formation of oxidation products during photo-oxidation of linear low density polyethylene under different natural and accelerated weathering conditions. *Polymer Degradation and Stability* 2000. 68(3): 465-469.

209. Kaci M., Sadoun T and Cimmino S. Crystallinity measurements of unstabilised and HALS stabilised LDPE films exposed to natural weathering by FT-IR, DSC and WAXS analysis. *International Journal of Polymer Analysis and Characterization* 2001. 6(5): 455-464.

210. Hamid S. H and Amin M. B. Lifetime prediction of polymers. *Journal of Applied Polymer Science* 1995. 55(10): 1385-1394.

211. Fernando S. S., Christensen P. A., Egerton T. A and White J. R. Carbon dioxide evolution and carbonyl group development during photodegradation of polyethylene and polypropylene. *Polymer Degradation and Stability* 2007. 92(12): 2163-2172.

212. Azapagic A., Emsley A and Hamerton I. *Polymers, the environment and sustainable development* New York: John Wiley and Sons, 2003. 235.

213. Stark N. M and Gardner D. J. *Outdoor durability of wood-polymer composites* In: K. O. Niska and M. Sain, editor. Wood-polymer composites. Boca Raton: CRC press, 2008. 143-165.

214. Stark N. M and Matuana L. M. Characterization of weathered wood–plastic composite surfaces using FTIR spectroscopy, contact angle, and XPS. *Polymer Degradation and Stability* 2007. 92(10): 1883-1890.

215. Fengel D and Wegen W. *Wood: Ultrastructure, chemistry, Reactions*. Berlin: Walter de Gruyter, 1984. 613.

216. Torikai A., Shirakawa H., Nagaya S and Fueki K. Photodegradation of polyethylene: Factors affecting photostability. *Journal of Applied Polymer Science* 1990. 40(9-10): 1637–1646

217. Schellenberg J and Fienhold G. Environmental stress cracking resistance of blends of high-density polyethylene with other polyethylenes. *Polymer Engineering & Science* 1998. 38(9): 1413-1419.

218. Srivastava D. Study of aging characteristics of ternary blends of polyethylenes—II. *Journal of Polymers and the Environment* 2004. 12(1): 27-33.

219. Bikiaris D and Panayiotou C. LDPE/starch blends compatibilized with PE-g-MA copolymers. *Journal of Applied Polymer Science* 1998. 70(8): 1503-1521.

220. Khan J. H. and Hamid S. H. Durability of HALS-stabilized polyethylene film in a greenhouse environment. *Polymer Degradation and Stability* 1995. 48(1): 137-142.

221. Rabello M. S and White J. R. Photodegradation of polypropylene containing a nucleating agent. *Journal of Applied Polymer Science* 1998. 64(13): 2505-2517.

222. Rowell R. M. Challenges in biomass-thermoplastic composites. *Journal of Polymers and the Environment* 2007. 15(4): 229–235.

223. Shah P. B., Bandopadhyay S and Bellare J. R. Environmentally degradable starch filled low density polyethylene. *Polymer Degradation and Stability* 1995. 47(2): 165-173.

224. Leong Y. W., Bakar A., Mohd Ishak Z. A and Ariffin A. Mechanical and morphological study of talc/calcium carbonate filled polypropylene hybrid composites weathered in tropical climates. *Jurnal Teknologi* 2003. 39: 23–34.

225. Hodzic A. *Re-use, recycling and degradation of composites*. In: Baillie C. A editor. Green composites: Polymer composites and the environment. Boca Raton CRC Press, 2004. 252-271.

226. Pagès P., Carrasco F., Surina J and Colom X. FTIR and DSC study of HDPE structural changes and mechanical properties variation when exposed to weathering aging during canadian winter. *Journal of Applied Polymer Science* 1996. 60(2): 153-159.

227. Rahman W. A. W. A, Lee T. S., Rahmat A. R., Isa M. N., Salleh M. S. N and Mokhtar M. Comparison of rice husk filled polyethylene composites and natural wood under weathering effects. *Journal of Composite Materials* 2011. 45 (13): 1403-1410.

APPENDIX

Appendix A: TGA thermograms showing the amount of moisture absorbed by the composites made from 37 wt% untreated and heat-treated at different conditionings

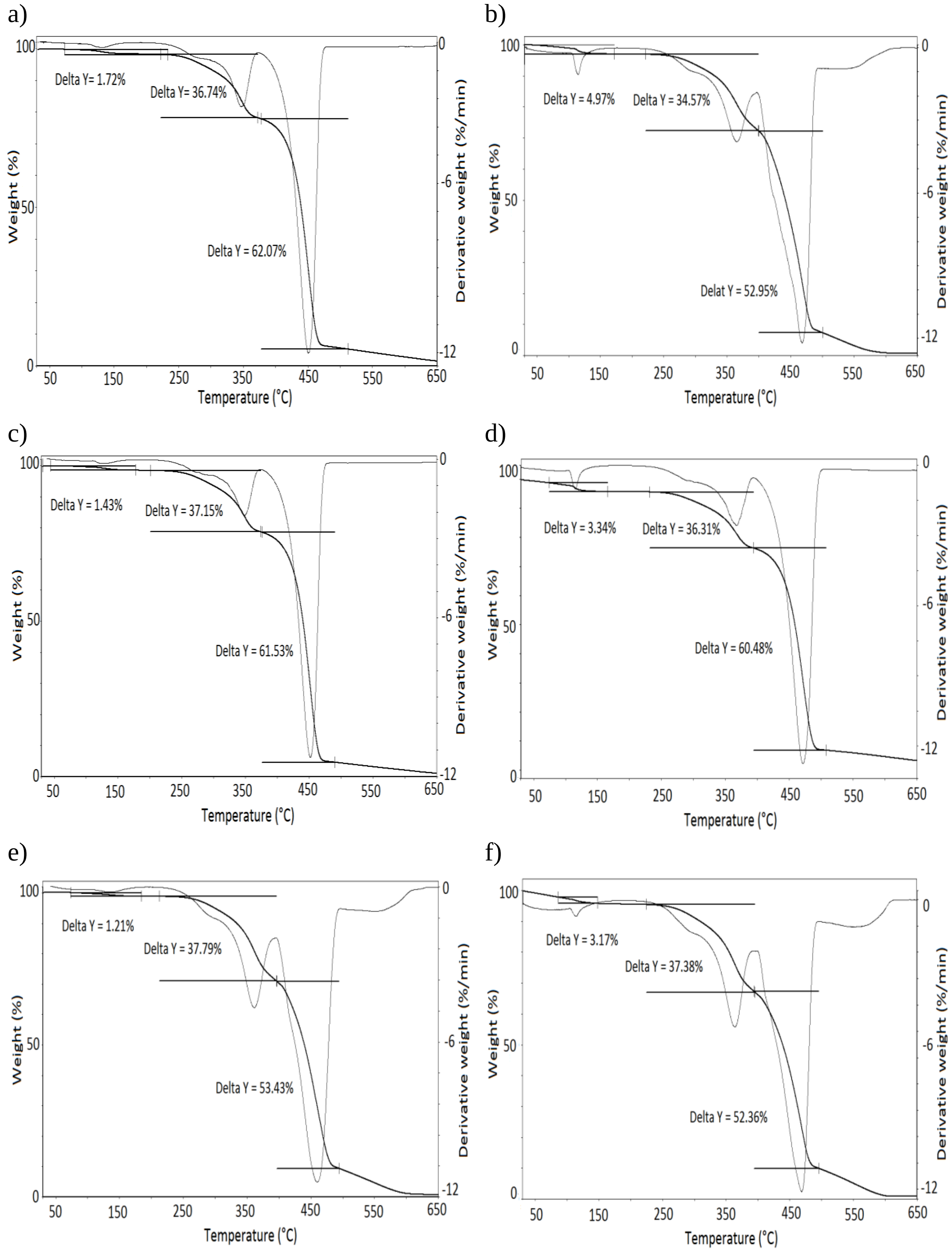


Figure A1: TGA/DTG curves of dry as-moulded: a) untreated, c) 180°C treated and e) 200°C treated and moisture saturated b) untreated, d) 180°C treated and f) 200°C treated 37 wt% WTC without compatibiliser

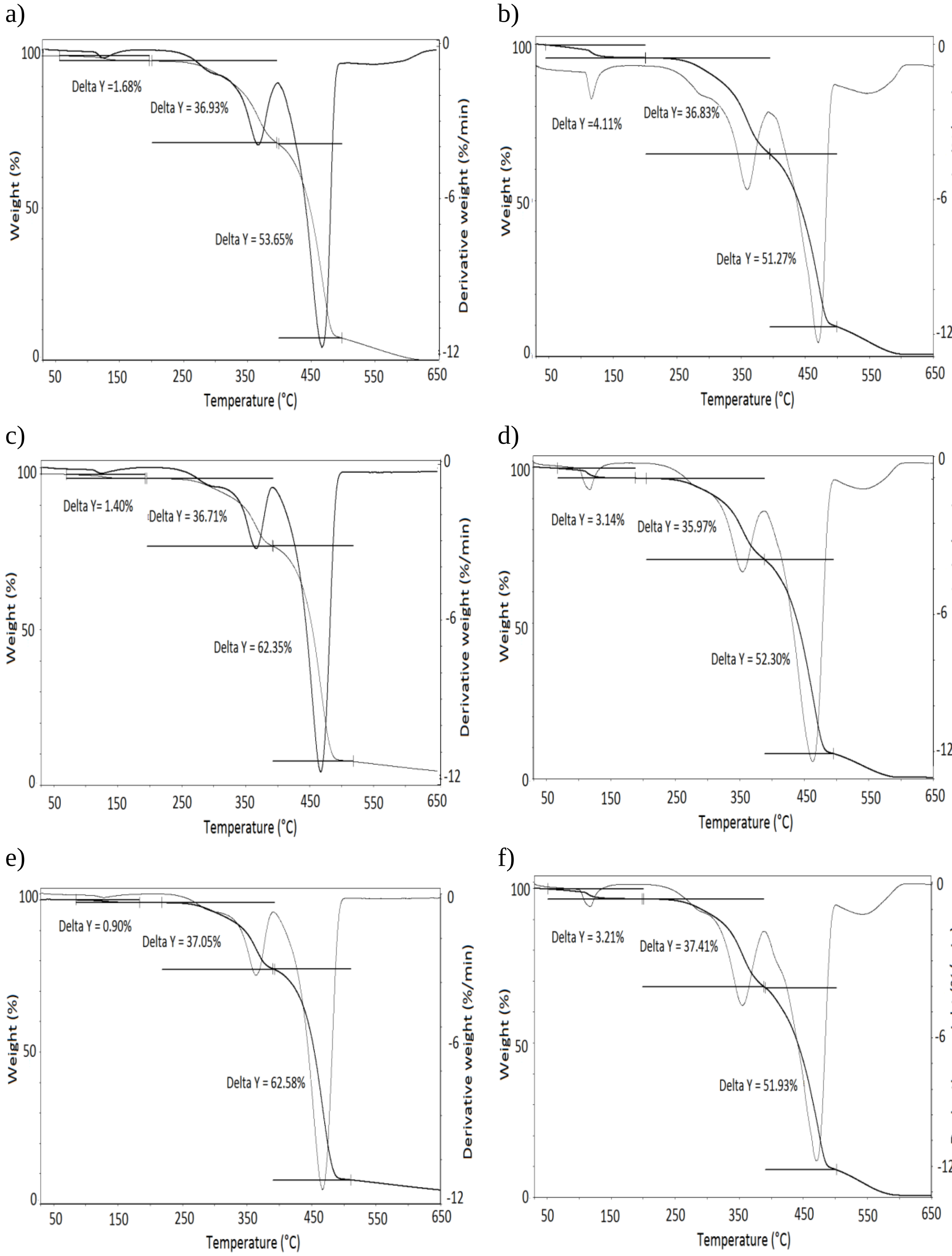


Figure A2: TGA/DTG curves of dry as-moulded: a) untreated, c) 180°C treated and e) 200°C treated and moisture saturated b) untreated, d) 180°C treated and f) 200°C treated composites with 6% MAPE

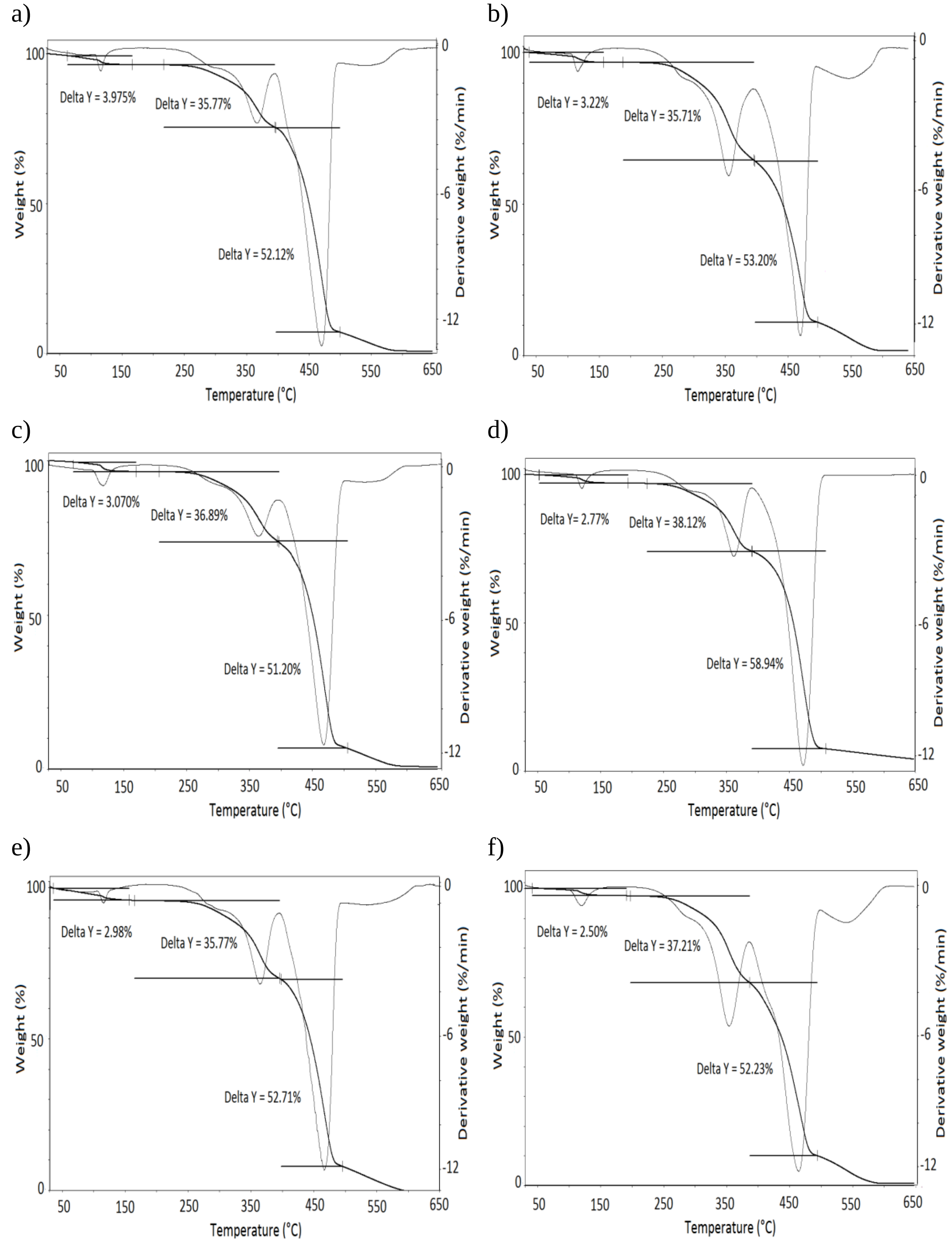


Figure A3: TGA /DTG curves of buried: a) untreated, c): 180°C treated and e) 200°C treated composites without MAPE and b) untreated, d) 180°C treated and f) 200°C treated composites with 6% MAPE

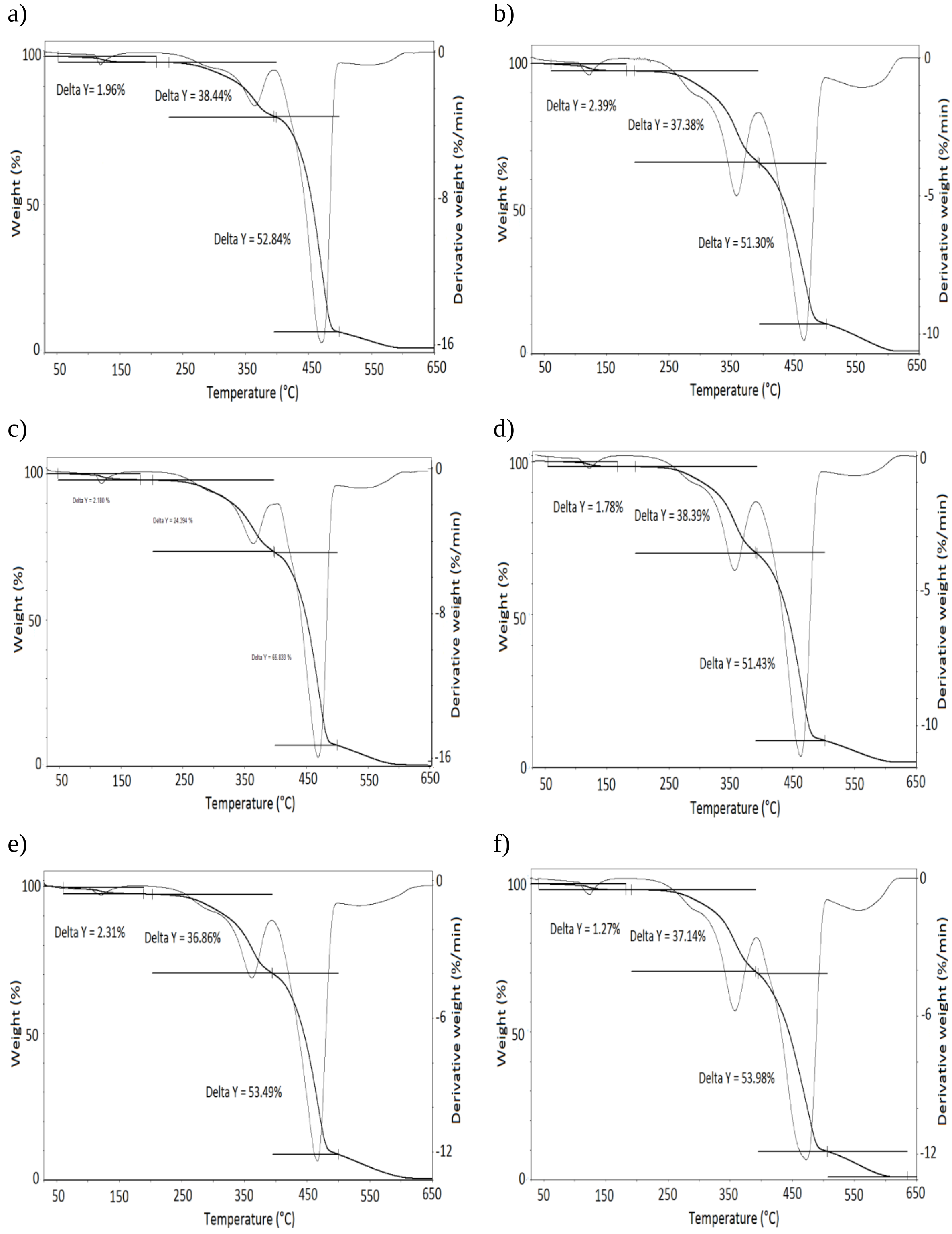


Figure A4: TGA /DTG curves of outdoor weathered: a) untreated, c) 180°C treated and e) 200°C treated composites without MAPE and b) untreated, d) 180°C treated and f) 200°C treated composites with 6% MAPE

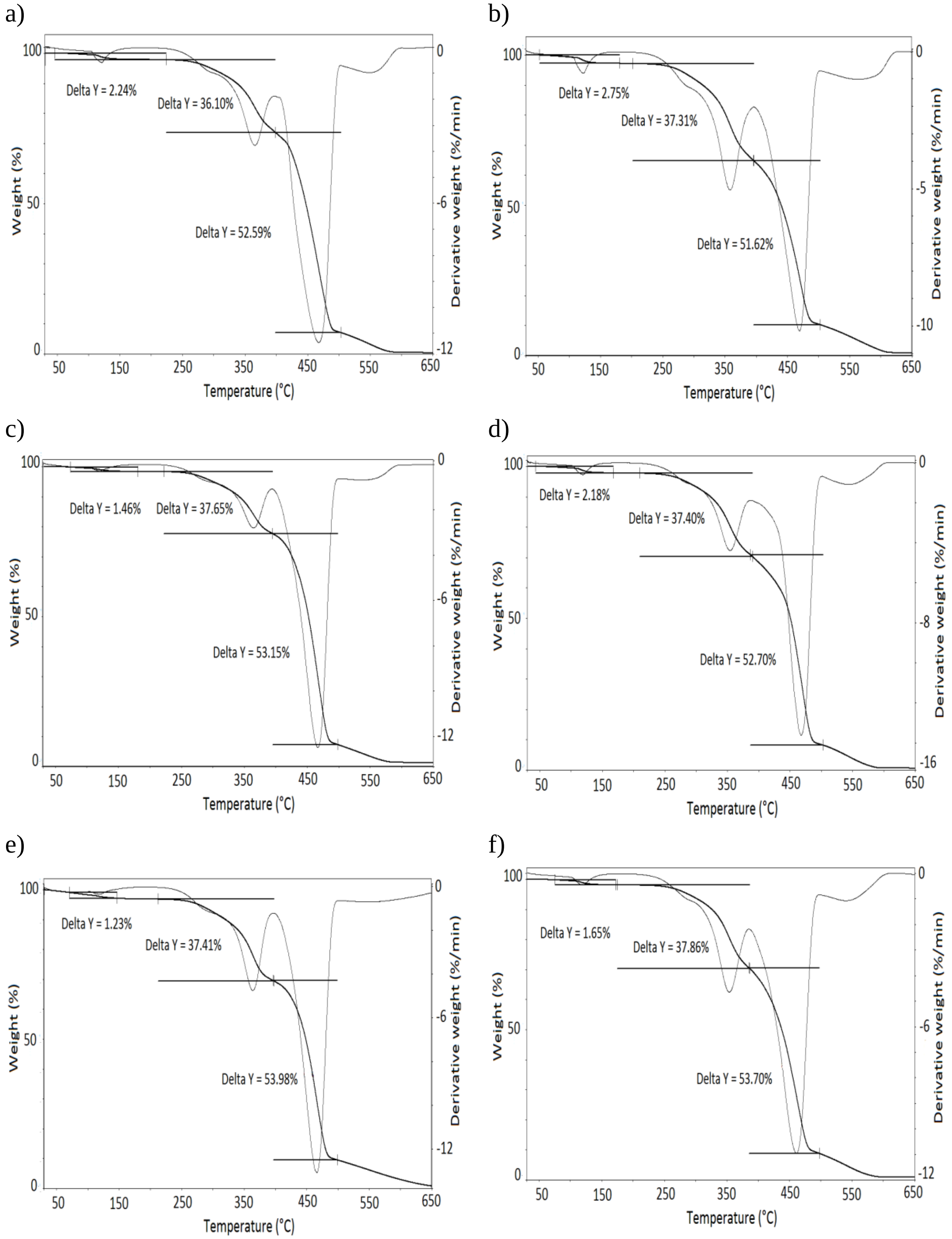


Figure A5: TGA /DTG curves of indoor exposed: a) untreated, c) 180°C treated and e) 200°C treated composites without MAPE and b) untreated, d) 180°C treated and f) 200°C treated composites with 6% MAPE

Appendix B: G_c calculations of dry as-moulded and conditioned samples

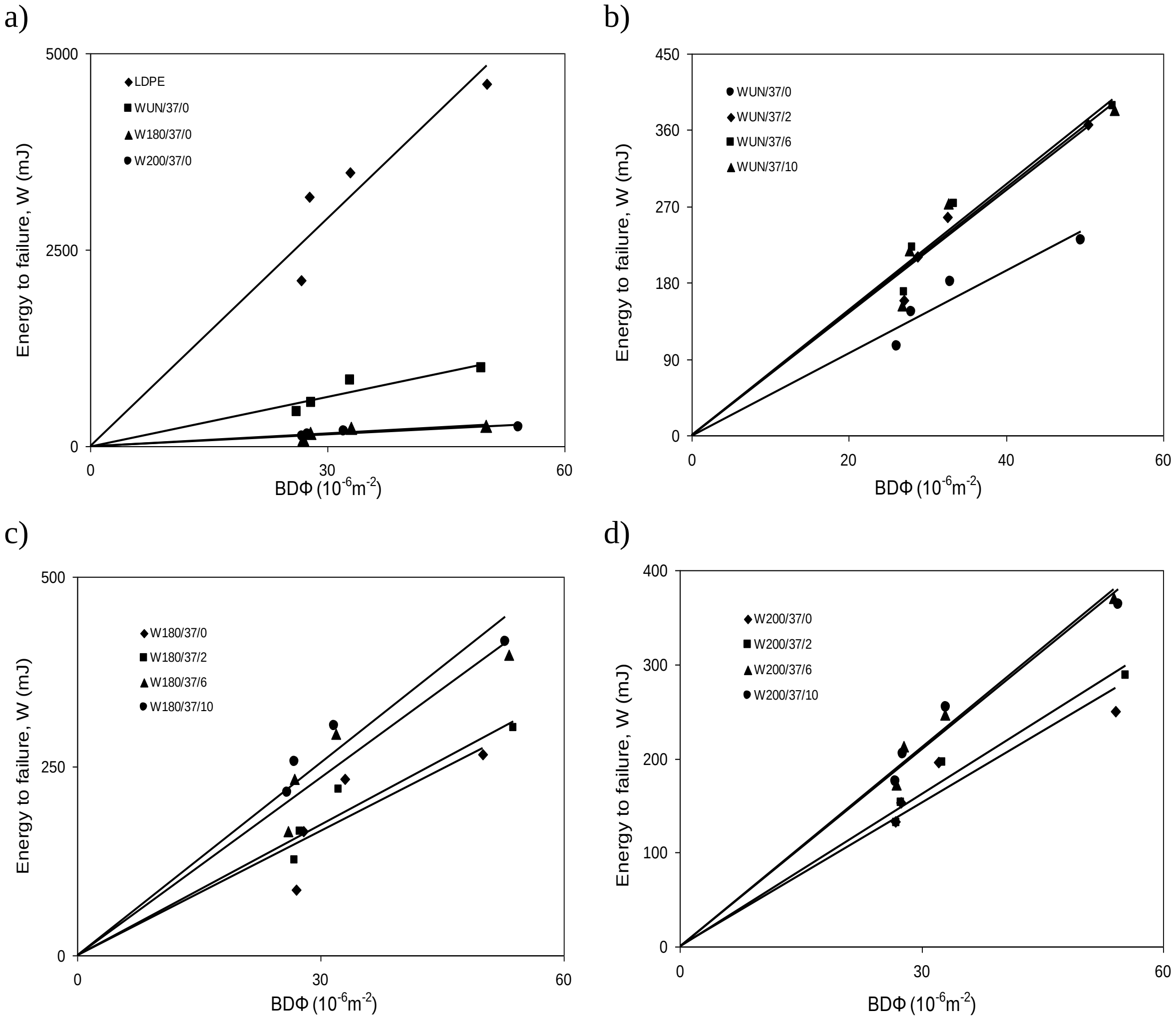


Figure B1: G_c calculations of dry as-moulded 37 wt% composites showing the effect of: a) different treatment and b-d) MAPE content

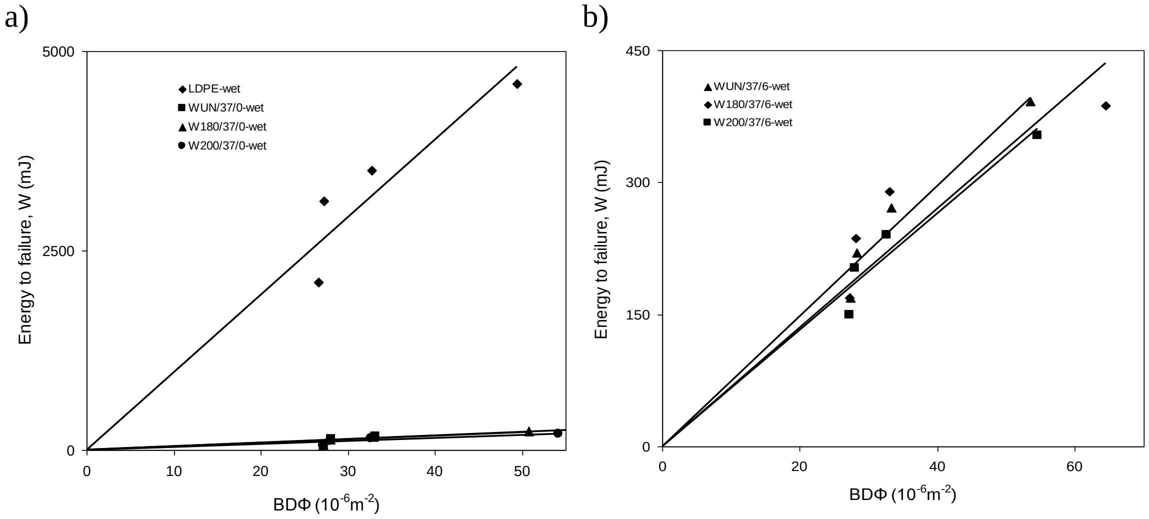


Figure B2: G_c calculations of dry as-moulded and moisture saturated 37 wt% composites containing: a) 0% and b) 6% MAPE

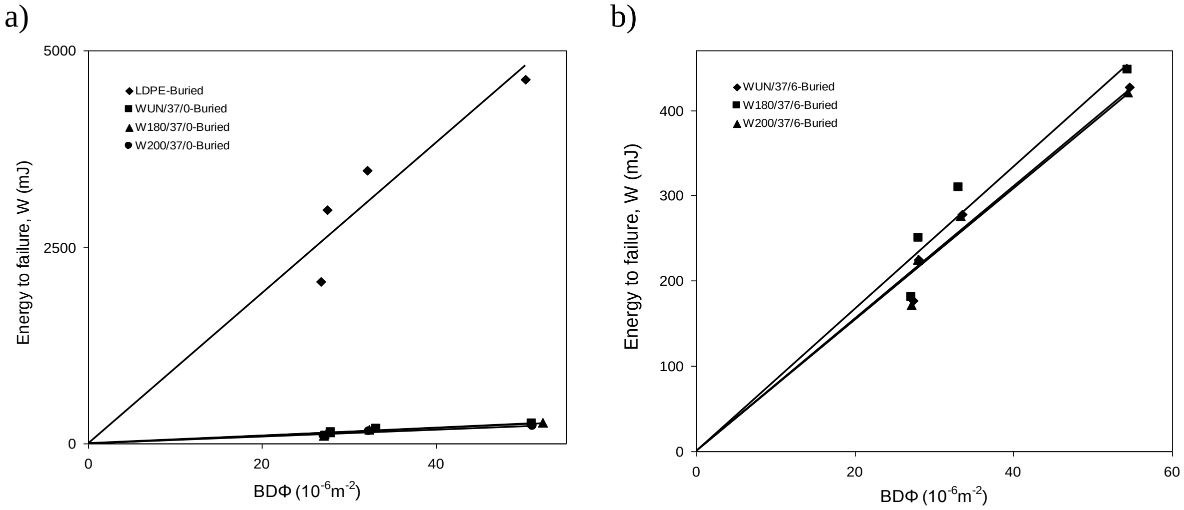


Figure B3: G_c calculations of dry as-moulded and buried 37 wt% composites containing: a) 0% and b) 6% MAPE

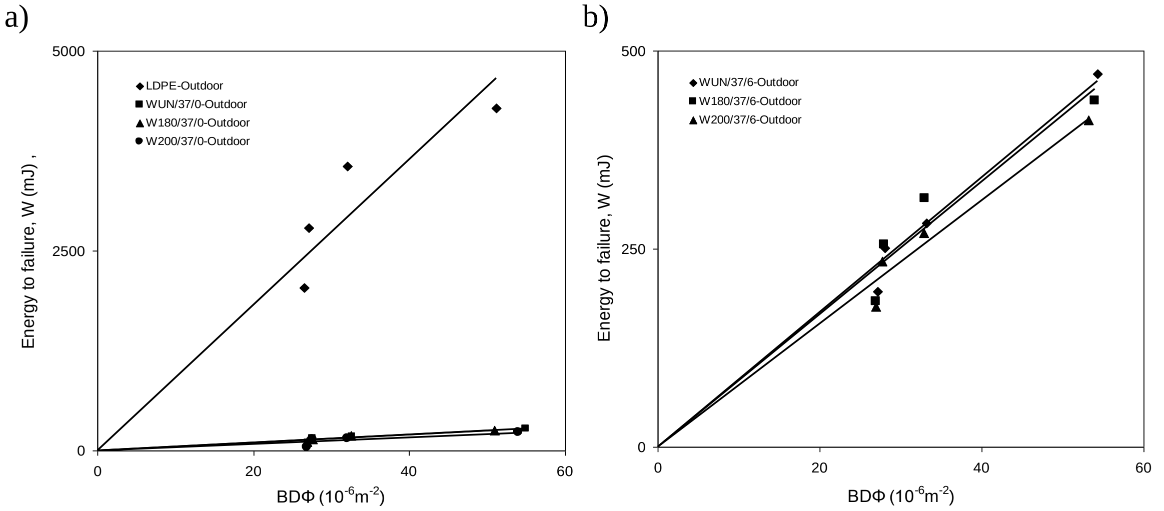


Figure B4: G_c calculations of dry as-moulded and outdoor weathered 37 wt% composites containing a): 0% and b): 6% MAPE

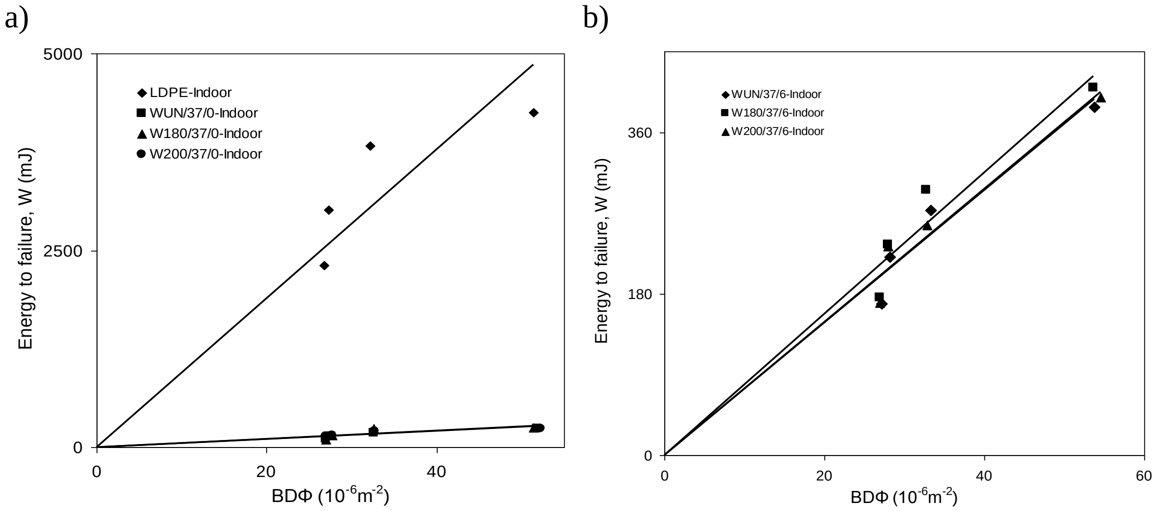


Figure B5: G_c calculations of dry as-moulded and indoor exposed 37 wt% composites containing: a) 0% and b) 6% MAPE

Appendix C: *K_c* calculations of dry as-moulded and conditioned samples

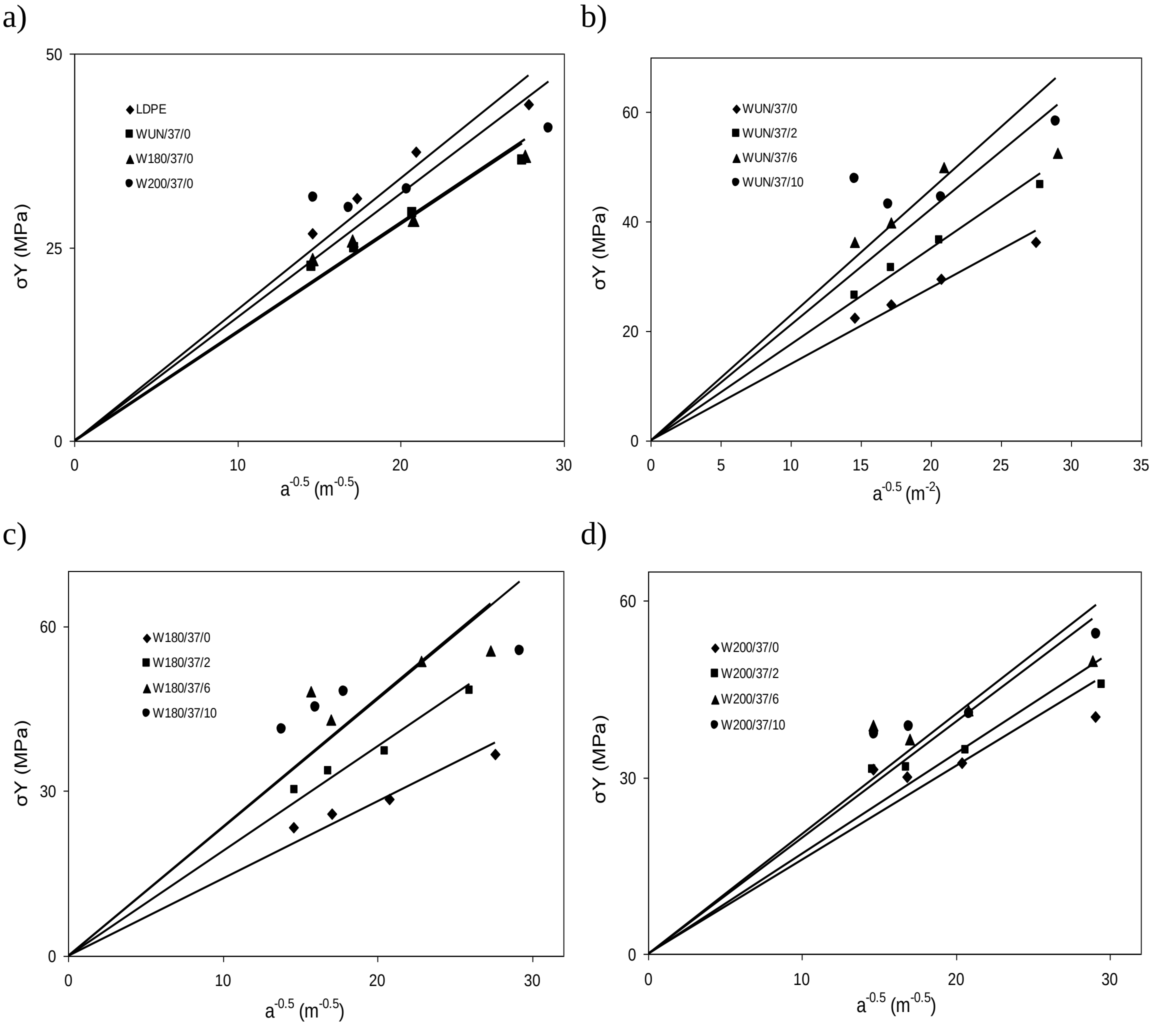


Figure C1: *K_c* calculations of dry as-moulded 37 wt% composites showing the effect of: a) different treatment and b-d) MAPE content

a)

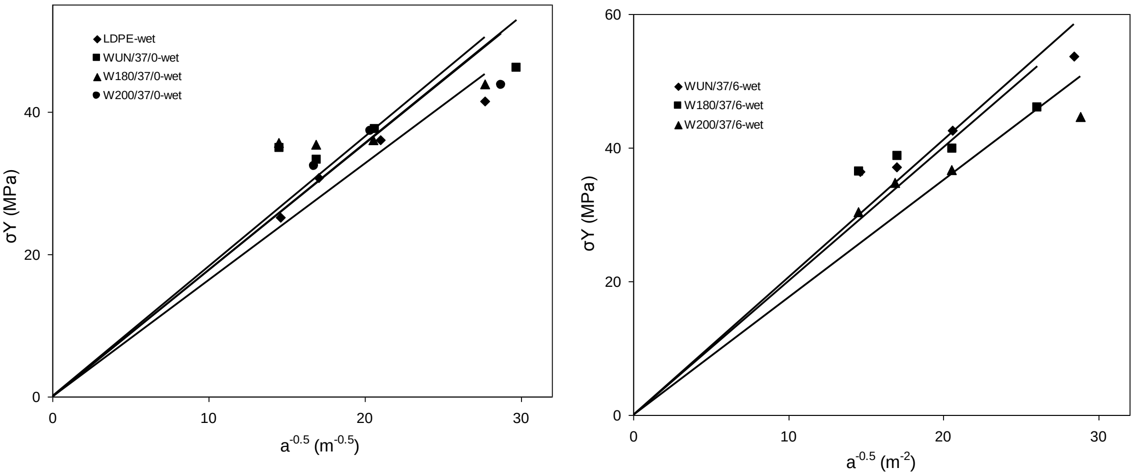


Figure C2: K_c calculations of dry as-moulded and moisture saturated 37 wt% composites containing: a) 0% and b) 6% MAPE

a)

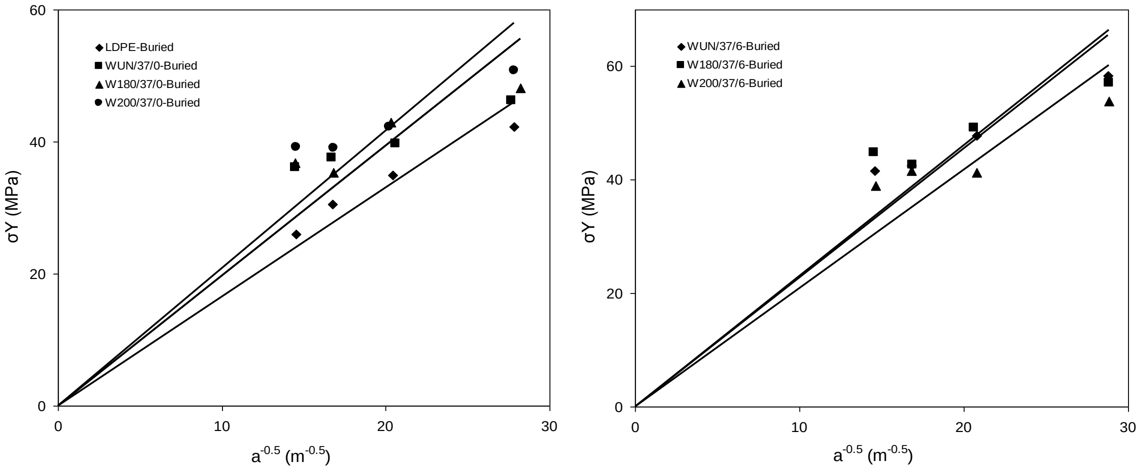


Figure C3: K_c calculations of dry as-moulded and buried 37 wt% composites containing: a) 0% and b) 6% MAPE

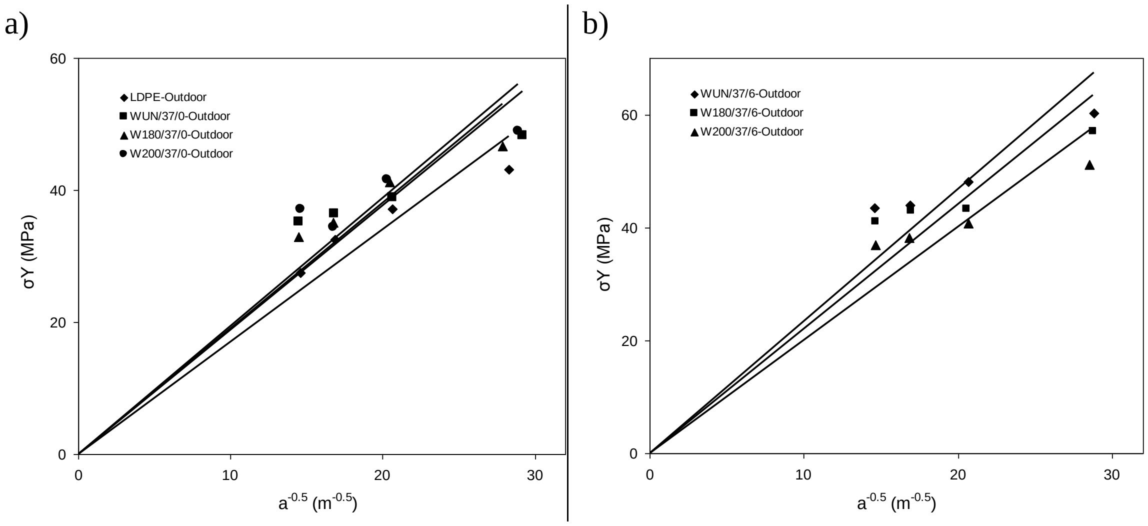


Figure C4: K_c calculations of dry as-moulded and outdoor weathered 37 wt% composites containing: a) 0% and b) 6% MAPE

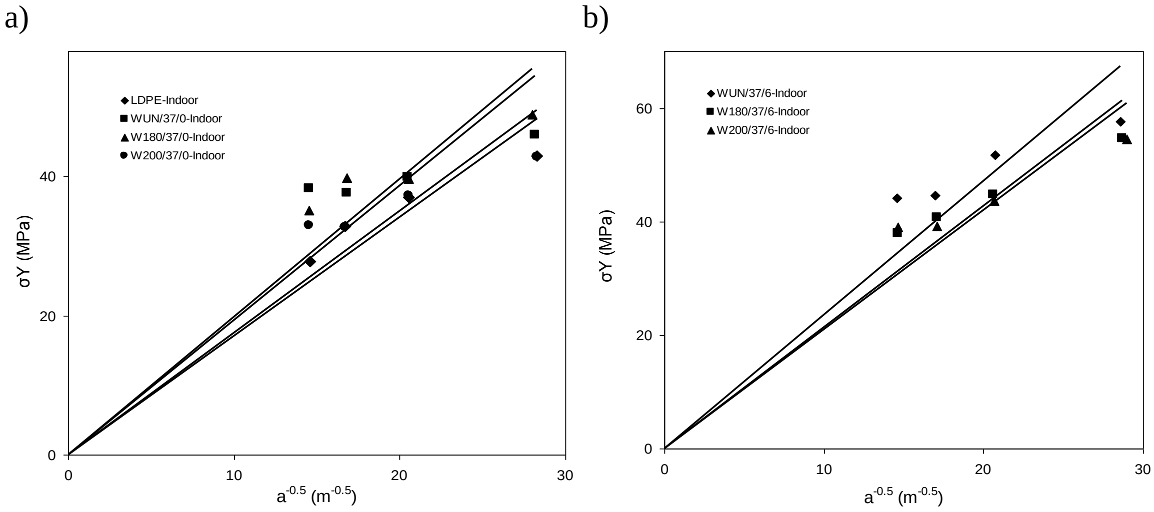


Figure C5: K_c calculations of dry as-moulded and indoor exposed 37 wt% composites containing: a) 0% and b) 6% MAPE

Appendix D: Publications and conference presentations

Appendix D1: Publications

i **Ruth Anayimi Lafia-Araga**, Aziz Hassan, Rosiyah Yahaya, Peter Hornsby, Nor Mas Mira Abd. Rahman and J. Heidarien (2012).Thermal and mechanical properties of treated and untreated red balau saw dust/LDPE composites. **Journal of Reinforced Plastics and Composites. 31(4): 215-224. (ISI, JCR 2011, Q2)**

ii **Ruth Anayimi Lafia-Araga**, Aziz Hassan and Rosiyah Yahaya (2011). Thermal and tensile properties of treated and untreated red balau (*Shorea dipterocarpacea*) fiiled LDPE composites. **Journal of Science and Technology. 2 (3): 17-28. (Scopus)**

iii **Ruth Anayimi Lafia-Araga**, Aziz Hassan and Rosiyah Yahaya and Nor Mas Mira Abd. Rahman, (2012). Water absorption behaviour of heat-treated and untreated Red Balau saw dust-LDPE composites-Its kinetics and effects on mechanical properties. **Iranian Polymer Journal** (under review).

iv **Ruth Anayimi Lafia-Araga**, Aziz Hassan and Rosiyah Yahaya and Nor Mas Mira Abd. Rahman, (2012). Effects of heat treatment of wood flour on the dynamic mechanical and impact properties of red balau/LDPE composites
(In preparation)

v **Ruth Anayimi Lafia-Araga**, Aziz Hassan and Rosiyah Yahaya and Nor Mas Mira Abd. Rahman, (2012). Effects of moisture absorption on the dynamic mechanical and impact properties of untreated and heat-treated red balau/LDPE composites (In preparation)

Appendix D2: Conference presentations

i **Ruth Anayimi Lafia-Araga**, Aziz Hassan, Rosiyah Yahaya and Nor Mas Mira Abd. Rahman (2012). Effect of heat treatment of wood flour on the mechanical properties of outdoor weathered red balau/LDPE composites. Editor; Buhri Arifin, **Universiti Malaysia Terengganu Annual Symposium on Sustainability Science and Management (UMTAS 2012)**, Ri-Yaz Heritage Marina Resort and Spa, Kuala Terengganu, Malaysia. July 9-11.

ii **Ruth Anayimi Lafia-Araga**, Aziz Hassan, Rosiyah Yahaya and Nor Mas Mira Abd. Rahman (2012). Effects of compatibiliser on the mechanical properties of red balau filled LDPE composites. **Asian International conference on Materials, Minerals and Polymers, (MAMMIP 2012),** Vistana Hotel, Penang, Malaysia 23-24 March.

iii. **Ruth Anayimi Lafia-Araga**, Aziz Hassan and Rosiyah Yahaya and Nor Mas Mira Ad. Rahman (2011). Studies on the water absorption behaviour of treated and untreated red balau (*Shorea dipterocarpaceae*) filled LDPE composites. **7th Mathematics and Physical Sciences Graduate Congress (MPSGC2012)**, National University of Singapore, Singapore. 12-14 December,

v **Ruth Anayimi Lafia-Araga**, Aziz Hassan, Rosiyah Yahaya and Nor Mas Mira Abd. Rahman (2011) Effects of water absorption on the mechanical properties of red balau saw dust/LDPE composites. **Malaysia polymer international conference**. Crystal Hotel, Putrajaya, Malaysia, 19-20 October.

vi **Ruth Anayimi Lafia-Araga**, Aziz Hassan and Rosiyah Yahaya

(2010).Thermal and tensile properties of treated and untreated Red Balau (*Shorea dipterocarpaceae*)/LDPE composites **National Seminar on the Applications of Science and Mathematics**, The Zon Regency Hotel, Johor Bahru, Malaysia. December 8-10. 171-177.

Appendix D3: Conference proceedings

i **Ruth Anayimi Lafia-Araga**, Aziz Hassan, Rosiyah Yahaya and Nor Mas Mira Abd. Rahman (2012). Effect of heat treatment of wood flour on the mechanical properties of outdoor weathered red balau/LDPE composites. Editor; Buhri Arifin, **In proceedings of the Universiti Malaysia Terengganu Annual Symposium on Sustainability Science and Management (UMTAS 2012)**, Ri-Yaz Heritage Marina Resort and Spa, Kuala Terengganu, Malaysia. Section 4, pp1050-1056. July 9-11.

ii **Ruth Anayimi Lafia-Araga**, Aziz Hassan, Rosiyah Yahaya and Nor Mas Mira Abd. Rahman (2012). Effects of compatibiliser on the mechanical properties of red balau filled LDPE composites. Editors ; Ahmad Zahirani and Ahmad Azhar. **In Proceedings of the Asian International conference on Materials, Minerals and Polymers, (MAMMIP 2012),** Vistana Hotel, Penang, Malaysia 23-24 March. Part two, pp 427-433.

iii **Ruth Anayimi Lafia-Araga**, Aziz Hassan, Rosiyah Yahaya and Nor Mas Mira Abd. Rahman (2011). Effects of water absorption on the mechanical properties of red balau saw dust/LDPE composites. **In: Proceeding of the Malaysia polymer international conference**. Crystal Hotel, Putrajaya, Malaysia. Pp 204-213, October 19-20.

iv **Ruth Anayimi Lafia-Araga**, Aziz Hassan and Rosiyah Yahaya (2010).Thermal and tensile properties of treated and untreated Red Balau (*Shorea dipterocarpaceae*)/LDPE composites. **In Proceeding of the National Seminar on the Applications of Science and Mathematics**, The Zon Regency Hotel, Johor Bahru, Malaysia. December 8-10. 171-177.