

**ENVIRONMENTAL FRIENDLY POLY (VINYL)  
ALCOHOL/KENAF FIBER COMPOSITES FOR  
AGRICULTURAL APPLICATIONS**

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KUALA LUMPUR**

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ENVIRONMENTAL FRIENDLY POLY (VINYL)  
ALCOHOL/KENAF FIBER COMPOSITES FOR  
AGRICULTURAL APPLICATIONS

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## ABSTRACT

In this study, poly(vinyl alcohol)/kenaf fibre (PVA/KF) based composites were prepared by casting from a mixture of kenaf fibre and aqueous solution of PVA. Certain amounts of urea could be loaded into the composite. The water solubility, release behaviour of urea and thermal stability of PVA/kenaf fibre/urea composites were evaluated. In a wet environment, urea was released from the composites through its dissolution in water. Around 57% of the urea was released from the PVA/KF composites in 24 hours. The composites also lost 25% of their weight after 7 days in water. Controlled amounts of methylene diphenyl diisocyanate (MDI) were added to introduce some crosslinking reactions between the diisocyanate and the –OH groups of the PVA and the fibre to improve the water barrier property of the composites for prolonged water submersion. Laboratory tests were performed on cross-linked and uncross-linked PVA/KF composites to examine the effect of MDI on the properties of the composites. Water-absorption test, morphological analysis, thermal-stability evaluation, and FTIR study were performed. This cross-linked structure was able to slow down the penetration of water and enhance water resistance, as confirmed by the water-absorption test and micrographs. Thermogravimetry analysis data revealed that cross-linking improved the thermal stability of the composites. The degradation of cross-linked and uncross-linked PVA/KF composites in soil was also investigated, where sample pieces of dimension of 20 x 20 x 1 mm were buried 5 cm deep under soil in flower pots. The evidence of degradation could be seen from FTIR spectroscopy. In addition, cracks and fungal growth on the surface of the materials could be clearly observed under the microscope. The rate of degradation could be monitored from the weight loss of the sample, which increased significantly when in wet environment. The observed weight loss of PVA/KF composite was 18% in 7 days and 50% after 28 days, while MDI cross-linked PVA/KF composite exhibited a slower weight loss of 7% in 7 days to 14% after 28 days. The composites were tested in

real life conditions by using them as biodegradable mulches for long bean plants in a small garden plot. The degradation of mulches and the plant growth were carefully observed. Their performance was also compared with the plastic mulch using black polyethylene films available in the market. It was found that the biodegradable mulches were able to protect the seedlings of long beans from moisture loss. As the plants have grown stronger within 30 days, the mulches have biodegraded completely, releasing the fibres as fertilizer to the soil without leaving any undegradable waste for disposal. Hence, they would not pose any risks to the land or biological systems. The composites could have great potential agricultural applications.

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## ABSTRAK

Dalam kajian ini, poli(vinil alkohol)/gentian kenaf (PVA/KF) komposit telah disediakan daripada campuran gentian kenaf dan larutan akueus PVA. Jumlah urea yang tertentu boleh ditambah ke dalam komposit. Kebolehlarutan air, tingkah laku pelepasan urea, sifat-sifat kimia dan kestabilan haba PVA/gentian kenaf/urea komposit telah dinilai. Dalam persekitaran yang basah, urea telah dibebaskan daripada komposit ke dalam air. Kira-kira 57% daripada urea yang telah dibebaskan daripada komposit dalam masa 24 jam. Komposit juga hilang 25% daripada berat mereka selepas 7 hari di dalam air. Jumlah metilena diphenyl diisocyanate (MDI) yang tertentu telah ditambah untuk memperkenalkan silang-seli antara diisocyanate dan kumpulan -OH daripada PVA dan gentian untuk meningkatkan ketahanan air untuk penenggelaman air dalam masa panjang. Ujian makmal telah dilakukan ke atas PVA/KF/MDI komposit untuk mengkaji kesan MDI pada sifat-sifat komposit. Ujian penyerapan air, analisis morfologi, penilaian kestabilan terma, dan kajian FTIR telah dijalankan. Struktur silang dapat melambatkan penembusan air dan meningkatkan ketahanan air, seperti yang disahkan oleh ujian air penyerapan dan mikroskop. Termogravimetri data analisis menunjukkan bahawa penyilangan dapat meningkatkan kestabilan terma komposit. Kajian biodegradasi PVA/KF dan PVA/KF./MDI komposit dalam tanah juga dijalankan, di mana kepingan sampel dengan dimensi 20 x 20 x 1 mm telah dikembumikan sedalam 5 cm di bawah tanah dalam pasu bunga. Bukti degradasi boleh dilihat dari FTIR spektroskopi. Di samping itu, retak dan pertumbuhan kulat pada permukaan bahan-bahan boleh dilihat dengan jelas di bawah mikroskop. Kadar degradasi boleh ditentukan dari peningkatan kehilangan berat sampel yang ketara apabila dalam persekitaran basah. Kehilangan berat sampel PVA/KF komposit adalah 18% dalam 7 hari dan 50% selepas 28 hari, manakala PVA/KF/MDI komposit menunjukkan penurunan berat badan yang lebih rendah sebanyak 7% dalam 7 hari dan 14% selepas 28 hari. Komposit turut diuji dalam

persekitaran sebenar dengan menggunakan mereka sebagai biodegradasi sungkup untuk tanaman kacang panjang di taman kecil. Degradasi sungkup dan penumbuhan tanaman telah diperhatikan dengan teliti. Keputusan juga dibandingkan dengan plastic sungkup dengan menggunakan filem polietilena hitam yang boleh didapati dari pasaran. Keputusan didapati bahawa biodegradasi sungkup dapat melindungi anak benih kacang panjang daripada kehilangan air. Tumbuh-tumbuhan telah membesar dengan lebih kukuh dalam tempoh 30 hari, lepas itu sungkup telah dibiodegradasi dengan sepenuhnya. Gentian kenaf telah dilepaskan sebagai baja di tanah tanpa meninggalkan apa-apa sisa yang tidak akan lupus. Oleh sebab itu, sungkup ini tidak akan menimbulkan apa-apa risiko kepada tanah atau sistem biologi. Komposit ini mempunyai potensi yang besar untuk aplikasi pertanian.

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## LIST OF SYMBOLS AND ABBREVIATIONS

### *Symbols*

|                        |                                   |
|------------------------|-----------------------------------|
| °                      | Degree symbol                     |
| %                      | Per cent                          |
| C                      | Celsius                           |
| cm                     | Centimetre                        |
| <i>D</i>               | Diffusion coefficient             |
| <i>E<sub>a</sub></i>   | Activation energies               |
| g                      | Gram                              |
| kD                     | kilo Dalton                       |
| <i>L</i>               | Thickness                         |
| mg                     | Milligram                         |
| mm                     | Millimetre                        |
| pH                     | power of Hydrogen                 |
| <i>P</i>               | Permeation coefficient            |
| RH                     | Relative humidity                 |
| <i>S</i>               | Sorption coefficient              |
| <i>t</i>               | Time                              |
| <i>T<sub>max</sub></i> | Maximum decomposition temperature |

|               |   |
|---------------|---|
| $\mu\text{m}$ | Micrometre  |
| $w_0$         | Weight of the dried samples before water absorption |
| $w_f$         | Dry weight of the samples after water immersion     |
| $w_t$         | Weight of the wet sample at time $t$                |
| wt. %         | Weight per cent                                     |
| $W_t$         | Water uptake at time $t$                            |
| $W_\infty$    | Weight gain at equilibrium                          |

### ***Abbreviations***

|      |  |
|------|--|
| 3D   | Three Dimensional                          |
| ASTM | American Society for Testing and Materials |
| ATR  | Attenuated total reflection                |
| DAS  | Days of sowing                             |
| DTG  | Derivative Thermogravimetric Analysis      |
| FDA  | Food and Drug Administration               |
| FTIR | Fourier transform infrared spectroscopy    |
| HMMM | Hexamethoxymethylmelamine                  |
| HMTA | Hexamethylenetetramine                     |
| KF   | Kenaf fibre                                |
| LDPE | Low density poly(ethylene)                 |

|       |  |
|-------|--|
| MARDI | Malaysia Agricultural Research and Development Institute |
| MDI   | Methylene diphenyl diisocyanate                          |
| MFC   | Microfibrillated cellulose                               |
| PA    | Phthalic anhydride                                       |
| PBS   | Poly(butylene succinate)                                 |
| PBSA  | Poly(butylene succinate-co-adipate)                      |
| PEG   | Poly(ethylene glycol)                                    |
| PHA   | Poly(hydroxyalkanoates)                                  |
| PHB   | Poly(hydroxybutyrate )                                   |
| PLA   | Poly(lactic acid)  |
| PP    | Poly(propylene)  |
| PVA   | Poly(vinyl alcohol)                                      |
| PVAc  | Poly(vinyl acetate)                                      |
| SEM   | Scanning electron microscopy                             |
| TGA   | Thermogravimetry analysis                                |
| USA   | United States of America                                 |
| USDA  | United States Department of Agriculture                  |

## CHAPTER 1: INTRODUCTION

### 1.1 Introduction

The plastic films produced with biodegradable polymers have found diverse applications in several fields particularly for agriculture sector. Poly(vinyl alcohol) (PVA) is a material that may have role as biodegradable mulches in the future because of their attractive properties such as biodegradability and water soluble characteristic. The positive effect of PVA to the soil had been confirmed in previous study (Chiellini *et al.*, 2003). At the end of life, the material can be incorporated into the soil, where the soil microorganisms would transform them into CO<sub>2</sub>, humus, water and so on. They will not contaminate the environment and can be ploughed in the field, resulting a significant savings in labour and disposal cost. In order to reduce the overall cost of mulches, previous research has been devoted towards the utilization of natural fibres and agricultural residues which are readily available from our environment.

Among our renewable resources in the environment, kenaf is one of the natural fibres which are well known for its economic and ecological advantages (Akil *et al.*, 2011). Kenaf is a high yielding crop that has been cultivated in more than 20 countries, including China, India, Thailand and Vietnam (Monti & Alexopoulou, 2013). Since 1960, United States Department of Agriculture (USDA) has identified kenaf as the most promising of a wide variety of annual plants for paper making. Owing to the functionality of PVA, kenaf fibre (KF) is suitable to combine with PVA to form PVA/KF biodegradable mulches. Besides that, the blending of PVA and kenaf can be manipulated easily in water solution and applied directly on the field. These kenaf fibres could later serve as fertilizer for plants upon the leaching of PVA. In order to assure the permanency of biodegradable mulches on soil, PVA/KF was treated with methylene diphenyl

diisocyanate (MDI) to introduce certain cross-links in the composites. These cross-links could be formed between the active isocyanate in MDI and hydroxyl groups in PVA. Efforts were made by USDA laboratories and the University of Pisa in developing mulches from PVA and lignocellulose fibres with suitable cross-linkers (Cinelli *et al.*, 2003; Imam *et al.*, 2005).

## **1.2 Problem Statements**

The old traditional practice of mulching method is by using dead leaves, residues and straw to cover the soil. These natural mulches can offer all the benefits of mulches if they are properly used. They help in maintaining soil organic matter, provide food and shelter for earthworms and other soil biota (Kasirajan & Ngouajio, 2012). However, these natural mulches are not very effective mulching method because they could be easily carried away by rain and wind. Besides that, their quality is inconsistent, depending on the material derived from animal or plants. The application of natural mulches is found to reduce the soil temperature and evaporation but do not invariably cause higher yields (Kasirajan & Ngouajio, 2012). Furthermore, those natural mulches that contain weed seeds may deplete the seedbed nitrogen due to their high Carbon/Nitrogen ratio, subsequently immobilizing the soil nitrogen as they decompose. Other disadvantages include their limited quantity and the needs of high labour force for spreading in field. This indicates that the natural straw mulches could not be used effectively in crop production. Therefore, plastic mulches have been developed to overcome such problems.

The plastic films, usually polyethylene (PE) was first introduced and used as mulches in the late 1950s. The widespread use of polyethylene mulches is due to their high durability, flexibility, excellent chemical resistance, easy process ability and low in cost (Kasirajan & Ngouajio, 2012; Moreno & Moreno, 2008). PE films help in

accelerating plant growth by increasing the soil temperature and stabilizing the soil moisture. Black polyethylene mulches in particular can reduce the weed emergence effectively. Since then, they have attracted a good deal of attention and have played a major role in the production of crops. Statistic from Applied Market Information (AMI) estimated that the European market uses about 500,000 tons/year in agricultural films, in which 25% are mulch films (Andrady, 2003). It is estimated that 1 million tons of mulch films is used worldwide every year in agriculture (Halley *et al.*, 2001). In 1999, over 30 million acres of agricultural land, in which 185,000 acres in the USA alone, were covered with plastic mulches and the number is increasing. In 2004, the data recorded 130,000 tons of mulch films was used (Warnick *et al.*, 2006).

Based on the statistics above, such petroleum-based plastic mulches have caused a considerable waste removal and disposal problem after use. Removal of these plastic mulches still requires hand labour which is very time-consuming, about 16h/ha despite the use of machine (Kasirajan & Ngouajio, 2012; McCraw & Motes, 1991). Landfilling has been a common way for disposing the used plastic films. According to the survey conducted at Pennsylvania, 66% and 27% of farmers disposed the used plastic films by on-site burning and landfilling, respectively (Lamont, 2004). Such plastics films do not decompose or degrade and will persist in the environment, reducing the aesthetic qualities of environment. Moreover, the local availability of landfill space has been an issue, and this may increase the disposal expense of farmers.

Due to the high disposal expense for landfilling, some farmers consider on-site burning as an option to discard the plastic wastes. The on-site burning of plastic mulches creates air pollution problem. The incomplete combustion of plastic films or combustion conducted at low temperature will generate toxic particles, so-called Dioxins which are known as endocrine disruptors and carcinogens (Levitan & Barro, 2003). The exposure to such toxic particles and compounds increase the risk of stroke, lung cancer, asthma,

respiratory disease, deteriorating our health and harming lives (Dockery & Pope, 1994; Hong *et al.*, 2002).

Some environmentalists have suggested that recycling may be a greener way for plastic removal and disposal. However, these relatively low prices of plastic materials do not encourage recycling and retrieval. In fact, plastic films with more than 5% contaminants by weight are not accepted for recycling (Clarke, 1996). Generally, there are 40-50% of contaminants appear in agricultural plastics, including fertilizers, pesticides, soil, debris, silage juice water, moist vegetation and additives. For uncleaned films, the contaminants (moisture and soil content) in agricultural plastics are 36%, making them as undesirable recyclable feed stocks (Brooks, 1996). According to Kotrba (2008), only 1% from 95 million lb. of agricultural plastic films and nursery containers were recycled between 1992 and 2008, clearly showing a very low amount of agricultural plastic films were recycled due to the high level of contaminations. Attempts to recycle the plastic films have been hampered by practical difficulties and high recycling costs.

Since large amounts of plastic films are involved, it is urgency to find an alternative to PE films. Paper mulches have been used in agriculture since 1941. However, the paper mulches are not effective in providing protection because they suffer rapid degradation after a few weeks of exposure to soil, rain and wind (Anderson *et al.*, 1995; Shogren, 1999, 2000). Although people have considered using a thicker paper or mats to increase their lifespan in soil, they are not economical in practice. Therefore, researchers worldwide are interested in developing plastic films that would self-degrade under suitable conditions. To reduce the cost of biodegradable mulches, some of the researchers have considered adding renewable resources such as natural fibres and agro-waste to form composite mulches. The use of such biodegradable mulches may be an alternative to petroleum-based mulches, helping the farmers to reduce labour, disposal and environmental cost in removing the plastic wastes after use.

### **1.3 Research Objectives**

The main aims of this research are to develop a novel biodegradable composite from poly(vinyl alcohol) and kenaf fibre for potential agriculture application. In order to achieve it, the following objectives are pursued:

1. To fabricate poly(vinyl alcohol)/kenaf fibre (PVA/KF) composites via solution casting method
2. To study the releasing properties of urea from PVA/KF composites for the use as fertilizer carrier
3. To investigate the effect of cross-linkings in PVA/KF composites.
4. To study the biodegradation behaviour of PVA/KF composites
5. To evaluate the mulching effect of PVA/KF composites through field trial.



## CHAPTER 2: LITERATURE REVIEW

### 2.1 Introduction

Natural fibres have attracted considerable attentions due to their renewability and availability. They have been considered as alternative materials to replace the inorganic fillers and fibres due to serious environmental issues. Natural fibres are naturally occurring polymers in our environment which appear pervasively in grasses, leaves, stalks of plants or even animals. In the composite industry, they are usually referred to as plant fibres and further categorized into wood or non-wood sources. They are also referred to as lignocellulose fibres since lignin and cellulose are the main components in their structure.

Besides natural fibres, agro-wastes such as rice husks, wastes from rubber plants, cocoa cultivation, sugar cane cultivation and oil palm cultivation have also been considered as filler in the composites. In Malaysia, oil palm industry is the biggest biomass producer. It was estimated 17 million tons of empty fruit bunches waste were produced annually. The wastes from palm oil (excess fibre, empty fruit bunches and shell) have been utilized on-site to provide energy for the mill and electricity exports to the grid. For low-pressure systems with an assumed conversion rate of 2.5 kg of palm oil waste per kWh, potentially 7,000 GWh could be generated (Chuah *et al.*, 2006). Table 2.1 presents the estimation of biomass energy productivity, biomass production and utilization in Malaysia. The Malaysian government strongly promotes the uses of palm diesel as a replacement for fossil fuel. The biofuel policy framework has been drafted by the government to encourage the use of biofuels.

Table 2.1: Estimates of the energy productivity, biomass production and utilization (Chuah *et al.*, 2006).

| Crops/<br>Activities | Energy<br>productivity<br>(boe/ha/year) | Current<br>amount<br>used<br>for<br>energy<br>purposes | annual<br>used<br>for | Current<br>potential<br>of<br>biomass<br>(million boe) | annual<br>of<br>energy<br>utilised |
|----------------------|---|--|-----------------------|--|------------------------------------|
| Oil palms            | 88.7                                    | Fruit shells   | 23.609                | Pruned fronds  | 77.665                             |
|                      |   | Fruit fibres   | 13.630                | Empty fruit bunches (EFB)                              | 11.444                             |
|                      |   |  |                       | Effluents  | 2.928                              |
|                      |   | Effluents  | 0.022                 | Replanting wastes                                      | 12.94                              |
| Rubber trees         | 29.5                                    | Wood   | 4.967                 | Wood   | 3.707                              |
|                      |   |  |                       | Effluents  | 0.210                              |
| Paddy plants         | 11.54                                   |  |                       | Rice husks   | 1.025                              |
|                      |   |  |                       | Rice straws  | 2.541                              |
| Coconut trees        | 28.21                                   | Fronds   | 1.578                 | Fronds   | 0.164                              |
|                      |   | Shells   | 0.785                 |  |                                    |
| Cocoa trees          | 80.33                                   | N.A.   | N.A.                  | Pruning wastes   | 16.850                             |
|                      |   |  |                       | Pod husks  | 0.085                              |
|                      |   |  |                       | Replanting wastes                                      | 0.630                              |
| Sugarcane            | 54.9                                    | Bagasse  | 0.421                 | Leaves and tops  | 0.298                              |
| Logging              | -                                       | -  |                       | Residues   | 19.060                             |
| Timber processing    | -                                       | Sawdust & waste  | 3.733                 | Tree bark and sawdust                                  | 1.0                                |

Apart from being used as sources of energy, the empty fruit bunches have found alternative uses such as fibreboard in furniture making, eventually reducing the waste at palm oil mills. In the making of nanocomposites, previous studies have also shown that nanocellulose could be extracted from agro-wastes and used as nano-reinforcement in various polymer matrices (Rosa *et al.*, 2012). Promoting the usage of agro-wastes in composites may help to solve part of the global agriculture refuse problem.

Huge loads of wastes could be converted into affordable value-added products which allow them to be more valuable for wider applications. Besides, they are renewable, cheap, completely or partially recyclable, and biodegradable. In automotive industries, the variety of bio-based automotive parts currently in production is astonishing. For example, DaimlerChrysler is the biggest proponent with up to 50 components in its European vehicles being produced from bio-based materials.

The properties of natural fibres are closely related to the nature of cellulose and its crystallinity properties. For example, fibres with higher cellulose content possess impressive specific mechanical properties but also tend to be more flammable than those with higher hemicellulose content. The mechanical properties of some common fibres are listed in Table 2.2. Fibres with higher hemicellulose content tend to absorb more moisture and char formation is generally better with fibres that have higher lignin content as they experience degradation at relatively lower temperatures (Azwa *et al.*, 2013; Dittenber & GangaRao, 2012). For reinforcement purposes, cellulose is extracted from the natural fibres and used for the production of composites due to its hierarchical structure and semicrystalline nature (Dufresne, 2013).

Table 2.2: Mechanical properties of some natural fibres (Célineo *et al.*, 2014).

| <b>Natural fibres</b> | <b>Density (g/cm<sup>3</sup>)</b> | <b>Young's modulus (GPa)</b> | <b>Tensile strength (MPa)</b> | <b>Elongation at break (%)</b> |
|-----------------------|-----------------------------------|------------------------------|-------------------------------|--------------------------------|
| Flax                  | 1.54                              | 27.5 – 85                    | 345 – 2000                    | 1 – 4                          |
| Ramie                 | 1.5 – 1.56                        | 27 – 128                     | 400 – 1000                    | 1.2 – 3.8                      |
| Hemp                  | 1.47                              | 17 – 70                      | 368 – 800                     | 1.6                            |
| Jute                  | 1.44                              | 10 – 30                      | 393 – 773                     | 1.5 – 1.8                      |
| Sisal                 | 1.45 – 1.5                        | 9 – 22                       | 350 – 700                     | 2 – 7                          |
| Coconut               | 1.15                              | 4 – 6                        | 131 – 175                     | 15 – 40                        |
| Cotton                | 1.5 – 1.6                         | 5.5 – 12.6                   | 287 - 597                     | 7 - 8                          |
| Kenaf                 | 1.2                               | 14 – 53                      | 240 – 930                     | 1.6                            |
| Bamboo                | 0.6 – 1.1                         | 11 – 17                      | 140 – 230                     | -                              |

In spite of their advantages, the major challenge of natural fibres is the difficulty manufacturing them into the desired form or film because they cannot be melted or

dissolved in a common solvent due to the strong intermolecular hydrogen bonding, high degree of polymerization, and high crystallinity degree (Abdulkhani *et al.*, 2013). In conjunction with the completely green environmental policy, it is preferable to add the natural fibres in biodegradable polymers such as polyvinyl alcohol (PVA) to produce eco-sustainable composites. PVA is a common and well-known polymer that possesses salient features such as water solubility, ease-of-use, film-forming property and biodegradability. The global production of PVA is approximately 650,000 tons per year (Lin *et al.*, 2014).

Unlike most of the polymers, PVA cannot undergo polymerization from its own monomer, but through poly(vinyl acetate) (PVAc) due to the instability of vinyl monomer. Hence, PVA can only be obtained through a saponification process from PVAc or alcoholysis by reacting PVAc with methanol (Goswani *et al.*, 2004; Odian, 2004). PVA can be hydrolyzed from PVAc into two different grades, fully or partially hydrolyzed based on their applications. The degree of hydrolysis indicates the number of residual acetate groups that are present in the polymer in which saponification or alcoholysis has not taken place (Goldschmidt & Streitberger, 2003). The degree of hydrolysis will eventually affect the properties of PVA including its solubility (Rolando, 1998).

The PVA/natural fibre composites have been well developed and documented. Although much work has been carried out on such a broad topic, the information is scattered in nature. This paper reviews PVA/natural fibres composites and their nanocomposites. The properties, processing techniques, biodegradability, applications of the composites, and future works will also be discussed. It is hoped that the researchers can continue to explore the new potentialities for such superior composites and increase their applications as a way to achieve long term environmental sustainability.

## 2.2 Natural fibre based composites

The performance of the natural fibre based composites relies on several factors including fibres loading, length, types, orientation and chemical nature. Kalapakdee and Amornsakchai (2014) studied the mechanical properties of Santoprene/pineapple leaf fibres composite with respect to fibres content and orientation, suggesting the composites exhibited clear anisotropy in mechanical properties. It was found that modulus at 10% strain and tear strength in the longitudinal direction increased significantly with increasing fibre contents, while tensile strength and elongation at break decreased after the addition of fibres. However, the effect of fibre content was less significant in the transverse direction. Similar result was also reported regarding the effect of hemp fibre content and anisotropy on the tensile properties of the composite. The tensile strength of composites with fibres in the perpendicular direction was 20-40% lower than those composites with fibres in parallel direction, suggesting the failure of fibres to act as load bearing elements when arranged in perpendicular direction (Hajnalka *et al.*, 2008).

The effect of fibres types, on the mechanical properties of polypropylene (PP) based composites was also compared in previous study (Kim *et al.*, 2008). It was observed that the tensile strength of PP/wood fibre composites decreased with increasing of wood fibre loading. However, the tensile strength of PP/cotton fibre composites displayed an opposite behaviour. This can be explained by the entanglement of the cotton fibres in the composite as confirmed by the scanning electron microscopy (SEM) micrographs. Study performed by Mwaikambo and Bisanda (1999) on polyester/cotton fabric composites demonstrated different results in comparison with Kim *et al.* (2008) whereby the composite tensile strength decreased with increasing cotton fabric content. They believed that this observation can be attributed to the increment of void content with increasing fabric volume fraction.

The addition of natural fibres as reinforcement materials in polymer composites also exhibits several shortcomings. Incompatibility between fibres and polymers matrices, aggregation during processing, poor moisture resistance and limited processing temperatures are some of the major barriers for the applications of natural fibres (Azwa *et al.*, 2013). Awal *et al.* (2015) fabricated poly(lactic acid) (PLA)/wood powder composite by using extrusion technique. The addition of 20 wt% of wood powder slightly improved tensile strength, tensile modulus, notched impact strength, flexural modulus as well as thermal stability but decreased the flexural strength and unnotched impact strength of the composite. However, the addition of 1.3% of bioadimide (bio-additive) could improve the processability of the composite and fibres/matrix adhesion, subsequently enhanced all the mechanical properties of the composites.

Yu *et al.* (2014) revealed the incompatibility between fibres and polymers matrices could be overcome by addition of compatibilizers. The mechanical properties of the ramie fibres reinforced PLA were improved with the presence of 3% maleic anhydride. Tensile strength, flexural strength and impact strength were rising from 59.3 to 64.3 MPa, 105.2 to 112.4 MPa and 5.0 to 7.1 kJ/m<sup>2</sup>, respectively. This improvement was also related to the better interface adhesion between the fibres and the matrix which facilitated more stress transfer through bonding to the fibres.

Other disadvantage of natural fibres is their poor moisture resistance property which can influence the overall properties of composite and eventually result in the failure of fabricating composite. Bayerl *et al.* (2014) revealed the biodegradability of the composite was promoted by the flax fibres. They act as the channels to distribute water and microorganisms into the composite, enlarging the polymer composite for potential hydrolysis reaction and deterioration by microorganisms.

Many works have addressed the poor moisture resistant of PVA/natural fibres and chemical modifications or applications of certain coatings were suggested to reduce their

moisture uptake. As work continues to improve the composites' properties, it is important to evaluate their environmental impact since chemical reagents are involved. Besides, high initial cost for some methods should be considered.

### 2.3 Poly(vinyl alcohol) based composites

PVA is often blended with starch because of the low mechanical properties and poor processability of starch. This makes PVA/starch composites as one of the most popular biodegradable polymers which are widely used in packaging and agricultural applications. In view of the PVA/starch composites mechanical properties, the tensile strength of the composite also decreased with increasing starch content (Chao *et al.*, 2012). Similar result was also reported by Ramaraj (2007), in which the tensile strength and elongation at break decreased whereas the tensile modulus increased with increasing starch content, due to stiffening effect of starch.

Thermogravimetry analysis (TGA) was exerted to provide a clear description about the thermal stability of PVA/cassava starch blending. It was found that blending of 40 and 50 wt% PVA with cassava starch exhibited enhancement in thermal stability in terms of activation energies ( $E_a$ ), suggesting high loading of PVA with cassava starch was synergistically compatible which contributes towards a higher energy stability hierarchy (Rahman *et al.*, 2010; Lee *et al.*, 2011). Moreover, stable carbonaceous residues were formed during heating process at temperature above 600°C, thus blending PVA/starch/glycerol is favourable to produce good thermal stability biodegradable compounds. Unfortunately, this thermal resistance effect was insignificant with the increment of starch content (Rahman *et al.*, 2010).

In addition, the PVA/starch/glycerol blends also exhibited a potential controlled release property which makes it an ideal carrier material for fertilizer. Yip *et al.* (2013)

analysed the urea released by using FTIR after immersed the sample in the water solution for 1 hour. It was found that the encapsulated urea was released in controlled manner through diffusion from the swollen polymer matrix into a damp environment. This observation was supported by the FTIR data whereby the strong peak of amide groups from urea compound was detected in the filtered water solution. However, Yip *et al.* (2013) failed to measure the rate of urea released and the percentage of urea released in a particular time frame. This is relatively important in order to estimate the service life of such composite as controlled release fertilizer.

Another similar report on PVA based composite as urea release carrier was reported by Niu and Li (2012). Niu and Li (2012) prepared starch-g- PVAc membrane to encapsulate urea. Such membrane has a core-shell structure, in which the hydrophilic starch as core and hydrophobic PVAc grafts as shell. These membrane exhibited low swell-ability and hence release urea in slow manner. The amount of urea release did not exceed 15 wt% on the second day and release about 78 wt% after 30 days. The fabricated PVA based composite fulfilled the requirements as carrier for slow release of fertilizers according to the Committee of European Normalization.

Biodegradability of PVA based materials is an essential aspect to be considered especially in application as mulch or fertilizer carrier materials. However, Chiellini *et al.* (2003) have pointed out that PVA could only be biodegraded by certain microorganisms. Therefore, PVA is blended with other biodegradable polymers to enhance its biodegradability (Jayasekara *et al.*, 2004). Maiti *et al.* (2013) blended PVA with starch and conducted biodegradation study on this composite in standard compost. The microorganism species were determined from this study. After 30 days of degradation, *Aspergillus flavus* and *Penicillium daleae* were identified to be responsible for the degradation of PVA/starch films. This showed the potential of PVA/starch blends as



packaging films since these fungi can be used for degrading the films after disposal (Maiti *et al.*, 2013).

PVA/xylan composite films were produced with addition of citric acid which acts as a both plasticizer and cross-linking agent. Xylan is the main component of hemicellulose containing abundance of hydroxyl groups. PVA was anticipated to have good compatibility with xylan. With the high loading of xylan (50%) as key drivers, the composite was more susceptible to microbial attack (Wang *et al.*, 2014). There is another biodegradable polymer developed by blending the PVA with corn gluten, yielding flexible films. Unfortunately, the mixture was immiscible for this composition (Corradini *et al.*, 2011).

#### **2.4 Poly(vinyl alcohol)/natural fibres composites**

The combination of PVA with natural fibres forms eco-sustainable composites. In particular, their nanocomposites have gained huge popularity around the globe due to their unique microstructure and superior properties. The interaction or compatibility of reinforcement-matrix, the dispersion of reinforcement in matrix and the properties of matrix and reinforcement are the 4 key factors that can affect the strength of polymer composites. The presence of –OH groups in natural fibres and their hydrophilic nature are compatible with PVA. Good interaction between fibres and PVA has been witnessed in many micrographs, resulting in good composite properties and satisfactory performance. The PVA/natural fibres composites processing methods and applications in various fields have been discussed. However, some properties and processing limitations of PVA/natural fibres composites have been pointed out. Fortunately, these limitations may be solved by a variety of approaches and techniques which will be discussed in detail later.

With these and many more specific treatments and modifications, these composites would gain a renewed interest as advanced materials in future.

Basically, the natural fibres are collected, dried, ground and sieved to obtain the desired size prior to processing. The common processing methods to prepare natural fibres based composites are extrusion or injection moulding (Cinelli *et al.*, 2006a). One of the disadvantages of natural fibres is their low thermal stability. It is preferred to process the natural fibres based composites at low temperature (usually limited to 200°C) with shorter processing time (Lee *et al.*, 2011). At lower processing temperatures, the degradation of natural fibres can be avoided. Cinelli *et al.* (2006a) found that compounding of PVA/corn fibres could be achieved at low temperatures (<160-170°C) in the presence of a plasticizer. In addition, the fibres decomposition could be avoided during processing. Addition of high loading plasticizer reduced the melt viscosity during extrusion indicated by the reduction of die pressure. Lower melt viscosity implies easier processing of composites.

The selected plasticizers reported by Cinelli *et al.* (2006a) were polyethylene glycol (PEG), pentaerythritol and glycerol. The utilization of plasticizer yields uniform and flexible PVA/corn fibres composites. PEG and glycerol have been commonly used in PVA. The addition of PEG plasticizer depressed the melting temperature, elastic modulus and also tensile strength of composites, while enhancing the elongation at break, thus inducing plastic behaviour to the composites (Laboulfie *et al.*, 2013). On the other hand, glycerol content in the PVA was important to predict the ultimate tensile strength of PVA based composites (Pang *et al.*, 2013). Glycerol was found to have more profound effect on the overall mechanical properties of the composite, suggesting that the glycerol is an effective plasticizer than the others.

This hypothesis was further validated by the determination of moisture effect on the tensile properties of the composite. In this case, the plasticization effect of water was

observed. Result elucidated the trend in the tensile properties of the composites was consistent with water acting as a plasticizer. Increasing the relative humidity from 25% to 50% decreased the strength and modulus but enhanced the elongation at break. However, the elongation at break was reduced slightly when the relative humidity was up to 80% for composite containing higher ratio of glycerol, due to the weakening of the matrix upon water absorption. Cinelli *et al.* (2006a) also pointed out that water is a better plasticizer than pentaerythritol because water might have a plasticization effect on the composites.

Some investigators have added both urea and glycerol as plasticizers in PVA/lignocellulose fibre based composites for mulch films application. TGA from this study showed a slight reduction of the onset temperature, illustrating the reduction of thermal stability due to initial decomposition of low molecular weight components such as urea and glycerol. In biodegradation study, Imam *et al.* (2005) observed the amount of CO<sub>2</sub> released from the glycerol and urea had exceeded the value corresponding to 100% mineralization, indicating that these additives could be the potential carbon and nitrogen sources for the microorganisms which enhanced the mineralization capacity of the soil. Similar findings were also reported by Cinelli *et al.* (2003).

Undoubtedly, the use of plasticizers in polymer composite offers a number of advantages to the polymers while at the same time sacrifices some of the properties. Plasticizer selection must be based on its efficiency in terms of necessary amount, compatibility with polymer and its permanency. Due to concerns about environmental protection, natural based plasticizers are believed to be the preference for the future. In fact, various types of natural based plasticizers have been well developed and studied.

### 2.4.1 Chemical and physical modifications of PVA/natural fibres composites

Generally PVA is compatible with natural fibres, owing to its ability to form hydrogen bonds between the hydroxyl groups in both PVA and the cellulose in the fibres. Cinelli *et al.* (2006a) found an increment in Young's modulus but a reduction in both the elongation and maximum yield force in the composites after blending the corn fibres with PVA. This result is mainly ascribed to the low flexibility of corn fibres. Research work from Toh *et al.* (2011) reported holes and embedded particles with obvious deformable phases (Figure 2.1b) appearing in the PVA/sago pith (20/80 wt %), highlighting the phase separation between PVA and sago pith under inappropriate composition. However, they have suggested that good compatibility exist between these two components as the texture was successfully improved compared to the pure sago pith (Figure 2.1a).

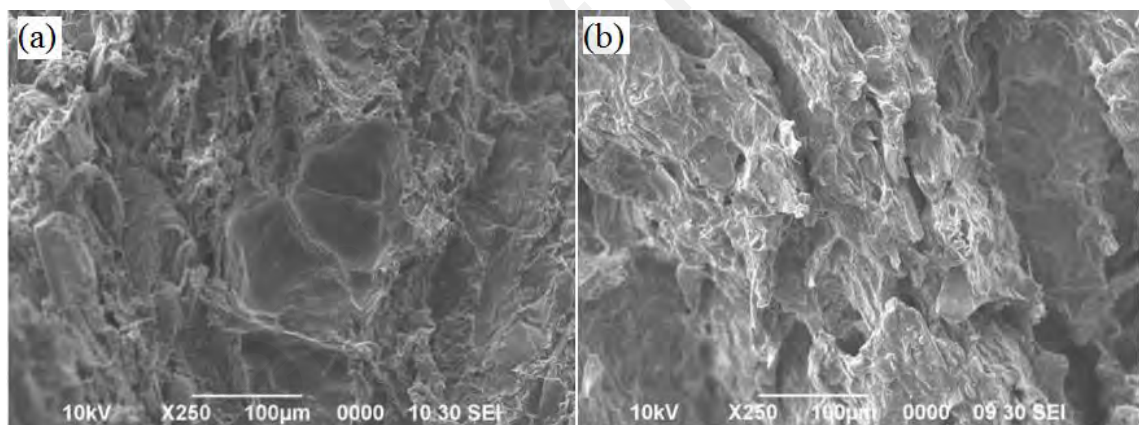


Figure 2.1: SEM images of the fracture surfaces of (a) sago pith and (b) PVA/sago pith (20/80 wt%) (Toh *et al.*, 2011).

The bonding ability between matrix and reinforcing phase is one of the key factors deciding the properties of a composite material (Mathew *et al.*, 2005). The composites based on PVA and cellulose is likely to produce materials with excellent mechanical properties since both materials are polar polymer. However, direct incorporation of pristine cellulose fibres into a PVA matrix may not obtain a composite with good mechanical properties, in spite of their compatibility. This is because most of the hydroxyl

groups in cellulose molecules have already formed either intra- or inter-molecular hydrogen bonds within each other. Hence, they are not able to form strong interaction with PVA, leading to unsatisfactory mechanical performance of the composites (Ozaki *et al.*, 2005).

One of the possible approaches to further strengthen the properties of composite is cross-linking both materials with desired molecules to increase their compatibility. Cross-linking is recognized as a phenomenon where a multifunctional compound is reacted to the hydroxyl groups in PVA, forming the network via chemical bonds. The effect of cross-linking agents has been reported extensively.

The PVA/tropical fruit waste composites were cross-linked with 1.5 wt % of either glutaraldehyde or hexamethylenetetramine (HMTA) cross-linker. HMTA appeared to be a better cross-linker than glutaraldehyde, due to its crosslinking effect to the properties of composites. A slight improvement on the tensile strength, Young's modulus, water resistance and moisture barrier properties were witnessed. However, both HMTA and glutaraldehyde cross-linked composites showed comparable weight loss and lower than non-cross-linked composites (Ooi *et al.*, 2012).

Considering the toxicity of glutaraldehyde, glyoxal as an alternative cross-linker was applied to PVA/MFC composites for environmentally positive purposes. The formation of cross-linking through the acetal linkages increased the glass transition temperature while reducing the melting temperature and crystallinity of PVA in the composites, due to the restricted segmental motion (Qiu & Netravali, 2012). Another environmentally friendly cross-linker is Borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) which is recognized as a non-toxic food additive, which has been successfully used in PVA/nanocellulose composites (Han *et al.*, 2013; Spoljaric *et al.*, 2014). The addition of small amounts of borax led to a remarkable increase in viscoelasticity and compressive strength of polymeric system due to the formation of complexes between borate ions and hydroxyl

functional groups of PVA. Moreover, the highly-crystalline nanocellulose not only tangled with PVA chains through numerous hydrogen bonds, but also formed chemically cross-linked complexes with borate ions as well, enhancing the stiffness and strength of hydrogel (Han *et al.*, 2013; Spoljaric *et al.*, 2014). These crosslinking reactions associated with the effect of microfibrils have successfully strengthened the mechanical and thermal properties of the composites as well as to make the PVA partially water-insoluble (Qiu & Netravali, 2012).

Ozaki *et al.* (2005) have exhibited the possibility of phthalic anhydride (PA) as a functional cross-linking agent in PVA/waste wood composites. The water hydrolyzed PA formed dicarboxylic acid which can participate with both carboxyl groups in the crosslinking reaction. The resulting composites displayed good mechanical properties and higher durability than solid wood even after 180 days of soil burial. The results were in opposition with the previous research that stated cross-linking retarded the composite degradation. In addition, the composites showed peculiar degradation behaviour where the composites that contain higher amounts of PA suffered higher weight loss. This observation was related to the fungi which developed better with acetate compared to glucose as a carbon source.

On the other hand, some researchers applied chemical treatment on the natural fibres as an alternative approach to improve the mechanical properties of the composites (Mohanty *et al.*, 2013; 2014). Acid such as acrylic acid was reported to be able to treat the date palm leaf fibres. In both studies, optimum properties were obtained at 28 wt % of treated date palm leaf fibres reinforced with PVA. This is because the acid has removed the impurities and thereby produced more sites for polymer penetration. However, the involvement of hazardous chemicals should be avoided particularly for biomedical applications such as wound dressings, medical implants, or drug delivery. Thus, physical cross-linking could be an alternative method for previous conditions because it has the

advantage of completely removing the chemical residue or/and causing no chemical leaching problem. In fact, it is frequently employed in improving the properties of biomaterials.

The PVA/nanocellulose hydrogels can be obtained by freezing-thawing technique. Under very low temperature ( $-20\text{ }^{\circ}\text{C}$ ), the water in the polymer system which acts as porogen freezes, expelling the PVA and forming PVA-rich and PVA-lean regions. The polymer chains come into contact with each other, resulting in local crystallization of polymer chains and formation of crystallites as cross-linking junction points in the porous network (Holloway *et al.*, 2010; Mihranyan *et al.*, 2013). The excellent compatibility between PVA and nanocellulose was established which was responsible for the increment of mechanical and bacterial barrier properties. Zheng *et al.* (2014) combined both chemical and physical methods to prepare PVA/nanocellulose composites by a freeze-drying process followed by silane-treatment via a simple thermal chemical vapour deposition process. The silane-treated PVA/nanocellulose aerogels were more thermally stable, possessed high elasticity, and presented superior hydrophobic and oleophilic properties.

In conclusion, the addition of cross-linking agents is a potentially powerful approach leading to superior improvement in composites. In chemical cross-linking methods, the desired cross-linking density can be obtained by tailoring the molar ratio of polymer/cross-linker. The number of hydroxyl groups of PVA and cellulose decreased with increasing cross-linkers loading. As a result, the cross-linking density was increased whereas for the freezing-thawing method, the desired properties can be tailored based on the number of freeze-thaw cycles and the freezing-thawing rate. The degree of polymer phase separation, crystallite formation and hydrogen bonding showed a climb up trend when the number of freeze-thaw cycles increased (Holloway *et al.*, 2010).

## 2.5 Applications of PVA/natural fibres composites

Since the biodegradable PVA/natural fibres composites are environmental-friendly products which benefit our environment, they can be applied in various areas, particularly for food packaging material and mulch films. PVA is an efficient binder for solid particles, including pigments, ceramic materials, cement based materials, plaster, cork, compressed waste products, nonwoven fabrics and ribbons. Li *et al.* (2011) prepared PVA/pinewood saw dust composites by hot press moulding for particleboard application. The tensile strength, shore hardness and tensile modulus are affected by the processing conditions. The optimum properties were obtained when the composite particleboard was pressed at 140°C for 10 to 12 minutes. The application of such PVA/wood composites in particleboard may provide long term benefit in infrastructure from the economic and environmental point of view.

Packaging materials usually request for certain barrier properties as well as mechanical resistance. Fibres tend to absorb moisture, grease and oil from the environment. However, PVA possesses certain resistance to grease, oils and solvents. This has led to the combination of cellulose packaging materials with PVA. The study conducted by Cerpakovska and Kalnins (2012) proved that the PVA/cellulose fibre composites meet the packaging requirements. Besides, the foam plate produced from potato starch, corn fibres, and PVA could be used to replace expanded polystyrene due to its biodegradability (Cinelli *et al.*, 2006b). The incorporation of essential oils such as clove and oregano oil could extend the shelf life of PVA/cassava wastes (14% fibres) food packaging by reducing their moisture sensitivity (Debiagi *et al.*, 2014). Additionally, the antimicrobial properties of essential oil prevent the occurrence of food-related diseases caused by pathogenic microorganisms.

In the agriculture sector, Imam *et al.* (2005) and Cinelli *et al.* (2003) suggested the application of PVA/natural fibres as mulch films. A few years later, Chiellini *et al.* (2008)



applied this material to the agricultural practice of mulching. The effectiveness of materials was assessed based on the growth and yield of lettuce and corn. Encouraging results on the plant growth and crop yields were obtained. The material also demonstrated positive effects on the maintenance of soil structure. The mulches based on PVA and agro-wastes showed achievement of similar enhancement in crop production compared to PE mulches. Such composites have higher cost effectiveness than plastic mulches while at the same time are able to reduce the environmental concern.

The invention and development of nanocelluloses has advanced the utilization of PVA based nanocomposites in more diverse applications. The unique water retention property of PVA/nanocellulose hydrogel possesses high water retention in soil, suggesting its suitability as super absorbents in desert regions (El-Salmawi, 2007). Additionally, their application was amplified as coating material for control-release fertilizer (Zhang *et al.*, 2013). Besides, the PVA/nanocellulose aerogel could be implemented as high capacity absorbent materials to overcome water pollution problems, either from oil, spillage or leakage of chemicals. This silane-treated aerogels also showed a remarkable scavenging capability for heavy metal ions but strongly repel water, making them a versatile absorbent medium for various applications (Zheng *et al.*, 2014).

In the medical field, PVA based nanocomposites was found suitable for tissue engineering applications such as scaffolds, drug delivery, medical implants and wound dressing (Xu *et al.*, 2013). Rahman *et al.* (2014) and Gonzalez *et al.* (2014) described the possibility of PVA/nanocellulose as wound dressing. Such nanocomposites may react to match the natural environment moisture of a wound surface and eventually lead to wound healing. The electrospun PVA/nanocellulose containing stryphnodendron adstringens bark extract with improved biological properties might be suitable for medical implants (Costa *et al.*, 2013). Highly porous scaffolds with good pore-interconnectivity were produced based on ovalbumin/PVA reinforced with unmodified and  $-NH_2$  modified

nanocellulose cross-linked with glutaraldehyde via freeze-drying process (Kumar *et al.*, 2014). Another interesting application of PVA/cellulose composites is used as taste sensor. The membranes showed characteristic response patterns for organic acids, mineral acids, salts, bitter substances, sweet substances and umami substances (Majumdar & Adhikari, 2005).

In a nutshell, it is evident that PVA/natural fibre composites have exhibited unlimited application potential for use in a wide range of fields, particularly when the attention has been shifted from synthetic materials to biodegradable materials. This phenomenon has created a lot of opportunities for such materials due to their environmentally friendly and user-friendly characteristics. In fact, the PVA has been included in the Handbook of Green Chemicals (Michael & Irene, 2004). DeMerlis and Schoneker (2003) have also pointed out that the oral administration of PVA is harmless, supporting the usage of PVA as a coating agent for pharmaceutical, medical, food and cosmetic applications. The US Food and Drug Administration (FDA) has approved the usage of PVA as indirect food additive in products which are in contact with food (DeMerlis & Schoneker, 2003).

Natural fibres are also considered as green materials since it is natural in origin. However, for the case of using agro-wastes or residues in the composites, extra consideration is needed because the mold spores may develop in it and lead to health problems. Previous studies have assessed the risk of nanocellulose via *in vivo* and *in vitro* model. No worrying effects on environment and life are noticed (Vartiainen *et al.*, 2011; Kovacs *et al.*, 2010; Clift *et al.*, 2011; Ni *et al.*, 2012). Thus, the full utilization of PVA/natural fibre composites and their nanocomposites is expected in the future for the benefit of the world.

## 2.6 Biodegradable mulches

Mulching is a common cultural practice to conserve the soil moisture, reduce water loss, control weed growth and improve crops yield. In early days, abundant by-products such as wheat straw, stalks and dry leaves were used as mulches. Mulching using this waste is a cost-effective way to improve the soil. They could be easily swept aside by rain water or blown away by strong wind. Over the last two decades, the use of PE mulches has become a very common practice because it has excellent properties such as high durability, easy processing, excellent chemical resistance and low cost. However, this material causes negative consequences to the environment. A large portion of these PE films were left on the field or burnt without considering the impact to the environment. Thus, a solution for the problem could be the use of biodegradable mulches.

The application of biodegradable mulches has been viewed as a more sustainable ecological alternative to replace plastic polyethylene mulches. At the end of life, these biodegradable mulches could incorporate into the soil where the soil microorganisms would transform them into CO<sub>2</sub>, humus, water and so on. Therefore, they do not require disposal which reduces the overall crops production cost. Currently, the developed mulches involved the use of natural fibres and biopolymers. As with natural fibres, there is a wide range of biodegradable polymers. Particularly, PVA is well suitable for blending with natural fibres and other natural polymers since it can be manipulated in water solution. Efforts were made by United States Department of Agriculture (USDA) laboratories and the University of Pisa in developing mulches from PVA and lignocellulosic fibres. A more details on PVA/natural fibres mulches will be presented as follow. Besides, the biodegradable mulches made from other materials will also be discussed further.

### 2.6.1 PVA and natural fibres based mulches

The unique water retention property and biodegradability of PVA/natural fibres composite has led them in agriculture sector. Imam *et al.* (2005) and Cinelli *et al.* (2003) suggested the application of PVA/natural fibres as mulch films. Imam *et al.* (2005) prepared several blends consist of PVA, orange fibres and corn starch and found that both starch and natural fibres degraded more rapidly than neat PVA. The presence of starch and orange fibres in the blends stimulated the PVA degradation in soil which can be indicated by high CO<sub>2</sub> production. Addition of fibres had surprisingly enhanced the degradation of PVA. The results have concluded the importance of environmental conditions and the biodegradation behaviour of PVA and PVA based materials are strongly affected by the present of microbial species. Moreover, the addition of cross-linker retarded the biodegradation of composite, subsequently expands the composite lifespan.

Cinelli *et al.* (2003) also evaluated the biodegradation of PVA/orange fibres and hexamethoxymethylmelamine (HMMM) cross-linked PVA/orange fibres films by soil respirometric test for 120 days. After the soil respirometric test, the samples were brittle, fragile and diminished in size, losing nearly 50% of their dry weight except for HMMM cross-linked samples which exhibited only 40% of weight loss. Whereas in controlled compost environment, the films biodegraded within 30 days and achieving 50-80% mineralization. A possible stimulating effect of natural fibres on PVA biodegradation has been observed.

Few years later, Chiellini *et al.* (2008) applied PVA/natural fibres for agricultural practice of mulching. The effectiveness of materials was assessed based on the growth and yield of lettuce and corn. Encouraging results on the plant growth and crops yield were obtained. The material also demonstrated positive effects on the maintenance of soil structure. The mulches based on PVA and agro-wastes showed similar enhancement in

crop production compared to PE mulches. Such composites are more cost effective than plastic mulches and able to reduce the environmental concern.

Besides PVA/natural fibres composites, PVA based hydrogel has also been applied in agriculture sector. The biodegradable hydrogels based on PVA and carboxymethyl cellulose possesses high water retention in soil, causing the reduction of water evaporation rate after addition of hydrogel to the soil. Therefore, such hydrogel can act as miniature reservoir on farmlands to retain and supply moisture to the crops. In this way, it would enhance water utilization efficiency, prolong irrigation cycles and thereby reduce irrigation frequency. Moreover, the prepared hydrogel also possessed high biodegradability in the soil, suggesting its suitability as super absorbents in the desert regions (El-Salmawi, 2007).

The application of PVA/cellulose films was also amplified as coating material for control-release fertilizer (Zhang *et al.*, 2013). The water permeability,  $\text{NH}_4^+$  permeability and water absorbency of films decreased with increasing PVA content due to the presence of plenty hydrogen bonding between PVA and cellulose. Their biodegradability was measured by using indoor soil burial method. The films decomposed to 60% after 50 days, appeared to be thinner, brittle and fragile. Such film has favourable biodegradability, suggesting its feasibility to be used as environmentally friendly film.

### **2.6.2 Mulches based on other materials**

Starch has been the common material for biodegradable mulches (Kapanen *et al.*, 2008). Most of the biodegradable mulches available on the market are either derived from or blended with starch because it is biodegradable, cheap and renewable. Such products are such as Biosafe<sup>TM</sup> (Xinfu Pharmaceutical Co., China), Eastar Bio<sup>TM</sup> (Novamont, Italy), Eco-Flex<sup>®</sup> (BASF, Germany), Ingeo<sup>®</sup> (NatureWorks, USA), Mater-Bi<sup>®</sup> (Novamont,

Italy) and Paragon (Avebe, Netherlands) (Hayes *et al.*, 2012). However, the starch based mulches exhibited poor mechanical properties and brittleness, which are their major drawback. Therefore, these starch based mulches must be blended with other polymers and/or plasticizers to overcome their limitation. For example, Halley *et al.* (2001) blended starch with polyester in order to determine the applicability of films to be processed on film blowing line and their performance on field. Encouraging results were obtained in terms of the processing method and their performance properties.

Among the biodegradable polymers, PLA based mulches has gained attention because it is bio-based and compostable. PLA is a hydrophobic polymer derived from renewable agriculture-based feed stocks such as corn starch or dairy whey. These renewable resources is fermented to lactic acid and then polymerized. PLA is nontoxic and able to promote plant growth (Kinnersley *et al.*, 1990). The mechanical properties of PLA is comparable to petroleum-based plastic. Thus enable it to be processed by common techniques such as extrusion and injection moulding. In view of its biodegradability, PLA can decompose into water, CO<sub>2</sub> and humus under normal soil or compost conditions. Previous research on biodegradability of PLA/corn meal-10% (w/w) observed that PLA showed approximately 60-80% degradation after 90 days with aerobic digestion at 60°C in compost conditions (Sarasa *et al.*, 2009). Moreover, the partially degraded PLA is ready to be ploughed into soil for new plant cultivation.

Another biodegradable polymer that may have role in biodegradable mulches is polyhydroxyalkanoates (PHA). It is produced naturally by a wide range of microorganisms under conditions of nutrient stress with an excess of environmental carbon. PHA is very attractive to the scientists and researchers due to its inherent biodegradability and interesting material properties, ranging from rigid and highly crystalline to flexible, amorphous and elastomeric. PHA is completely biodegradable and can decompose into water and CO<sub>2</sub> through natural microbiological mineralization in

various media such as soil, activated sludge, buffer solutions in laboratory atmosphere, sea water, and lake water. However, the price for PHA is expensive, hitting approximately \$2.50 per lb. Therefore, composite material with lower price can be produced by substituting a part of PHA with agriculture based filler. For example, Madbouly *et al.* (2014) developed horticultural crop containers (pots) by blending PHA with dried grains with solubles.

Besides, fermentation residues were added into polyhydroxybutyrate (PHB) to reduce the production cost of mulches. Fermentation is a way to convert biomass waste into alcohol or organic acids. In this process, carbon rich byproducts which composed lignin and unreacted carbohydrates were also produced inevitably. On the other hand, PHB is the main polymer of PHA family and it is brittle in nature due to its high crystallinity which may affect its biodegradability in environment (Wei *et al.*, 2015). Incorporation of fermentation residue in PHB can reduce the production cost of mulches and improve the biodegradability of mulches for the use on crops with short life cycles.

Since both of the PLA and PHB are biodegradable polyesters, they can be combined to form polymer blends. Both of them are partially miscible in nature according to their thermodynamic miscibility constant values. For this reason, maleic anhydride was used to further enhance the interaction between these two polymers. The maleic anhydride acts like a bridging unit between PLA and PHB through dipole–dipole or intermolecular hydrogen bonding. As a result, an improved interaction between the two partially miscible polymers was witnessed. Moreover, the presence of physical interactions results a transition of fracture behaviour from brittle of PLA to ductile characteristics of blends. This result indicated the incorporation of PHB enhances the flexibility of PLA.

Shi *et al.* (2012) also proposed utilization of fermentation residues and combined with PVA as mulches. The authors agreed with Wei *et al.* (2015) that fermentation

residues could reduce the final cost of products. Moreover, the fermentation waste is a good source of low cost natural polymeric materials because it is rich in natural microbial protein, mycelium, polysaccharides and lipids. With certain treatments, mycelium can be made into a good cross-linking material with biodegradable properties. This is because the sauce residue and citric acid fermentation residue have a large amount of bio-macromolecules such as lipids, proteins and cellulose; thereby adding cross-linker is essential to form good biodegradable films.

Other waste materials such as protein based waste materials are also attractive as mulch materials because of their intrinsic agronomic values bound to the high nitrogen content. Moreover, they can be easily blended with synthetic and natural polymers. The wastes from pharmaceutical industries were also used by blending with PVA for same application. The pharmaceutical waste gelatine was blended with PVA, cross-linker and sugarcane bagasse in order to improve water resistance, thermal stability and mechanical properties of films. The resulted films were red in colour, translucent and flexible due to the moisture and glycerol content that originally in waste gelatine. Addition of limited PVA content (20%) improved the water resistance for 2 days whereas the addition of sugarcane bagasse lowered time of permanence in water. Therefore, treating the films with glutaraldehyde modestly improved the water resistance and maintained the cohesiveness of films for a longer period (Chiellini *et al.*, 2001).

In recent years, an innovative water based solution used as biodegradable mulch spray coating has been introduced. The selected polymer is the sodium salt of alginic acid. Sodium alginate (NaAlg) has excellent features such as biocompatibility, biodegradability and pH-responsive property. NaAlg has reflected its ability to form hydrogel which it can absorb large amount of water without dissolving. In a water solution and in the presence of calcium ions in soil, the sodium salt give rise to insoluble gels due to the strong cross-linked network between divalent cations and the (COO-)



groups of the base residual of guluronic acid. They can entangle the cations to form stable and insoluble three dimensional (3D) arrangements, showing an egg box structure (Figure 2.2). The resulted cross-linked network is rigid and stiff. They have good mechanical properties and good water resistance coating to withstand environmental factors such as rain and humidity.

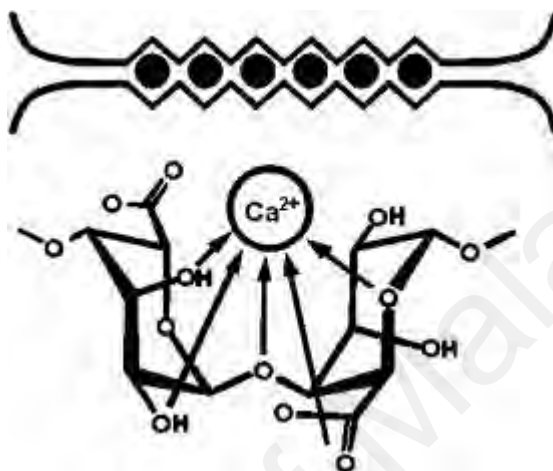


Figure 2.2: Scheme of alginate crosslinking with calcium ions.

Immirzi *et al.* (2009) obtained this polymer from seaweed and used as matrix on soil. Moreover, the authors also introduced hydroxyethylcellulose as secondary biodegradable component of the sodium alginate solution. According to the literatures, hydroxyethylcellulose is compatible with a wide range of water-soluble polymers such as NaAlg and shows better mechanical performance than NaAlg. They can form intermolecular hydrogen bonds between available hydroxyl groups, producing physically entanglement with the three-dimensional networks of calcium alginate, thus assuring a long-lasting plasticising contribution to the polysaccharide. For plasticization, polyglycerol was added.

### 2.6.3 Field performance

In order to be a viable alternative to conventional polyethylene mulches, biodegradable mulches should have comparable performance and crops yield to the polyethylene mulches. The major concerns of biodegradable mulches are cost, biodegradability, crops yield and quality. By considering the overall cost, the added cost of biodegradable mulches would be offset by eliminating the need for removing and disposing used polyethylene mulches. The use of wastes such as fermentation residues and biomass wastes could help to lower the overall cost to a more competitive range whereas their biodegradation period is depends on the material used and environment factors. One important point that worth noted is the biodegradable mulches should not have negative impact to the soil after biodegradation and incorporation into the soil.

Kitamoto *et al.* (2011) studied the biodegradation of biodegradable mulches and claimed that the efficiency of isolation of microorganisms that degrade solid forms of biodegradable plastic is low. Therefore, the authors suggested finding a reliable source of microorganisms that could degrade such biodegradable plastic and recruit them to improve the biodegradability efficiency of plastic. With this intention in mind, Kitamoto *et al.* (2011) carried out a study to search for reliable microorganisms to degrade poly(butylene succinate) (PBS) or poly(butylene succinate-co-adipate) (PBSA) which are the main component in biodegradable mulches. From the result, it was found that the *Pseudozyma spp.* yeasts which are common in the phyllosphere and are easily isolated from plant (eg. leaves and husks of rice) surfaces, displayed strong degradation activity on PBS and PBSA mulch films. Thus, proper utilization of these yeasts in mulches or treating the plastic with their enzymes can accelerate the degradation of biodegradable plastic wastes.

The works from Kitamoto *et al.* (2011) is very useful but only feasible for polyester type mulches. Moreover, extra treatment on the films may also increase the

production cost. A more cost effective method is to employ the versatile natural fibres into various types of materials to form composite mulches. Finkenstadt and Tisserat (2010) prepared PLA/orange wood fibre composites for use as an agricultural mulch film. The prepared composites had comparable mechanical properties (in dry and wet conditions) with the existing mulch film products. According to the authors, this is due to the high concentration and large particle size of orange wood fibres which contributed to the enhancement of mechanical properties especially the modulus. The crystallinity of PLA was significantly higher when 25% of orange fibres are filled into the PLA. In addition, the organic compounds of orange fibres are readily available for release into the environment. The authors suggested such films has several advantages to be used as mulch films over the existing products including biodegradability, growth promotion and controlled release of organic compounds.

Biodegradable mulches developed based on fermentation residues and biomass wastes also demonstrated good biodegradability. The utilization of such wastes could help to minimize the disposal cost of wastes. The prepared composites showed extremely high biodegradation rate compared with pure PHB. 50% of fibres in PHB composites were completely decomposed by 8 months whereas the composites that filled with less than 50% fibres were partially degraded. The fibre content in potato peel fermentation residues was shown to have a significant effect on the surface hydrophobicity and water absorption of the PHB biocomposites. However, the adhesion between fermentation residue and PHB decreased with increasing fibre loading. The tensile, flexural and water resistance of the composites were also decreased with increasing fibre loading (Wei *et al.*, 2015).

Jandas *et al.* (2013) also observed similar problem in PLA and PHB blends mulches. For this reason, maleic anhydride was used to enhance the interaction between these two polymers. Furthermore, the authors also added organically modified nanoclays

like hexadecyl trimethylammonium bromide modified natural montmorillonite and cloisite 30B to modify the performance characteristics of the blend films. Blending of PHB with PLA and compatibilized with MA enhanced the flexibility and impact modification considerably compared to virgin PLA. Moreover, the biodegradation rate of PLA was also enhanced. The authors suggested the films can be applied for short term crops which their crop cycle around 100-150 days.

Shi *et al.* (2012) investigated the field performance of PVA blended with waste mycelium from sauce residue and citric acid fermentation residue as covers for pak choi growth under semi-arid climatic conditions. Generally, the use of these films recorded a total of 50% higher water retention than a control (unmulched) after 96-h treatment at 40 °C. With such high water retention on soil, the yield of pak-choi was increased by 80% in weight compared with the control. The yield of pak-choi was also 22% higher than low density poly(ethylene) (LDPE) mulching. This is because the waste mycelium/PVA films released certain ions such as  $K^+$ ,  $NO_3^-$ ,  $Mg^{2+}$  and organics which are beneficial for plant growth during their biodegradation process. It was estimated that over 56% of  $K^+$ ,  $NO_3^-$ ,  $Mg^{2+}$  and organics were released during mineralization of films. The films were biodegraded within 14 weeks under natural conditions. However, the degradation rate of citric acid fermentation residue/PVA was higher than the sauce residue/PVA composite film. The observation could be explained by the fact that sauce residue mainly contains certain fibres such as soybean hull and wheat bran which need longer degradation time than citric acid waste mycelium.

Sartore *et al.* (2013) and Chiellini *et al.* (2001) developed mulches based on waste products from leather and pharmaceutical industry. The leather waste based mulch films cross-linked by PEG could last on field up to 12 months keeping the mulching effect, subjected to a cumulative solar radiation equal to 4,343 MJm<sup>-2</sup>. On the other hand, the PVA/waste gelatine films showed high biodegradability under soil burial conditions. The

films appeared to be suitably used as self-fertilising mulches. Blending the film with lignocellulose and cross-linking with glutaraldehyde improved films cohesiveness and time of permanence when films were applied on the soil. In view of biodegradability, the waste gelatine did not increase the degradation of PVA. The biodegradation rate decreased with increasing PVA content could be tentatively attributed to a sort of physical entanglement exerted by the vinyl polymer on the protein. In the same time frame (30 days), the pure waste gelatine films undergoes about 60% biodegradation whereas films containing variable amounts (17–20%) of both PVA and bagasse showed a fairly limited biodegradation less than 40%. As expected, the overall effect of crosslinking resolved in a significant reduction of the biodegradation rate and extent of films.

For NaAlg mulches, the introduction of hydroxyethylcellulose improves the mechanical performance of plain NaAlg, lowering the Young's modulus from 4627 to 3144 MPa, and increasing the strain at break from 6.4 to 8.2%. The addition of polyglycerol provoked a drastic drop of the Young's modulus, from 3144 to 171 MPa, in favour of an enhancement of elongation at break, from 8.2 to 20.0%. This result indicated an improvement on the film flexibility. These biodegradable water-based polysaccharides mulches showed a biodegradation of 65.25% after 190 days could be tilled into the soil to be biodegraded. In the field testing of strawberry cultivation, the authors stated that different mulches did not significantly influence yield. In conclusion, the authors agreed that the cost of these spray mulches cannot be compared with the cost of LDPE extruded films and suggested more research works are needed. It is also important to consider the social objective of environmental protection and sustainable development when counterbalance any higher cost of biodegradable mulching materials (Immirzi *et al.*, 2009).

#### 2.6.4 Challenges and future aspects

Biodegradable plastics are defined by American Society for Testing and Materials (ASTM) as broken down by naturally occurring microorganisms (ASTM, 2012a), and ultimately converted to carbon dioxide and water under aerobic conditions (Narayan, 2010). According to the new ASTM in-soil plastic biodegradation standard D5988-12 and WK29802, *in situ* biodegradation of mulches should occur within 2 years and the soil and should not negatively impact the soil quality (Corbin *et al.*, 2013a, 2013b; Goldberger *et al.*, 2013; Miles *et al.*, 2009). Currently, the use of biodegradable plastic mulches in USA and Europe for certified organic plantation is still remains prohibited; therefore the use of polyethylene mulching is still allowed in organic production. However, given that ASTM has developed in-soil plastic degradation standards, it can be used to assess the product suitability for use in certified organic production. Sufficient data is still needed to support the feasibility of biodegradable mulches for agricultural system.

Another major limitation of these biodegradable mulches is their high production cost, preventing them to be adopted by farmers. Many literatures have emphasized on this issue (Kasirajan & Ngouajio, 2012). Due to higher costs and processing complexity, the research frontiers shifted towards developing low cost, easily processibility and environmental friendly materials. Kitamoto *et al.* (2011) suggested treating the plastic with biodegradable microorganisms or their enzyme for higher biodegradation efficiency. This suggestion involves process complexity and hence increases the operational cost. Although the cost of starch based mulches is low, but the use of starch based material increase the food and feed product competition. However, replacing the starch material with biomass wastes could be an alternative method to avoid such competition. Besides, these wastes are truly biodegradable and low in cost. Furthermore, the use of biomass waste can help to solve part of the agriculture refuse. It is hoped that the cost of

biodegradable mulches can be significantly lowered so that it can gain widespread use on low value agricultural crops.

University of Malaya

## CHAPTER 3: MATERIALS AND METHODS

### 3.1 Introduction

This chapter describes the methodology and characterization techniques used to fabricate PVA/kenaf fibre mulches in our work. Most of the characterizations and tests were conducted under indoor conditions (in laboratories). At the final stage, the feasibility of using biodegradable mulches in real life applications was evaluated by monitoring their performance under outdoor conditions.

### 3.2 Materials

Poly(vinyl alcohol) (PVA-220S, molecular weight = 26.3-30 kD, hydrolysis degree = 87-89 mole%) was purchased from Kuraray Asia Pacific Pte. Ltd. Urea was supplied by System ChemAR whereas 4,4'-methylene diphenyl diisocyanate (MDI) was obtained from Bayer. Toluene was from Merck Ltd and the kenaf was kindly donated by National Kenaf & Tobacco Board, Malaysia. The kenaf was washed properly with distilled water, air-dried, grinded and screened to the desired mesh size of 65  $\mu\text{m}$ . These fibres were conditioned in the vacuum oven at 50°C for 24 hours to remove the excess moisture before using. For field testing, the seeds of beans plant (*Vigna sinensis var. sesquipedalis*) were kindly provided by Malaysia Agricultural Research and Development Institute (MARDI). The black polyethylene film (thickness = 0.07 mm) was the commercial mulch film and used in this field testing.



### **3.3 Methodology**

#### **3.3.1 General preparation procedure for PVA/kenaf fibre composites**

PVA solution was prepared by dissolving 1 part of PVA powder in 9 parts of distilled water under constant stirring at 80°C for 1 hour. 10 g of kenaf fibres was added to the 100 g of PVA solution. The mixture was stirred continuously for more than 20 minutes, and cast on a non-stick mould and dried overnight at 60°C in a vacuum oven. PVA/kenaf fibre (PVA/KF) composites with thickness of  $1 \pm 0.5$  mm were prepared.

#### **3.3.2 Preparation of PVA/kenaf fibre/urea composites**

The composites were prepared according to procedure mentioned in previous literature (Yip et al., 2013), with some minor modifications. A predetermined amount of PVA powder was first dissolved in cold water to produce a PVA solution with 10% solids content. The solution was homogenized under constant stirring at 80 °C for 1 h. A 100-g portion of the PVA solution was transferred into a 250-mL beaker, and kenaf fibre was added until it represented 10 wt% of the PVA solution. Various levels of urea loading (3, 5, 7, and 10 wt%) were added and the mixture was stirred continuously. Finally, the mixture was cast on a 20-cm × 20-cm non-stick mold and left to dry overnight at ambient temperature (27 to 28 °C). The sample was then hot pressed at 150 °C for 8 min to obtain a sheet with a uniform thickness of around  $1 \pm 0.5$  mm. The prepared samples were stored in a drying cabinet for 7 days at  $25 \pm 0.5$  °C and 35% relative humidity (RH) before characterization.

### 3.3.3 Preparation of cross-linked PVA/ kenaf fibre composites

The samples were prepared based on the formulation as shown in Table 1. First, PVA was dissolved in distilled water to prepare a 10% PVA solution. Kenaf fiber (<65 micron) was added to the PVA solution and the mixture was stirred continuously until well mixed. The mixture was then cast on a non-stick mold and dried in an oven at 60 °C overnight in a vacuum oven. MDI at a concentration of 0%, 2.5%, 5.0%, 7.5%, and 10.0% (g MDI/100g sample) in toluene was applied onto the composite surface using a brush and dried in a fume hood for 24 h. The composites produced were stored in a drying cabinet for 7 days at  $25^{\circ} \pm 0.5^{\circ}$  under 35% relative humidity (RH) before characterization to ensure complete reaction of MDI. The thickness of the sample was measured using a digital thickness gauge (Mitutoyo Corp).

Table 3.1: Formulation for preparation of PVA/KF based composites.

| Samples          | PVA (g) | Kenaf fibre (g) | MDI (g) | Toluene (g) |
|------------------|---------|-----------------|---------|-------------|
| PVA/KF           | 100     | 10              | 0       | 0           |
| PVA/KF/MDI-2.5%  | 100     | 10              | 2.5     | 5           |
| PVA/KF/MDI-5.0%  | 100     | 10              | 5.0     | 10          |
| PVA/KF/MDI-7.5%  | 100     | 10              | 7.5     | 15          |
| PVA/KF/MDI-10.0% | 100     | 10              | 10.0    | 20          |

### 3.3.4 Biodegradability study of PVA/kenaf fibre based composites

The soil burial degradation experiment was conducted according to the procedure by Maran et al. (2014) with a slight modification. The soil was screened with 2 mm mesh size before burial of samples. The pH of the soil was around 5.5 according to ASTM D4972 with water content around 10%. The dried sample was cut into dimension of 2 x 2 x 1 cm. A set of five sample pieces were buried at least 2 cm apart and 5 cm depth from the soil surface in a flower pot for 28 days at the outdoor under shelter shade. Water was sprinkled on the soil from time to time to maintain 20 - 40% humidity.

### **3.3.5 Field testing of PVA/kenaf fibre based composites**

Long beans plant (*Vigna sinensis var. sesquipedalis*) was selected to test the agronomic effect of the mulching soil. The performance of mulches on selected bean plants was conducted at the experimental garden in University of Malaya (3.1208° N, 101.6564° E) following the method described by Chiellini et al. (2008) with minor modifications. The characteristics of the soil were as follow: 39% sand, 21% slit and 40% clay. Before conducting the experiment, ridges with the surface area of 0.6 m<sup>2</sup> and 0.15 m height were created, with a ridge-to-ridge spacing of approximately 15 cm. For the purpose of bench-marking, a black polyethylene (PE) film with thickness 0.7 mm was used as in the conventional mulching method. An untreated plot was also prepared to serve as control in this experiment. Both the PVA/KF composite and MDI cross-linked PVA/KF composite were used in this experiment. The mulches were applied on the soil surface and holes (4 cm diameter) were made around 15 cm part, and the seeds were sowed. Each group consisted of 4 plants, and their heights were measured after 10, 20 and 30 days after sowing (DAS).

## **3.4. Analysis and characterizations**

### **3.4.1 Characterization of kenaf fibres**

The physical appearance and size of kenaf core fibres were observed by using metallurgical microscope, model MT7100, Meiji Techno Co. Ltd., Japan. The holocellulose content was calculated by using ASTM D1104-56. After the holocellulose content was determined, the  $\alpha$ -cellulose content was determined by using ASTM D1103-55T. On the other hand, the lignin content of kenaf was determined according to ASTM D1106-56.

### 3.4.2 Water absorption and solubility test

For water absorption experiments, samples measuring 20 mm by 20 mm were dried in a vacuum oven at 50 °C overnight until the weight was constant. The weight was measured using a digital balance to an accuracy of 0.0001 g. The samples were then immersed in 100 mL of distilled water for 5 min, 10 min, 30 min, 1 h, 3 h, 8 h, 12 h, 24 h. After time  $t$ , the samples were removed from the water, and any visible moisture on the surface of samples was wiped off with soft absorbent paper. The samples were weighed again and recorded as  $w_t$ . The samples were dried again in a vacuum oven at 50 °C overnight until the constant weight was found and the final weight  $w_f$  was obtained. The tests were conducted five times for each formulation. The water uptake at time  $t$ ,  $W_t$ , and weight loss (solubility,  $SL$ ) were calculated using the following formulas.

$$W_t = (w_t - w_0) / w_0 \quad (1)$$

$$SL = (w_0 - w_f) / w_0 \quad (2)$$

where  $w_t$  is the weight of the wet sample at time  $t$ ,  $w_0$  is the weight of the dried samples before water absorption and  $w_f$  is the dry weight of the samples after water immersion. For evaluating the rate of water absorption at early stages of water uptake where  $W_t / W_\infty \leq 0.5$  by using the equation as follows (Tang et al., 2008; Unemori et al., 2003):

$$W_t / W_\infty = 2(Dt / \pi L^2)^{0.5} \quad (3)$$

where  $W_\infty$  is the weight gain at equilibrium (hereafter is maximum water uptake),  $L$  is the thickness of the sample and  $D$  is the diffusion coefficient.  $W_t / W_\infty$  against  $t^{0.5}$  were plotted and the diffusion coefficient was calculated from the gradient of the plot by using least-squares method.

The sorption coefficient,  $S$  indicates the extent of sorption which the degree of interaction of water with the polymer and can be calculated using the following equation (Sreekala & Thomas, 2003):

$$S = W_{\infty} / W_0 \quad (4)$$

where  $W_{\infty}$  is the maximum water uptake and  $W_0$  is the initial weight of the sample.

The permeation coefficient,  $P$  is the function of diffusion and sorption which can be obtained by the following equation:

$$P = DS \quad (5)$$

### **3.4.3 Thermogravimetric Analysis (TGA)**

The thermogravimetric measurements were performed by using a TGA 851/LF instrument from Mettler-Toledo, Switzerland. The samples (approximately 6 to 8 mg) were placed in a clean platinum pan and heated from 30 °C to 600 °C at a scanning rate of 10 °C/min under a nitrogen atmosphere.

### **3.4.4 Attenuated total reflection-Fourier transform infrared (ATR-FTIR) study**

The functional groups of the composites were characterized by the attenuated total reflection (ATR) technique using a Perkin Elmer Spectrum 400 (U.S.) spectrometer. The sample was lightly placed, then clamped in a position of direct contact with the crystal surface. The probe was then gently pressed down into the sample. A series of FTIR spectra were recorded, consisting of 16 scans in the wavelength range of 4000-400  $\text{cm}^{-1}$ .

### **3.4.5 Estimation of urea content by Kjeldahl method**

The urea content in the water was determined by using the Kjeldahl method, with minor modifications (AOAC, 1995). The water used in the solubility test was mixed with 25 mL of a 50 wt% sodium hydroxide solution in a conical flask fitted with a rubber

stopper that carried a delivery tube. The mixture was heated to boiling point, and the released ammonia gas was directed through the delivery tube into a known volume of 0.1-M hydrochloric acid solution. The acid/ammonia solution was then back-titrated using a 0.1-M sodium hydroxide solution. The number of moles of ammonia was calculated by subtracting the moles of base added from the moles of acid at the end point of the titration. Finally, the urea content released in the water was determined based on number of moles of ammonia. For comparison with the experimental results, another standard solution was prepared by mixing urea in distilled water at concentrations of 3, 5, 7, and 10 wt%. This experiment was carried out in triplicate.

#### **3.4.6 General analysis by digital microscopy**

The morphological images of the composites were examined by a Dino-Lite AM3113T (Taiwan) digital microscope. The samples were stored in a desiccator for at least 48 hours at room temperature before the observation.

#### **3.4.7 Gravimetric measurement**

The buried samples were retrieved, one at a time, every 7 days interval. Adhered soil particles were carefully removed and the samples were dried in a vacuum oven at 60°C before its weight was measured. The % weight loss was determined from the ratio of weight lost to its original weight.

### **3.4.8 Evaluation of plant performance**

The plants on each formulation were carefully observed. The height, number of primary branches and leaves per plant from 6 plants were recorded in 10, 20 and 30 days of sowing (DAS).

### **3.4.9 Evaluation of soil**

Visual mulches degradation behaviour on soil surface was also assessed. The soil temperature was measured according to the method suggested by Ramakrishna et al. (2006) with slight modification. The soil temperature at 5 cm and 10 cm depth was taken by thermometers to the accuracy of  $\pm 0.1$  °C. The measurements were recorded on 0800, 1200 and 1600 h at 7, 20 and 30 DAS. Three measurements were taken at each depth. After 30 DAS, the samples of the soil surface were collected to determine the soil aggregate stability by wet sieving method (Dane & Topp, 2002).

## CHAPTER 4: RESULTS AND DISCUSSION

### 4.1 Characteristic of kenaf fibres and PVA

Kenaf fibres were ground into smaller dimensions prior to usage. The fibres were sieved to the desired mesh size of 65  $\mu\text{m}$  after grinding. The average diameter and length of the fibres were measured randomly from 100 pieces of fibres using digital microscope. In order to determine the chemical composition of kenaf fibre, the raw kenaf fibres were used as received. Their physical dimension and chemical composition were determined and presented in Table 4.1.

Table 4.1: Size and chemical composition of kenaf fibres.

| Material    | Physical dimension ( $\mu\text{m}$ ) |                 | Chemical composition (wt%) |               |        |
|-------------|--------------------------------------|-----------------|----------------------------|---------------|--------|
|             | Diameter                             | Length          | Cellulose                  | Hemicellulose | Lignin |
| Kenaf fibre | $18.0 \pm 11.8$                      | $59.5 \pm 12.5$ | 54                         | 44            | 20.19  |

TGA of kenaf fibres and PVA were individually performed to define the thermal stability of the starting raw materials. This is because the thermal stability of the prepared composites is influenced by the thermal stability of each component present in the composites. The thermal stability of kenaf fibres and PVA were presented in Figure 4.1 and Figure 4.2, respectively. The maximum decomposition temperature,  $T_{\text{max}}$  and other thermal properties of kenaf fibres and PVA were tabulated in Table 4.2.

In Figure 4.1, it was shown that there were two decomposition steps in the curve at 331 and 424.4  $^{\circ}\text{C}$ , respectively. On the other hand, PVA showed three decomposition steps in the curve at 350, 420 and 450  $^{\circ}\text{C}$ . The presence of such multiple decomposition peaks is as expected because it is very much in accordance with the composite characteristics of the materials. The thermal stability of PVA and kenaf fibre are relatively high with maximum decomposition temperature ( $T_{\text{max}}$ ) recorded at 350 and 331  $^{\circ}\text{C}$ ,



respectively. This indicated that it can be processed at high temperature (such as hot pressed) and useful for application such as mulching films.

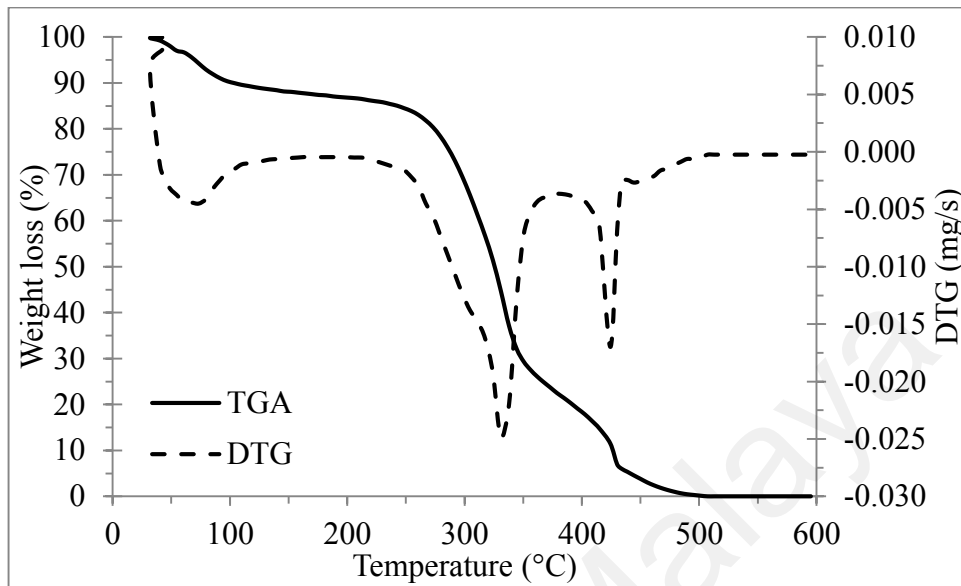


Figure 4.1: TGA and DTG curves of kenaf fibre.

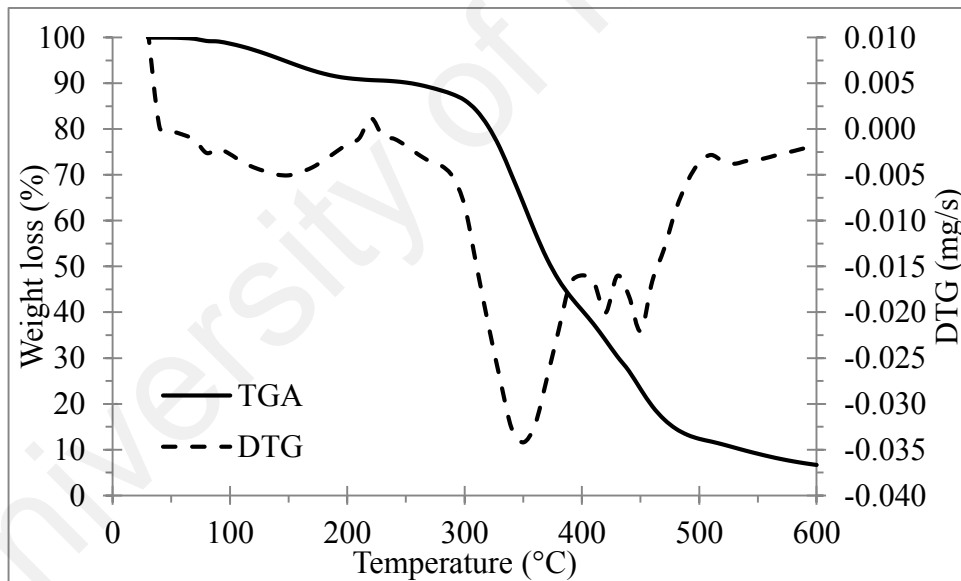


Figure 4.2: TGA and DTG curves of PVA.

Table 4.2: Thermal properties of kenaf fibre and PVA.

| Materials   | T <sub>5</sub> (°C) | T <sub>25</sub> (°C) | T <sub>50</sub> (°C) | T <sub>75</sub> (°C) | T <sub>max</sub> (°C) |
|-------------|---------------------|----------------------|----------------------|----------------------|-----------------------|
| Kenaf fibre | 73.4                | 287.7                | 324.2                | 367.4                | 331.0                 |
| PVA         | 150.0               | 332.0                | 373.0                | 445.0                | 350.0                 |

**Remarks:** T<sub>5</sub> - temperature at 5% weight loss, T<sub>25</sub> - temperature at 25% weight loss, T<sub>50</sub> - temperature at 50% weight loss, T<sub>75</sub> - temperature at 75% weight loss, T<sub>max</sub> – maximum decomposition temperature.

## **4.2 Verification of PVA concentration in PVA/kenaf fibre composites**

### **4.2.1 Water absorption test**

PVA is well known as adhesives in paper converting applications such as fibre board, box board laminating, wallboard joint compounds, wallpaper pastes, etc (Nickerson, 1973). By using its excellent adhesive property in bonding cellulose, PVA was used to bind the kenaf fibre together to form a uniform sheet of mulches. To form a strong composite, the concentration of PVA has to be verified. Since both kenaf fibres and PVA are hygroscopic materials, therefore the effect of PVA concentration on the water absorption property of composites was studied.

The water absorption capacities of PVA/kenaf fibre composites at different PVA concentration were illustrated in Figure 4.3. Generally, all the composite samples absorbed water initially and then started to dissolve after 1 hour of immersion. The samples reached saturation in water absorption after 4 hours of immersion in water. Finally, the water absorption capacity of the respective sample dropped gradually after prolonged immersion time.

Satisfactory water absorption result was observed for the sample with 15 wt% of PVA because of its lowest water absorption percentage at the first hour and slow disintegration rate after 4 hours of immersion. However, such high concentration of PVA in the mixture resulted in processing difficulty. With such high content of PVA, the mixture's viscosity would be further increased during the mixing of kenaf fibres. Eventually, this resulted in non-uniformity of the films casted as high viscosity of solution during mixing rendered homogenous dispersion of kenaf fibres to be impossible. For the ease of processability, low concentration of PVA is favourable in this case. However, when low concentration of PVA (4 wt%) was used, the sample was fragile and it cracked easily during manual handling. This indicated that the bonding between PVA and kenaf

fibre was poor and weak to support the stress transfer. Poor adhesion causes debonding of kenaf fibre from the composites, consequently results in breakage in composites. Therefore, the best PVA concentration was determined to be at 10 wt%.

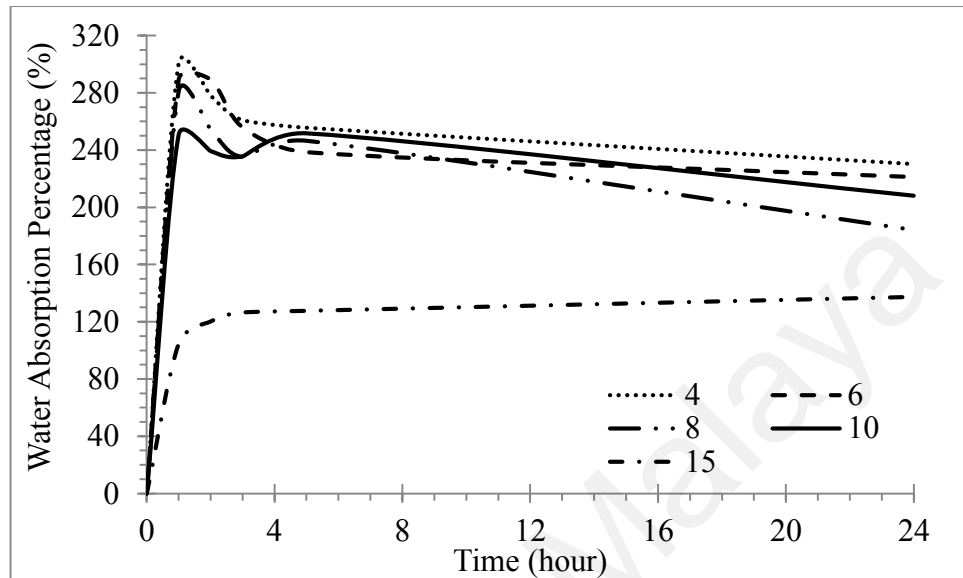


Figure 4.3: The water absorption percentage of PVA/kenaf fibre composite at various PVA loading.

### 4.3 Urea release behaviour in PVA/KF/Urea composites

#### 4.3.1 Water solubility test

Figure 4.4 presents the results of water solubility test the composites after 1 week of water immersion. It was found that the water solubility of the composites was not affected by the loading of small amounts of urea. The entrapped urea in the PVA/KF composites dissolved much slower than urea in the water. All of the samples presented similar patterns and the water solubility percentage increased with increasing time. The 10-wt% PVA/KF/U composite achieved the highest water solubility percentage after 7 d of water immersion. The composite reached 12% solubility in 24 h and gradually increased to 14% in 3 d. The composite achieved 25% solubility after 7 d in the water, implying that the composite could last for a reasonable length of service time in static aquatic conditions.

When the composite was immersed in water, the water molecules diffused into the composite, and presumably the hydroxyl groups in PVA and kenaf fiber could take part in intermolecular hydrogen bonding with water, causing the lower molecular weight fractions to diffuse out and dissolve (Nosbi *et al.*, 2010). The water-solubility of the composite gradually increased over 24 h (Figure 4.4). This effect was enhanced by the cellulose content of kenaf fiber, which contributed to more water penetration into the composites (Tan *et al.*, 2014). Mazuki *et al.* (2010) also reported the same observation when pultruded kenaf fiber reinforced composites were immersed in water. They claimed that this phenomenon was attributable to the penetrability of water and capillary action.

Azwa *et al.* (2013) also reported that moisture is one of the factors that influence the degradation of natural fiber/polymer composites. The leaching of water-soluble substances from PVA/KF composites would cause the debonding of kenaf fibers from the composite. Thus, the dissolution of a composite in water would ultimately lead to the degradation of the composite (Azwa *et al.*, 2013). Similar findings have been reported by Dhakal *et al.* (2007), who investigated the water absorption behaviour of hemp fibre-reinforced unsaturated polyester composites.

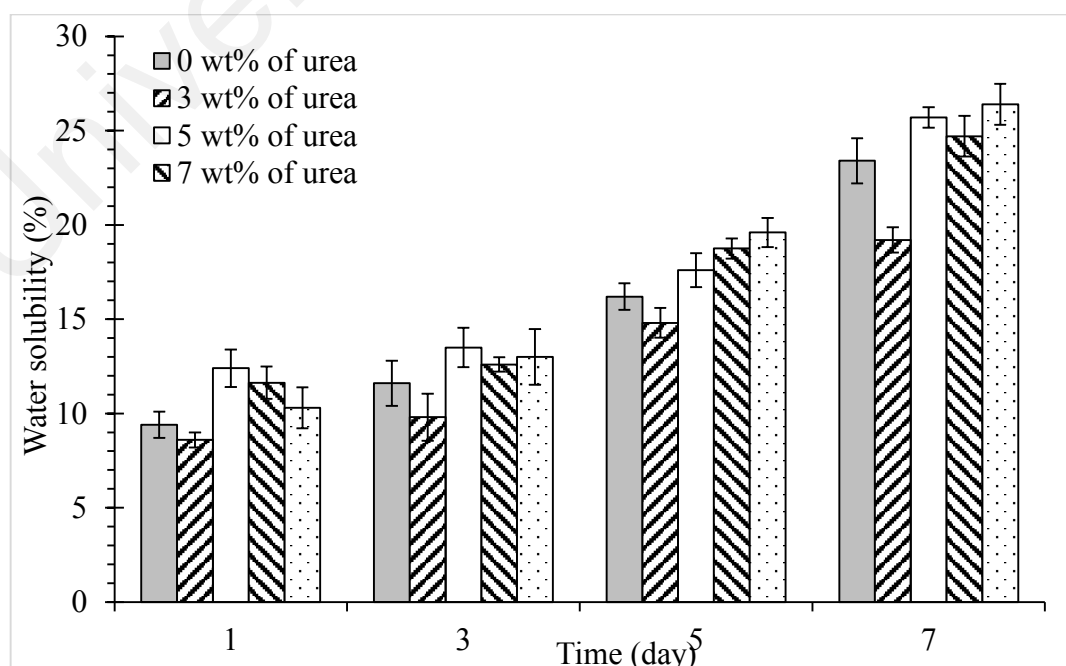


Figure 4.4: Water solubility of PVA/kenaf fibre composites with different urea loading.

### 4.3.2 Content of urea released

The controlled release property of the composites was investigated by measuring the amount of urea released into the water. The nutrients released through the polymer carrier are mainly dependent on the temperature and moisture permeability of the polymer carrier. Therefore, it is possible to estimate the nutrient release from the polymer carrier for a given time (Trenkel 1997). In Figure 4.5, all of the samples displayed a similar pattern and the content of urea released from the composites increased with increasing time and urea loading. The 10-wt% PVA/KF/U composite released the highest amount of urea after 24 h; 25% of the urea content was released in the first hour. The urea content in the water increased to 36% after 10 h, while a total of 57% of the urea was released into the water after 24 h. This finding indicated that the urea was released in a controlled and delayed manner after being entrapped in the composite.

Figure 4.6 compares the leached urea content with the standard urea solution. Apparently, the leached urea content was reduced after the urea was entrapped in the composites. This result indicated that the poly(vinyl alcohol)/kenaf fiber composites had a controlled release profile. Niu *et al.* (2012) also found that the rate of urea release had been evidently slowed down by starch-g-poly(vinyl acetate) matrices because the pure urea usually dissolved very quickly in water within several seconds. The 3-wt% PVA/KF/U composite released around 48% of the urea content, whereas the 5-wt% composite released up to 55 % in 24 h. The leached urea content continued to increase with increasing urea loading in the composites. The 7- and 10-wt% PVA/KF/U composites released approximately 56% and 57% of the urea content, respectively. Niu *et al.* (2012) reported that the urea was released slowly in the first (about 10% of urea) and third (about 15% of urea) stages. The release of urea from starch-g-poly(vinyl acetate) membrane depends on the graft efficiency of poly(vinyl acetate). The data in Figure 4.6

were shown in units of g/g in order to compare the amount of urea released between the composites and the standard urea solution.

According to the nutrient release rate requirements published by the International Fertilizer Industry Association, the desired nutrient release rate should not exceed 15% in 24 h (Trenkel 1997). Despite the observed increment in the nutrient release rate, these composites still retained the necessary characteristics for a mulching film and acted as a potential carrier for fertilizer. However, depending on the polymer coating material used, the incorporation of a cross-linking agent could reduce the moisture permeability of the polymers, which would subsequently reduce the nutrient release rate (Hussain *et al.*, 2012).

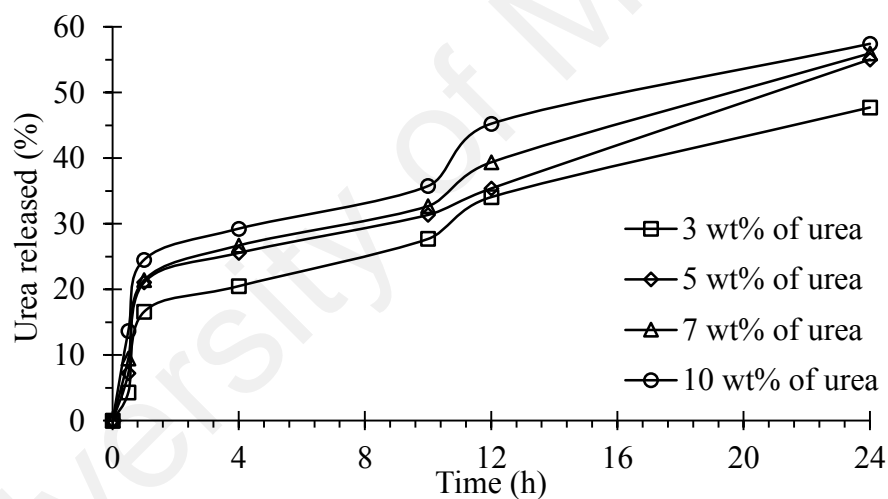


Figure 4.5: Urea content released from the composites in 24 h at different urea loading.

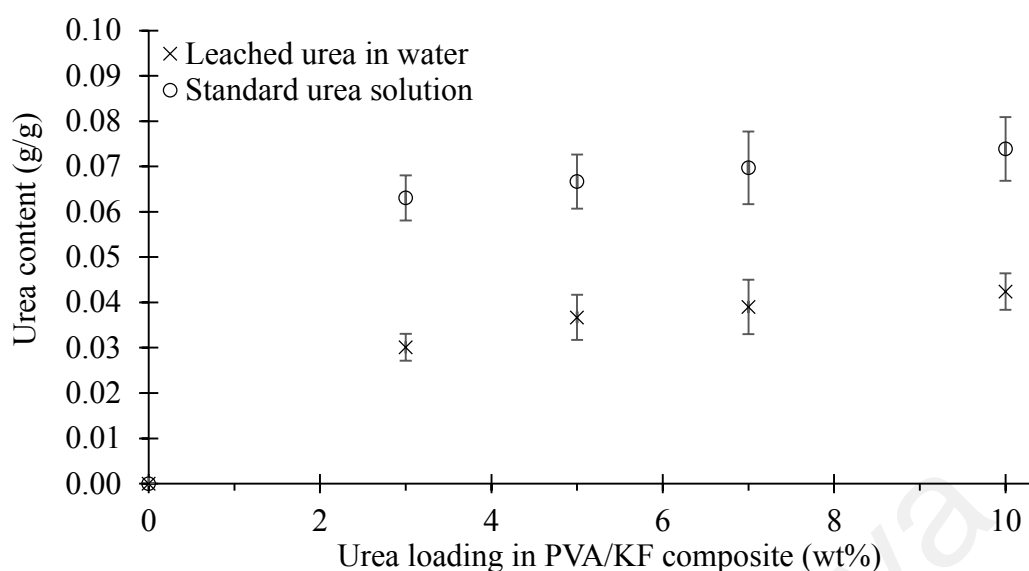


Figure 4.6: Urea content in water after 24 h for PVA/KF composites at different urea loading.

### 4.3.3 ATR-FTIR study

FTIR was used to identify the characteristics peaks of the various components in the composites. Figure 4.7 shows the IR spectra of PVA, KF, PVA/KF, and the 10-wt% PVA/KF/U composite. The region between  $833\text{ cm}^{-1}$  and  $837\text{ cm}^{-1}$  indicated the presence of PVA skeletal backbone. The PVA and kenaf fibre shared the same band, at  $3299\text{ cm}^{-1}$  and  $3334\text{ cm}^{-1}$ , respectively, which were assigned to the  $-\text{OH}$  groups (Ali *et al.* 2014). The stretching of  $-\text{OH}$  groups from the intermolecular and intramolecular hydrogen bonds among PVA chains was ascribed to the high hydrophilic forces (Reis *et al.*, 2006; Yong *et al.*, 2015). However, the existence of this band in kenaf fibre was due to the stretching of hydroxyl groups, which were present in cellulose, hemicellulose and lignin. The peak at  $3297\text{ cm}^{-1}$  was related to the stretching of  $-\text{NH}$  groups in urea. Similarly, the stretching of  $-\text{CH}$  alkyl groups were also seen at  $2928\text{ cm}^{-1}$  and  $2921\text{ cm}^{-1}$  for PVA and KF, respectively.

Figure 4.8 illustrates the IR spectrum of the 10-wt% PVA/KF/U composite before and after the water solubility test. Both curves showed a similar trend even though the

upper curve represented the water solubility profile following 24 h of water solubility testing. The band at  $1647\text{ cm}^{-1}$  was associated with the bending of  $\text{-NH}$  groups, while the band at  $1662\text{ cm}^{-1}$  corresponded to the stretching of  $\text{C=O}$  bonds in urea molecules. This observation supported the controlled release property of PVA/KF and its potential as a carrier for fertilizer. The main IR bands were summarized in Table 4.3.

Table 4.3: Main FTIR bands of PVA, kenaf fibre PVA/KF and PVA/KF/U-10wt%.

| Chemical Structure                       | Peak location ( $\text{cm}^{-1}$ ) * | PVA  | KF   | PVA/KF | PVA/KF/U-10wt% |
|--|--------------------------------------|------|------|--------|----------------|
| OH Stretching                            | 3300-3400                            | 3299 | 3334 | 3300   | 3297           |
| $\text{CH}_2$ & $\text{CH}_3$ Stretching | 3000-2800                            | 2928 | 2921 | 2921   | 2921           |
| $\text{CH}_2$ Bending                    | 1461-1417                            | 1424 | 1457 | 1423   | 1418           |
| $\text{C=C}$ Stretching                  | 1667-1640                            | 1647 | 1633 | 1644   | 1653           |
| $\text{C=O}$ Stretching                  | 1750-1625                            | 1720 | 1737 | 1720   | 1712           |
| $\text{C-O}$ Stretching                  | 1300-1000                            | 1088 | 1238 | 1034   | 1036           |
| PVA Skeletal Bone                        | 833                                  | 834  | -    | 837    | 834            |
| N-H Stretching                           | 3500-3100                            | -    | -    | -      | 3297           |
| N-H Bending                              | 1640-1550                            | -    | -    | -      | 1647           |
| $\text{C=O}$ Urea                        | 1670-1550                            | -    | -    | -      | 1662           |

\* Adopted from Zhan *et al.*, 2004; Imam *et al.*, 2005

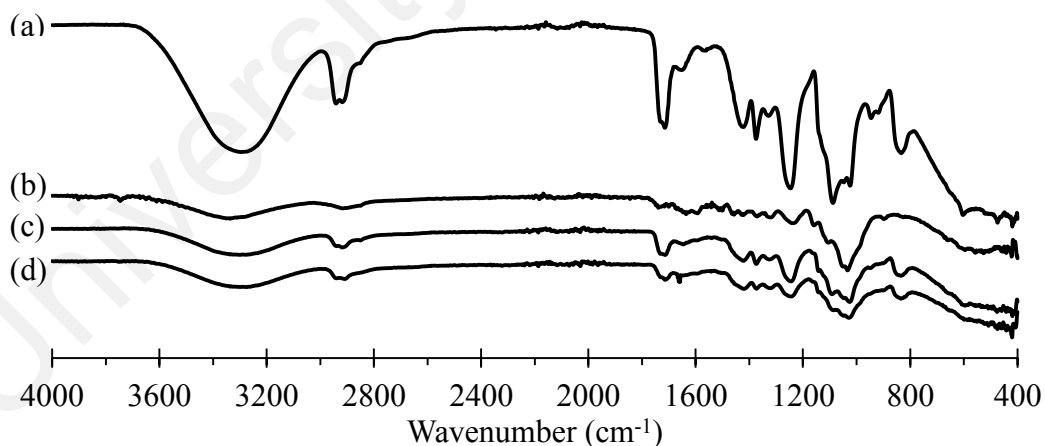


Figure 4.7: FTIR of (a) virgin PVA, (b) raw kenaf, (c) PVA/KF and (d) PVA/KF/U-10wt%.



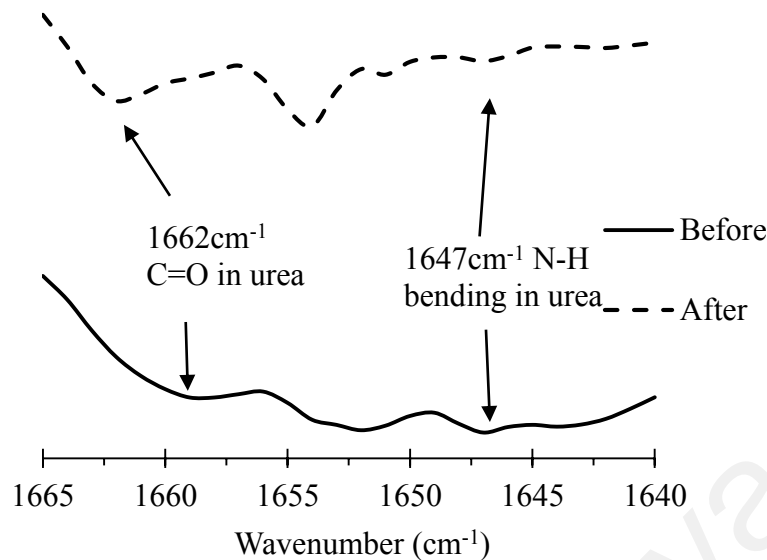


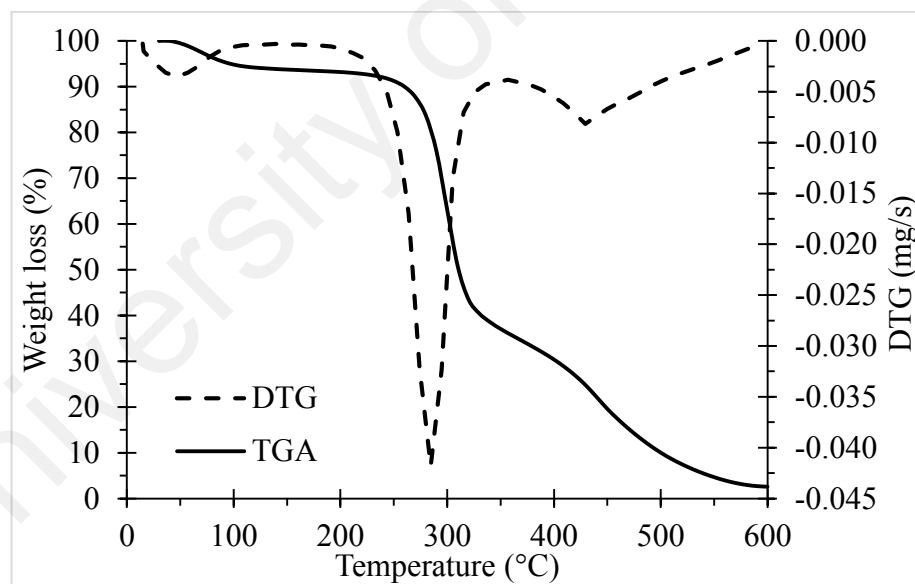
Figure 4.8: FTIR of PVA/KF/U-10wt% before and after soaking in water.

#### 4.3.4 TGA study

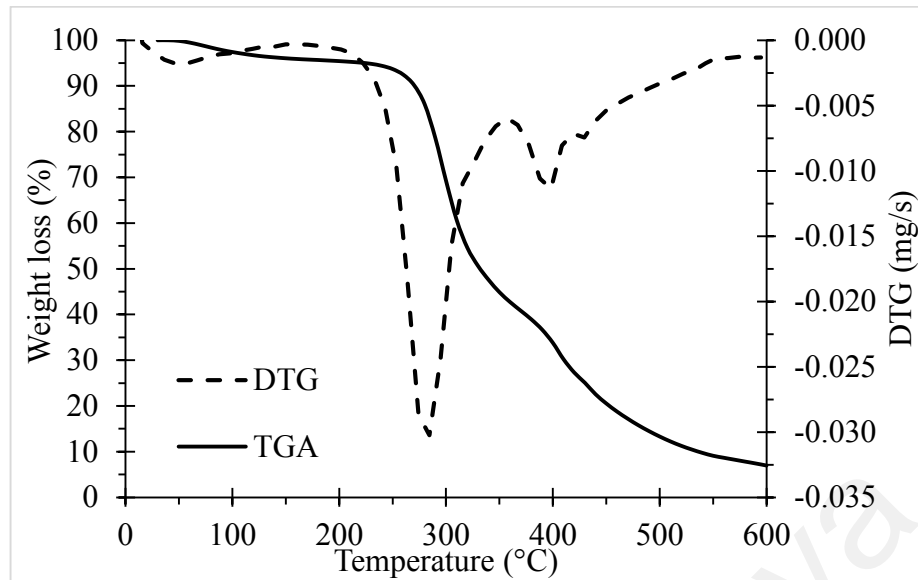
In the application as agricultural mulches, the materials are not subjected to high temperatures. Nevertheless, thermogravimetric analysis was carried out to check-whether the weight losses at different temperature ranges could be related to the wt% of the components. With reference to Figure 4.9, both samples (a) and (b) exhibited a small weight loss (around 10%) at 50-150 °C due to volatile component (water). The next major weight loss (about 60%) occurred from 250-350 °C due to thermal degradations of lower molecular weight fraction of PVA and the finer fibres. The higher molecular weight fraction of PVA and larger fibres has been broken down at temperatures higher than 350 °C. In curve (b), the 10% urea was seen to break down at around 400 °C, as indicated by  $dW/dT$  with a sharper peak. The maximum decomposition temperature ( $T_{max}$ ) for each sample is listed in Table 2. The result was in good agreement with the findings of Azwa *et al.* (2013), who found that approximately 60% of the thermal decomposition of most natural fibres occurred within the-temperature range between 215 and 310 °C.

Table 4.4 shows that the incorporation of fibres into the composites had a profound effect on the thermal stability of the PVA matrix (Ng et al. 2014). The

composites showed a lower degradation temperature (by about 50 °C) than pure PVA. A similar observation was reported using poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) composites with bamboo fibre (Lee & Wang 2006). Julkapli and Akil (2010) also reported that addition of kenaf dust in chitosan film reduced the thermal stability of chitosan film and that the reduction was proportional to the amount of kenaf dust added. The incorporation of urea into the composites did not influence the thermal stabilisation of the composites, even at a loading of 10 wt%. Imam *et al.* (2005) reported a decrease in the thermal stability of PVA/starch/orange peel composites, particularly because the addition of a high amount of low-molecular-weight components, such as urea and glycerol, resulted in early decomposition of the composites. Therefore, the low decomposition temperature of urea must be considered during the preparation of composites for high temperature applications (Imam *et al.*, 2005).



(a)



(b)

Figure 4.9: Comparison of TGA and DTG curves for a) PVA/KF composites and b) composite containing 10 wt% of urea.

Table 4.4: TGA characterisation of PVA, PVA/KF and composite containing 10 wt% of urea in the temperature range of 150 to 450 °C.

| Samples        | Weight loss (%) in temperature range |        |        |        |        |        | $T_{\max}$ (°C) |
|----------------|--------------------------------------|--------|--------|--------|--------|--------|-----------------|
|                | 150 °C                               | 250 °C | 300 °C | 350 °C | 400 °C | 450 °C |                 |
| Virgin PVA     | 5.38                                 | 9.81   | 13.68  | 36.18  | 59.54  | 76.80  | 350             |
| PVA/KF         | 6.26                                 | 8.74   | 36.92  | 62.93  | 69.63  | 80.42  | 300             |
| PVA/KF/U-10wt% | 3.94                                 | 6.30   | 30.75  | 55.12  | 66.19  | 79.46  | 300             |

#### 4.4 Effect of cross-linking in PVA/KF composites

##### 4.4.1 Water absorption test

PVA and KFs are well known for their hygroscopic nature. They are ready to absorb moisture from the air even at room temperature. The water uptake ratio ( $W_t/W_\infty$ ) versus  $t^{0.5}$  for all the control and cross-linked PVA/KF composites is depicted in Figure 4.10. Two phases were observed; rapid water was absorbed into the composite in the initial stage and very slow uptake thereafter.

The rapid water uptake characteristics of PVA/KF composites were due to the contribution of hydrophilic hydroxyl groups in the PVA and KFs. During the initial 50 s, water molecules diffused into the composites and attached to the hydroxyl groups via intermolecular hydrogen bonding. The absorbed water would cause the composite to expand whereby more water could diffuse in. After 50 s, the sample becomes more or less saturated with water, and thus the rate of water penetrating into the composites slowed down. Therefore, treating the composites with MDI first can reduce the moisture absorption of the composites because the active isocyanate groups in MDI would react with the active hydroxyl groups in PVA and KFs to form urethane linkages in the composites. Thus, the available water-attracting sites were reduced. The crosslinks in the composites had restricted the expansion, which in fact improved the moisture barrier property of the composites.

The rapid water absorption at initial stage showed a good linear relationship between water uptake ratio ( $W_t/W_\infty$ ) and  $t^{0.5}$ , indicating the composites approached the Fickian type of diffusion wherein the initial water uptake was rapid (Unemori *et al.*, 2003). Therefore, the diffusion coefficient could be calculated from the gradient of the plot. Table 4.5 summarises the diffusion coefficient for all the samples with different MDI loading. From the diffusion coefficient data, the diffusion rates of the control and samples with different MDI concentration could be identified. The control sample had the highest diffusion coefficient as expected. For cross-linked samples, the diffusion coefficient decreased with increasing MDI loading, suggesting water hindrance by the MDI. 10 wt% of MDI in the sample successfully decreased 55% of diffusion coefficient compared with the control sample. When the composite surfaces were treated with MDI, there was an improvement on the barrier properties of the composites. Similar observation was found when polyamide 6 was filled with impermeable silicate layers (Abacha *et al.*, 2009).

The weight loss or solubility is shown in Table 4.5. Although the samples were partially cross-linked by MDI, some of the remaining hydrophilicity in the composites would attract water, causing the water to diffuse into the composites through the edges. The cellulose and hemicellulose structures of KFs would absorb water and swell, developing stress at the interface regions, leading to the formation of micro-cracks in the matrix. This phenomenon would further promote the capillarity and transportation of water molecules into the bulk matrix via micro-cracks along the fibre/matrix interface. As a result, KFs were percolated from the composite, leading to the ultimate disintegration of the composites. The images in Figure 4.14 support this explanation. Similar observations have been found in the case of hemp fibre reinforced unsaturated polyester composites (Dhakal *et al.*, 2007).

The maximum water uptake and sorption coefficient were independent of the MDI loading because some portions of the composites disintegrated in the water after prolonged immersion time, which in turn reduced the maximum water uptake. The sorption coefficients of PVA/KF composites were generally higher, indicating good interaction between water and the composites. The permeation coefficient measured the transport rate of water molecules that penetrate through the material's thickness (Tang *et al.*, 2008). The increasing MDI loading successfully reduced the permeation coefficients of the composite as shown in Table 4.5. PVA/KF/MDI-10.0% showed 66% lower permeation coefficient compared with the control sample, reflecting that MDI is effective in hindering water molecules from penetrating into the composites. Previous researchers, Saijun *et al.* (2009) and Tan and Chow (2011) also reported similar results that the cross-linked polymeric systems possess lower water absorption characteristics.

Table 4.5: Summary of water absorption data.

| Samples          | Average samples thickness (mm) | $W_{\infty}$ (g/mm <sup>3</sup> ) | $D_t$ ( $\times 10^{-9}$ m <sup>2</sup> s <sup>-1</sup> ) | $SL$ (g/mm <sup>3</sup> ) | $S$ (g/g) | $P$ ( $\times 10^{-6}$ m <sup>2</sup> s <sup>-1</sup> ) |
|------------------|--------------------------------|-----------------------------------|---|---------------------------|-----------|---|
| PVA/KF           | 1.44 $\pm$ 0.11                | 0.43                              | 6.37  | 0.050                     | 860.63    | 5.48  |
| PVA/KF/MDI-2.5%  | 1.40 $\pm$ 0.07                | 0.37                              | 4.12  | 0.049                     | 723.74    | 2.98  |
| PVA/KF/MDI-5.0%  | 1.42 $\pm$ 0.10                | 0.40                              | 3.64  | 0.046                     | 809.59    | 2.95  |
| PVA/KF/MDI-7.5%  | 1.49 $\pm$ 0.06                | 0.45                              | 3.00  | 0.040                     | 883.67    | 2.65  |
| PVA/KF/MDI-10.0% | 1.44 $\pm$ 0.09                | 0.32                              | 2.88  | 0.036                     | 645.06    | 1.86  |

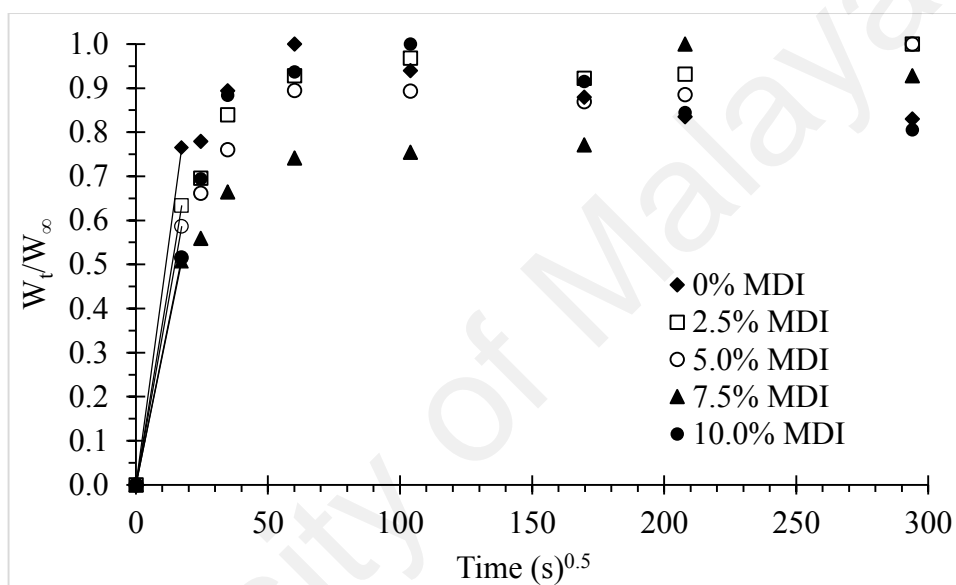


Figure 4.10: Plots of the  $W_t / W_{\infty}$  versus  $t^{0.5}$  for all the samples containing various loading of MDI.

#### 4.4.2 ATR-FTIR study

Figure 4.11 displays the FTIR spectra of the control and cross-linked PVA/KF samples with detailed IR bands summarised in Table 4.6. The overlapping broad and strong band corresponded to the stretching of OH group which occurred between wavenumber 3400 cm<sup>-1</sup> and 3200 cm<sup>-1</sup>. Characteristic transmittance bands in the range of 3000 cm<sup>-1</sup> to 2800 cm<sup>-1</sup> corresponding to the stretching of CH<sub>2</sub> and CH<sub>3</sub> groups were observed in the spectra for all the samples.

Significant chemical changes in the spectra are shown in Figure 4.12. The chemical changes implied structural changes of the composite when MDI was added to the sample. The isocyanate groups from MDI would react with the hydroxyl groups on the KFs fibres' surface and PVA to give urethane groups. A signal of the carbonyl groups (C=O) vibration from the urethane linkages was generated in the range of 1730  $\text{cm}^{-1}$  to 1720  $\text{cm}^{-1}$ , overlapping with the band of C=O stretching between 1750 and 1625  $\text{cm}^{-1}$ . The band of NH bending was also observed in the wavenumber ranging from 1650  $\text{cm}^{-1}$  to 1590  $\text{cm}^{-1}$ , which was also overlapped with the peak of C=C vibration at 1600  $\text{cm}^{-1}$ . Meanwhile, other characteristic peak of amide II occurred around 1510  $\text{cm}^{-1}$  in the spectra for the composites treated with 5%, 7.5%, and 10% of MDI.

Figure 4.12 also shows the peak of PVA skeletal bone at 833  $\text{cm}^{-1}$  decreasing at higher MDI concentration, confirming that a reaction between isocyanate and hydroxyl groups in PVA occurred. In addition, no peaks were observed between 2270  $\text{cm}^{-1}$  to 2100  $\text{cm}^{-1}$ , which was related to the isocyanate (N=C=O) groups, indicating all isocyanate groups had been reacted completely. The aforementioned peaks demonstrated the formation of urethane groups and they were the significant bands that identified the presence of polyurethane. Further addition of excess MDI would result in isocyanate end-capped prepolymer and ultimately become polyurethane in the presence of amines (Fink, 2013). The carcinogenic aromatic diamines have been reported as the degradation products from polyurethane incorporating aromatic diisocyanates (Guelcher *et al.*, 2005). Considering the potential release of these toxic degradation products to the environment, further addition of MDI is not favourable for the production of eco-friendly mulches.

Table 4.6: Main FTIR bands of cross-linked and uncross-linked PVA/KF composites.

| Chemical structure                           | Peak location* | PVA/K F    | PVA/K F/MDI-2.5% | PVA/K F/MDI-5.0% | PVA/K F/MDI-7.5% | PVA/KF /MDI-10.0% |
|--|----------------|------------|------------------|------------------|------------------|-------------------|
| OH stretching                                | 3400-3300      | 3330       | 3322             | 3320             | 3330             | 3324              |
| N-H stretching                               | 3400-3200      | -          | 3322             | 3320             | 3330             | 3324              |
| N-H bending                                  | 1650-1590      | -          | 1600             | 1600             | 1595             | 1595              |
| CH <sub>2</sub> & CH <sub>3</sub> stretching | 3000-2800      | 2915       | 2918             | 2918             | 2923             | 2923              |
| CH <sub>2</sub> bending                      | 1461-1417      | 1421       | 1420             | 1420             | 1420             | 1420              |
| C=C Aromatic vibration                       | 1600           | -          | 1600             | 1600             | 1595             | 1595              |
| C=O stretching                               | 1750-1625      | 1740       | 1733             | 1730             | 1720             | 1725              |
| C=O Urethane vibration                       | 1730-1720      | -          | 1733             | 1730             | 1720             | 1725              |
| C-O stretching                               | 1300-1000      | 1241, 1026 | 1239, 1025       | 1236, 1021       | 1236, 1033       | 1236, 1033        |
| PVA skeletal bone                            | 833            | 837        | 839              | 828              | -                | -                 |
| H-N-C=O Amide II Combined motion             | 1540-1500      | -          | -                | 1509             | 1511             | 1510              |

\* From Imam *et al.*, 2005; Zhan *et al.*, 2004

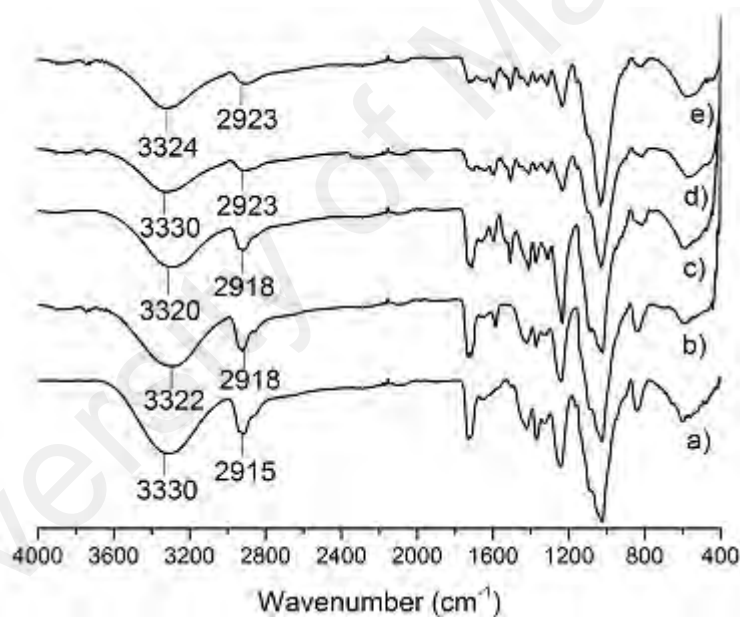


Figure 4.11: FTIR spectra for (a) PVA/KF, (b) PVA/KF/MDI-2.5%, (c) PVA/KF/MDI-5.0%, (d) PVA/KF/MDI-7.5% and (e) PVA/KF/MDI-10.0%.



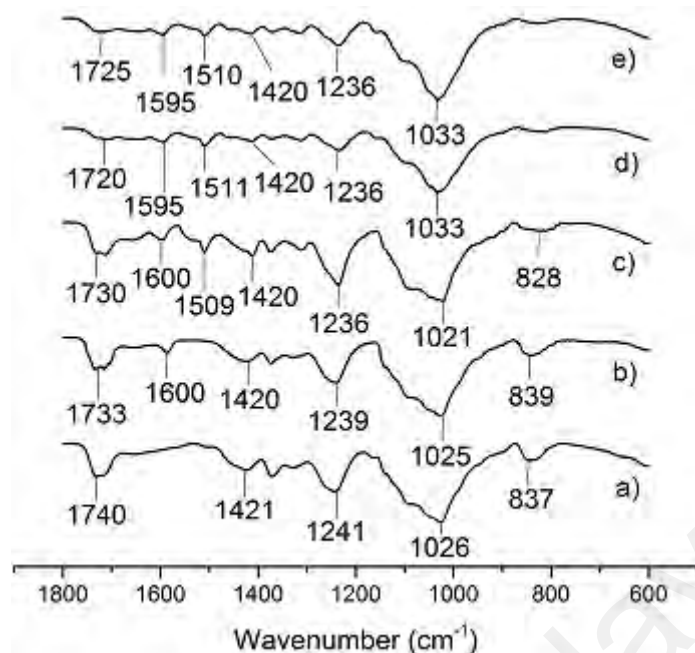


Figure 4.12: Significant chemical structure changes in the range of 1800-600  $\text{cm}^{-1}$  for (a) PVA/KF, (b) PVA/KF/MDI-2.5%, (c) PVA/KF/MDI-5.0%, (d) PVA/KF/MDI-7.5% and (e) PVA/KF/MDI-10.0%.

#### 4.4.3 TGA study

TGA has been carried out to determine the thermal stability of cross-linked PVA/KF composites. Figure 4.13 displays the TGA curves as a function of temperature for 0 wt%, 5 wt%, and 10 wt% MDI cross-linked PVA/KF composites. The result showed that there are three stages of thermal decomposition, implying three different stages of degradation occurring in the cross-linked PVA/KF composites. These three degradation stages were identified at nearly 100°C, 300°C, and 450–550 °C, respectively. Imam *et al.* (2005) reported similar decomposition behaviour for PVA/starch/fibres blended in the presence of three different thermal decomposition stages.

The minor weight loss in the first degradation stage at 100 °C was attributed to the evaporation of water molecules. The degradation at the second stages was where the composites experienced major decomposition as indicated by the maximum weight loss at the decomposition temperature. There was an increment of 2%–3% in the maximum decomposition temperature of control, 5% and 10% MDI treated composites, rising from

287 °C, to 295 °C, and to 303 °C, respectively were observed. PVA was also degraded at this temperature range from 250–350 °C, as reported by Gohil *et al.* (2006).

The overall thermal properties of the composites were significantly enhanced with the incorporation of MDI, which could be due to the formation of cross-linking in the composite because of the reaction between isocyanate and hydroxyl groups as supported by the FTIR result. According to Gohil *et al.* (2006), the three dimensional network structure of cross-linked PVA also exhibited higher thermal stability than those systems with lower cross-linking density.  $T_5$ ,  $T_{25}$ ,  $T_{50}$ ,  $T_{75}$  and  $T_{max}$  also increased with increased MDI content in the composites.

Third degradation stage has shifted to a higher temperature range of 450–550 °C. PVA/KF/MDI-10wt% was at the highest temperature, reaching 530 °C compared with the control and PVA/KF/MDI-5wt%, which was at 460 and 490 °C, respectively. The enhancement of thermal stability could be due to an increased cross-link density in the composites. Hence, the sample treated with the highest MDI content was determined to be most thermally stable. This finding is in good agreement with the result reported by El-Shekeil *et al.* (2012) who found that the thermoplastic polyurethane/KF composite treated with 6% pMDI is more thermally stable than those composites treated with 2% and 4% pMDI.

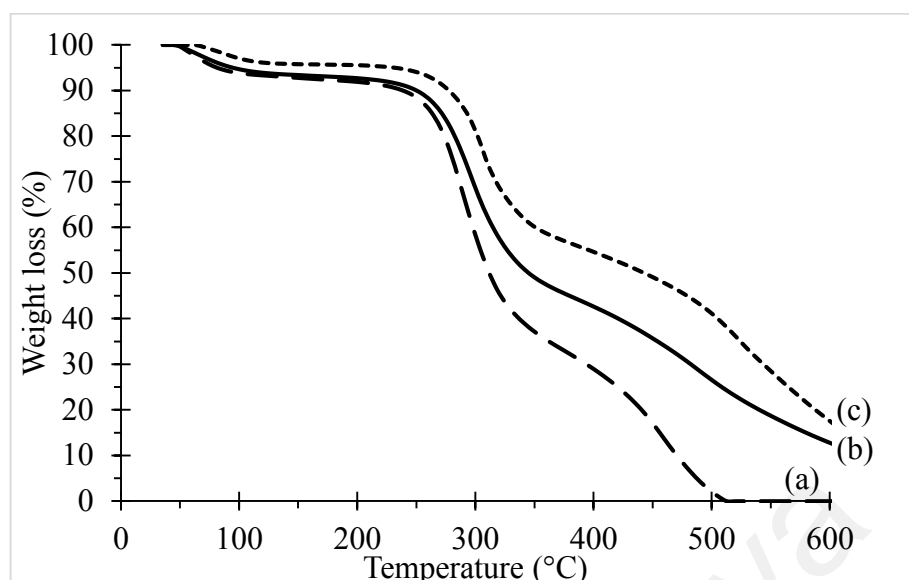


Figure 4.13: TGA curves of PVA/KF based composites, (a) PVA/KF, (b) PVA/KF/MDI-5%, (c) PVA/KF/MDI-10%.

#### 4.4.4 Morphological analysis

The surface of PVA/KF composites before and after water absorption test was visualized via digital light microscope to examine their degradation behavior. The images and micrographs of the composites are presented in Figure 4.14 and Figure 4.15, respectively. The appearance and micrograph of PVA/KF composite before water absorption test as shown in Figure 4.14(a) and Figure 4.15(a) reveal smooth and homogeneous surface without bubbles of PVA/KF composite. After 24 hours of immersion in water, all the samples were very different in appearance (Figure 4.15b–4.15f). They showed signs of degradation on the surface of the composites, as evident in the micrographs Figure 4.14b–4.14f. In particular, the control samples showed the most serious degradation effect compared with MDI treated samples. The greater part of the surface has dissolved in the water, and was in the process of disintegration.

Compared with the control samples, the cross-linked samples exhibited less degradation on their surfaces (Figure 4.15c–4.15f). After water absorption, all the cross-linked samples had rough surface with large number of holes or pits and cracks. A portion of PVA/KF/MDI-2.5% was broken into pieces (Figure 4.15c), whereas PVA/KF/MDI-5%

showed a greater number of deep cracks than PVA/KF/MDI-7.5% (Figure 4.15d and 4.15e). For 10% MDI treated composites, small pits, and shallow crevices developed on the surface of the samples (Figure 4.15f). More details of degradation effect could be observed from the micrographs. The number of cracks and pits were reduced with increased MDI loading. Hence, the degradation effect diminished with increased MDI loading, suggesting the effectiveness of MDI in improving water barrier property, which in turn prolonged the submersion time of PVA/KF composite under static aquatic condition. These observations are in good agreement with the aforementioned water absorption result.

From the appearance of cross-linked samples, degradation began from the edges of the samples, changing from shallow crevices into deep cracks, because the samples were treated with MDI. Water diffused into the composite from the edges and cross-section surface area. By contrast, the surface of the control samples was not coated with MDI, thereby increasing their surface area for water absorption. Such exposure increased the risk of water attack, leading to rapid degradation compared with the cross-linked samples. Besides, the KFs that absorbed water would also swell and develop stress at the interface region, forming voids and cracks. Since the composites were partially cross-linked, the water molecules could attack the unreacted hydroxyl groups in the composites. The pits and cracks were further enlarged and deepened because of the water attack. The water would also weaken the PVA binder, causing the composites to break into pieces and eventually lead to disintegration.

This observation was discussed based on the static aquatic condition at room temperature. These composites may differ in terms of lifespan under real field cultivation conditions, depending on soil moisture and climate, such as rainfall density, sunlight, and temperature (Kijchavengkul *et al.*, 2008). Based on the result above, the cross-linked composites are able to hinder the moisture attack, which in turn provide longer service

time than uncross-linked composites. Schettini *et al.* (2013) also utilized ionic cross-linking process to spontaneously cross-link the natural fibers/sodium alginate composite for the production of water resistant biodegradable pots. These cross-linking methods can assure the permanency of biodegradable materials in terms of longer service time compatible with agricultural cultivation. Despite the short lifetime of biodegradable PVA/KF mulches, they offer special benefits over the conventional polyethylene mulches. Earlier degradation of PVA/KF mulches allows the leached KFs to serve as fertilizer for successful seedlings establishment.

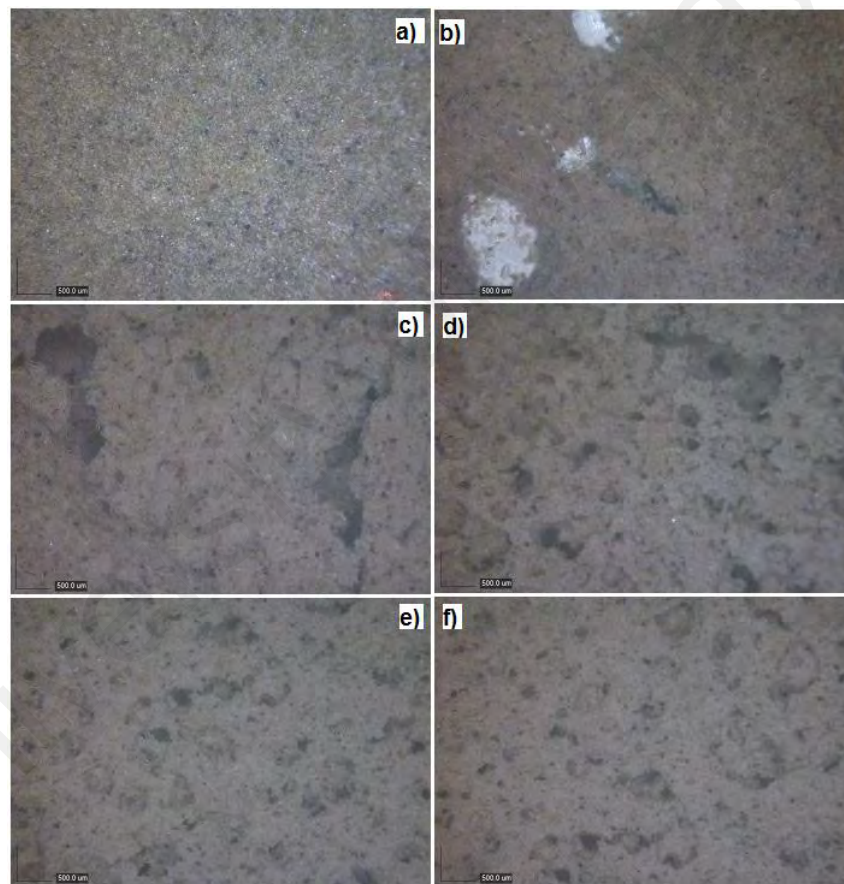


Figure 4.14: Micrographs (200x) of control and cross-linked PVA/KF composites before (a) and after 24 hours of water absorption (b-f), in which (a) PVA/KF, (b) PVA/KF, (c) PVA/KF/MDI-2.5%, (d) PVA/KF/MDI-5.0%, (e) PVA/KF/MDI-7.5%, (f) PVA/KF/MDI-10.0%.



Figure 4.15: The appearance of control and cross-linked PVA/KF composites before (a) and after 24 hours of water absorption (b-f), in which (a) PVA/KF, (b) PVA/KF, (c) PVA/KF/MDI-2.5%, (d) PVA/KF/MDI-5.0%, (e) PVA/KF/MDI-7.5%, (f) PVA/KF/MDI-10.0%.

## 4.5 Biodegradation of PVA/KF based composites

### 4.5.1 ATR-FTIR study

Evidence of degradation of the PVA/KF composite and MDI cross-linked PVA/KF composite could be clearly seen from the FTIR spectra as shown in 4.16. Since the PVA (PVA-220S) was manufactured from hydrolysis of 88 mole % of poly(vinyl acetate), the small amount of unhydrolysed acetate group has given rise to a weak peak around  $1750\text{ cm}^{-1}$  of the carbonyl group  $\text{-C=O}$  (spectra a and b). There was no significant difference between spectra (a) and (b), consistent with the fact the cross-linked PVA/KF composite was carried out with very small amount of MDI.

After 4 weeks of soil burial, a new peak around  $1639\text{ cm}^{-1}$  has emerged (spectra c and d). This peak is much higher in PVA/KF composite than in MDI cross-linked PVA/KF composite. Similar biodegradation behaviour of PVA based composites has been previously reported by other researchers (Imam *et al.*, 2005; Kibédi-Szabó *et al.*, 2012; Qiu & Netravali, 2013). The appearance of the peak around  $1638\text{ cm}^{-1}$  was attributed to the formation of  $\beta$ -diketone due to random polymer chains scission by enzymatic attack (Chiellini *et al.*, 1999). Further chain scission of activated  $\beta$ -diketone could produce a carboxylic group as explained by Leja and Lewandowicz (2010). Kibédi-Szabó *et al.* (2012) also reported the formation of many  $\text{C=O}$  groups around  $1649$

$\text{cm}^{-1}$  after 28 days of PVA-based membrane being broken down under aerobic environment by microorganisms.

Qiu and Netravali (2013) found the reduction of band at  $3500\text{-}3200\text{ cm}^{-1}$  during PVA degradation due to the disappearing of  $\text{-OH}$  groups. After 28 days in the soil, the loss of peaks at  $1200\text{-}1500\text{ cm}^{-1}$  and  $900\text{-}800\text{ cm}^{-1}$ , particularly at  $833\text{ cm}^{-1}$ , is related to the disappearance of PVA, which is a sign of composites degradation. As expected the FTIR results showed that the degradability of PVA/KF composite was faster than MDI cross-linked PVA/KF composite. With reference to spectrum d, the intensities of  $\text{C=O}$  peaks at  $1644$  and  $1637\text{ cm}^{-1}$  respectively were smaller than those of spectrum c. Apparently, the cross-linking has retarded the biodegradation of composite. The findings were similar to the biodegradability studied of hexamethoxymethylmelamine (HMMM) cross-linked PVA/starch/lignocellulosic fibers (Imam *et al.*, 2005).

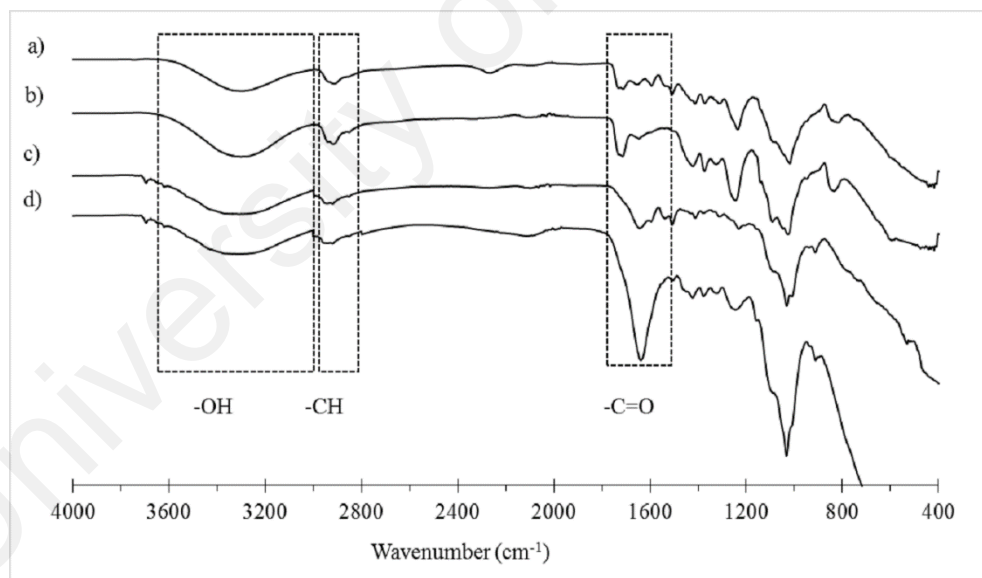


Figure 4.16: FTIR spectrum of (a) PVA/KF, (b) cross-linked PVA/KF, (c) degraded PVA/KF, (d) degraded cross-linked PVA/KF.

#### 4.5.2 Weight loss

Figure 4.17 displays the variation of weight loss of the composites with respect to burial time. As expected, the weight loss of all the samples increased gradually with time. The weight loss of PVA/KF composite increased from 18% in 7 days to 50% after 28

days. On the other hand, the weight loss of MDI cross-linked PKV/KF composite increased at a much slower rate, from 7% in 7 days to 14% after 28 days of biodegradation. Such weight loss was in similar trend as reported by other researchers (Kim *et al.*, 2006).

It was plausible that the degradation was promoted by the surface moisture absorption, which promotes the growth of microorganisms such as bacteria and fungi (Mohan & Srivastava, 2010). In addition, the kenaf fibres, being cellulosic materials are easily attacked by microorganisms (Cao *et al.*, 2002). The cross-linked PVA/KF composite displayed lower rate of weight loss, presumably the cross-links have improved barrier properties against moisture.

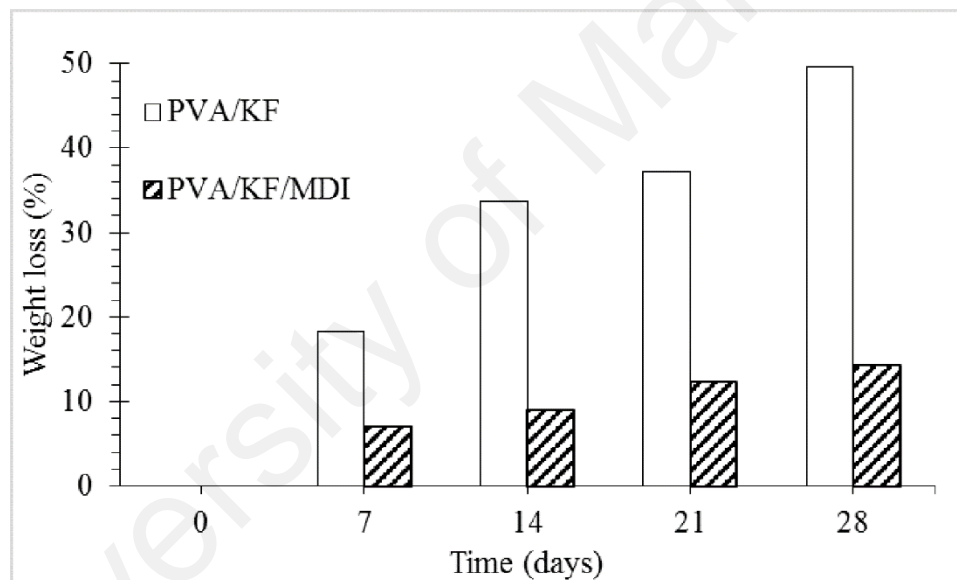


Figure 4.17: Weight loss of the buried composite samples in soil.

### 4.5.3 Morphological analysis

Figure 4.18 and Figure 4.19 are images of the surfaces of the PVA/KF mulches before and after soil burial. Initially, both of the composites showed smooth surfaces. After 28 days of degradation in soil, the PVA/KF composite showed large cracks and white spots on its surface due to the attack by microorganisms (Figure 4.18b). It has been reported earlier by Qiu and Netravali (2013) that during composting of PVA by fungal hyphae, deep cracks were formed on the surface. The cross-linked sample showed only



micro-cracks, smaller and less white spots (Figure 4.19b) on the surface after 28 days of soil burial. The cross-links have reduced the moisture penetration and lower the microbial activities.

It is plausible that the biodegradation of PVA/KF composites could have occurred in two stages. Initially, moisture affected the composites by slowly dissolving the PVA and swelling the kenaf fibres, causing the composite to loss mechanical strength, leading to cracks on the surface. Subsequently the growth of microorganisms would cause further breaking down of the PVA as well as the kenaf fibres.

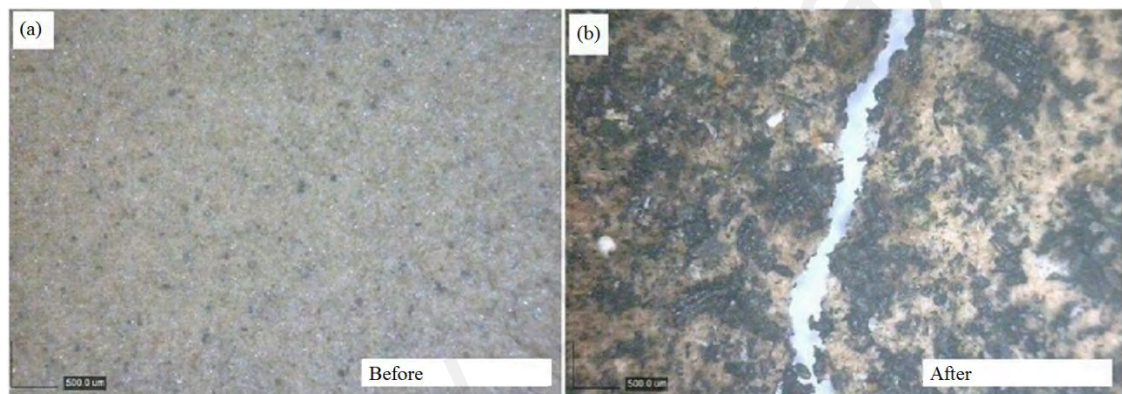


Figure 4.18: Optical micrographs of PVA/KF samples before and after degradation test.

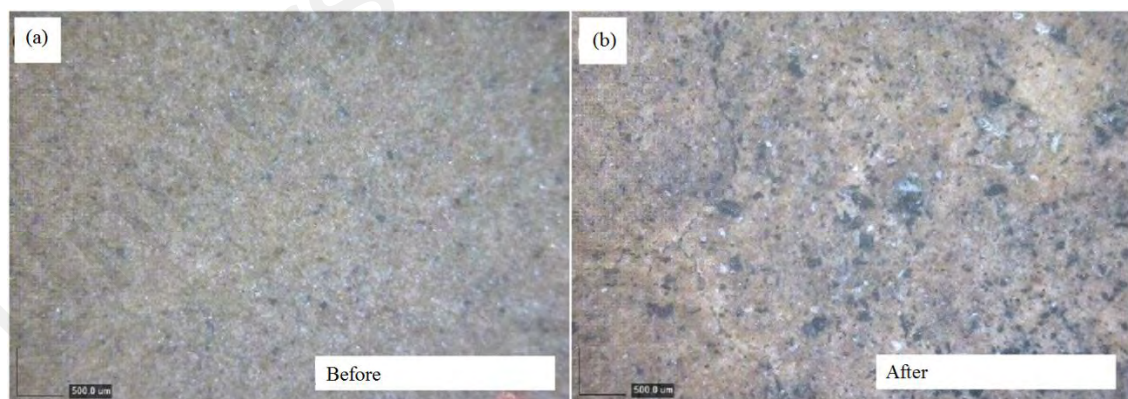


Figure 4.19: Optical micrographs of cross-linked PVA/KF samples before and after degradation test.

## **4.6. Field performance of PVA/KF based composites**

### **4.6.1 Behaviour of mulches**

For the countries located in the equatorial region such as Malaysia, their environment is characterized by tropical rainforest climate, being hot and humid throughout the year, with short spell of heavy rain during the wet seasons. The temperature range is between 28 to 36°C throughout the year. According to the data obtained from Malaysian Meteorological Department, the total rainfall at Petaling Jaya state is around 400 mm throughout these 30 days experimental period.

The rainfall that occurred in this area may have triggered the start of biodegradation. As a result of these humid conditions, the first degradation sign of biodegradable mulches appeared in around 5 to 7 days by forming holes on the soil surface. The PVA/KF was the most affected by showing large holes and breakage. Despite their early decomposition, they remained functional because the soil was still covered by kenaf fibres. Chiellini *et al.* (2008) had confirmed the strong interaction of PVA with soil as a binding agent and proposed that the renewable resources filler had improved the life span of PVA on soil. All the biodegradable mulches degraded gradually from time to time. At the end of days, the biodegradable mulches were not visible because they were incorporated into the soil. On the other hand, the PE mulches were still remained on the soil and required hand pick-up for removal.

### **4.6.2 Plants growth**

The growth performance of plants at different ages was measured. Table 4.7 shows the mulching materials had significant influence on the plant growth. The images of field trial are shown in Figure 4.19 and Figure 4.20. Generally, the plants in the control plot are the shortest. In comparison with PVA/KF, PVA/KF/MDI and PE plot in 30 DAS

(days of sowing), the plants at control soil were 9.7%, 1.9% and 5.3% shorter, respectively. In addition, the plants also suffered lower number of primary branches and leaves compared to all the mulched soil. This result is expected due to the vigorous competition between the plants and weeds. In the plot without mulches, the plants compete with weeds for available space, sun lights and soil nutrients. As a result, the plants were weaker and less healthy than the plants under protection of mulches.

On the other hand, the plants under the care of biodegradable mulches were healthy and strong. In plot which PVA/KF/MDI mulches were adopted, the plants had more leaves and branches compared to the plants in PVA/KF-mulched plot. In terms of plant height, the plants were also 5.4% higher than the plants in PVA/KF-mulched plot at 10 DAS, indicating the effectiveness of cross-linked PVA/KF in protecting the small plants. This is because MDI cross-linked mulches could last longer on the soil than PVA/KF to provide sufficient protection.

Surprisingly, a reversed result of plant height was observed at 20 and 30 DAS. The plants under the care of PVA/KF mulches were 3.5% (20 DAS) and 7.7% (30 DAS) higher than the plants in PVA/KF/MDI plot. These findings probably can be explained by the rapid disintegration of PVA/KF mulches compare to PVA/KF/MDI mulches, leaving kenaf fibres on the soil to act as fertilizer to the plants. From another point of view, the early degradation of PVA/KF could also provide growth advantage to the plants by supplying organic matter or nutrients to the plants. Both of these biodegradable mulches showed similar growth performance despite the shorter lifespan of PVA/KF than PVA/KF/MDI.

For conventional mulching method using PE films, the plant height, number of primary branches and leaves per plant also increased steadily in 30 DAS. This is because PE films are able to provide basic protection to the plants, preventing the emergence of weeds and competition of nutrients to occur. However, the two biodegradable mulches

formulations, PVA/KF and PVA/KF/MDI performed slightly better than PE mulches. The biodegradable mulches are able to conserve the soil moisture, and subsequently reduce the irrigation frequency. Moreover, the PE films require proper disposal system whereas biodegradable mulches would self-degrade in the field, resulting in significant savings in cost and time.

The results suggest that biodegradable mulches could be alternative mulch to PE from the environment point of view. Other researchers also reported the similar suggestion. In a field experiment conducted under continental Mediterranean conditions, Martin-Closas *et al.* (2008) also reported the plant growth performance for biodegradable mulches was comparable to PE films. Martin-Closas *et al.* (2008) reported that the highest production in terms of fruits weight and number of fruits per plant was found with the biodegradable mulches and PE films.

Table 4.7: The growth performance of plants within 30 days.

| Mulch materials | Average plant height |       |       | Number of primary branches per plant |      |      | Number of leaves per plant |      |      |
|-----------------|----------------------|-------|-------|--------------------------------------|------|------|----------------------------|------|------|
|                 | 10                   | 20    | 30    | 10                                   | 20   | 30   | 10                         | 20   | 30   |
|                 | DAS                  | DAS   | DAS   | DAS                                  | DAS  | DAS  | DAS                        | DAS  | DAS  |
| Control         | 10.12                | 12.50 | 13.45 | 1.20                                 | 2.00 | 1.30 | 5.00                       | 6.30 | 5.70 |
| PE              | 10.16                | 13.59 | 14.16 | 0.80                                 | 1.00 | 1.70 | 5.40                       | 7.00 | 7.80 |
| PVA/KF          | 9.75                 | 12.84 | 14.75 | 1.00                                 | 1.30 | 1.80 | 5.00                       | 7.00 | 8.00 |
| PVA/KF/MDI      | 10.28                | 12.41 | 13.70 | 0.80                                 | 1.00 | 2.00 | 4.30                       | 5.00 | 8.50 |



Figure 4.20: Images of the field trial, (a) PVA/KF on the soil at 3 DAS, (b) cross-linked PVA/KF after 7 DAS, (c) PVA/KF after 7 DAS.

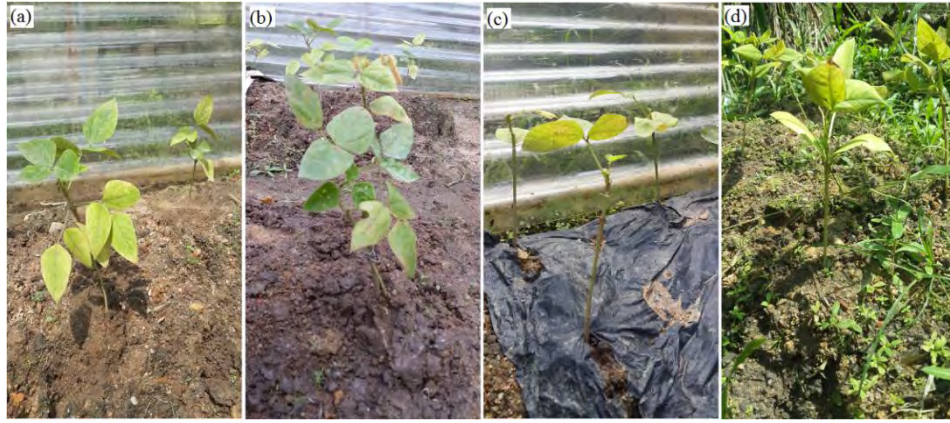


Figure 4.21: Images of plants after 30 DAS: (a) PVA/KF, (b) cross-linked PVA/KF, (c) PE, (d) control.

#### 4.6.3 Soil temperature

Soil temperature has a major influence on plant growth. It can be conditioned by soil water effects, rainfall and the seasonal changes. Table 4.8 shows the soil temperature at 5 and 10 cm depth for morning (0800 h), afternoon (1200 h) and evening session (1600 h). The results show that different mulching materials would have varying effects on the soil temperature. From Table 4.8, the soil was cooler under biodegradable mulches and highest under PE mulches. The soil temperature was also decreased with increasing soil depth for all the mulches as expected. In all cases, the soil temperature increased gradually during the days and decreased slightly in the evening. The differences in the soil temperature could be attributed to the composition of PE and biodegradable mulches.

For the control soil, the soil temperature fluctuated from time to time. The soil was warm in the afternoon because it was unprotected from direct sun lights but cooled down rapidly due to heat transfer on ground. The soil temperature recorded for PE mulches was the highest for all times. This is because the black PE mulches tend to absorb radiant energy during the days. The thermal effect of PE mulches remained until at night because they were less likely to reduce the heat loss from ground. The highest increment in soil temperature took place in the afternoon 1200 h with a record of 32.3 °C at 30 DAS.

The soil temperature at 5 and 10 cm soil depth for PVA/KF and PVA/KF/MDI was similar. Lowest soil temperature was marked for both of these mulches during the beginning of crops growth stage. The temperature measured on the soil covered by biodegradable mulches was marked at 26 °C for most of the time, indicating that PVA/KF is effective in reducing the fluctuations of soil temperature. According to Moreno and Moreno (2008), 26 °C is the optimum temperature for vegetable (particularly for tomato) and fruits to grow. However, the soil temperature was 1-2°C higher at 20 DAS when the plants grew higher. The soil temperature recorded for control and biodegradable mulches in particular for PVA/KF was almost similar at 30 DAS. This is because some part of the biodegradable mulches were decomposed, exposing the soil to sun lights. These results are in good agreement with the result reported by Moreno and Moreno (2008).

Table 4.8: The soil temperature data.

|                       | 10 DAS |      |      | 20 DAS |      |      | 30 DAS |      |      |
|-----------------------|--------|------|------|--------|------|------|--------|------|------|
|                       | 0800   | 1200 | 1600 | 0800   | 1200 | 1600 | 0800   | 1200 | 1600 |
| <b>at 5 cm depth</b>  |        |      |      |        |      |      |        |      |      |
| Control               | 27.7   | 29.7 | 28.0 | 27.7   | 31.5 | 29.5 | 27.3   | 30.0 | 29.0 |
| PE                    | 27.3   | 29.3 | 29.0 | 27.5   | 31.0 | 30.3 | 27.7   | 32.3 | 30.0 |
| PVA/KF                | 26.7   | 28.3 | 28.0 | 27.0   | 29.7 | 29.0 | 26.5   | 29.7 | 28.0 |
| PVA/KF/MDI            | 26.7   | 27.3 | 27.0 | 27.3   | 28.3 | 28.0 | 26.3   | 29.0 | 28.3 |
| <b>at 10 cm depth</b> |        |      |      |        |      |      |        |      |      |
| Control               | 26.3   | 28.7 | 27.0 | 26.3   | 28.5 | 27.0 | 26.3   | 29.0 | 28.0 |
| PE                    | 27.0   | 28.7 | 28.0 | 27.0   | 29.5 | 29.3 | 27.3   | 29.0 | 28.7 |
| PVA/KF                | 26.3   | 27.0 | 27.0 | 26.0   | 28.5 | 28.7 | 26.3   | 28.5 | 28.3 |
| PVA/KF/MDI            | 26.0   | 27.0 | 27.0 | 26.0   | 27.0 | 27.0 | 26.0   | 28.0 | 28.0 |

#### 4.6.4 Soil aggregate and stability

According to the Soil Science Society of America, soil aggregate is defined as a group of primary soil particles that cohere to each other more strongly than to other surrounding particles (Dane & Topp, 2002). From Figure 4.22(d), it is expected that

heavy weeds growth was observed on the bare soil without an evident of soil aggregates after 30 DAS. On the other hand, the soil aggregates were observed in the plot where biodegradable mulches were adopted. However, the soil aggregate size and stability were difficult to measure due to the presence of kenaf fibres used in the mulches. Despite that, the soil aggregates were evident on the soil surface as shown in Figure 4.22(b-c). Kenaf fibres in biodegradable mulches conferred a brown colour to the soil.

Besides, it is also observed that biodegradable mulches were partially incorporated into the soil. During the degradation of PVA/KF, the PVA was first degraded by moisture from soil and migrated into the soil. Interestingly, a layer of kenaf fibres and soil was formed which may be due to the adhesive characteristic of PVA to the soil. The soil under these mulches was moist, indicating the soil moisture was well conserved under biodegradable mulches. Similar observation was also reported when hydro-mulching based on PVA and bio-based filler was carried out on field (Chiellini *et al.*, 2008). Soil aggregates were seen in the plot of PVA/KF/MDI but they were not visible in the plot of PE-mulched soil and control soil. Under PE films, the soil was well structured without weeds but appeared in dry condition (Figure 4.22a). These observations supported the high temperature recorded for PE films in Table 4.8, suggesting the loss of soil moisture.

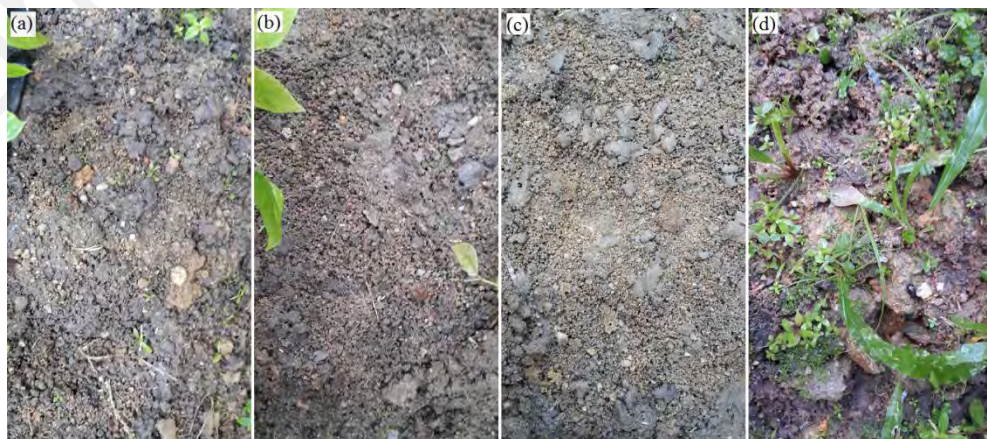


Figure 4.22: Appearance of soil surface after 30 days: (a) PE, (b) PVA/KF, (c) cross-linked PVA/KF, (d) control soil.

## CHAPTER 5: CONCLUSION

### 5.1 Conclusion

Biodegradable mulches are considerably part of green technologies. Unlike the conventional PE films, they do not end up in landfills at the end of their life instead they would self-degrade in suitable environment. The present study shown that biodegradable mulches were developed based on PVA and sustainable resources, kenaf fibre by simple solution casting methods. These biodegradable mulches were are easy to manipulate and they are completely environment and cost-friendly. The research trend is to improve their properties and further broaden their applications.

The biodegradable PVA/kenaf fibre composites with different urea loading were produced using simple blending and casting method. These composites exhibited good water solubility and controlled release property. The water solubility of the composites was not affected by the loading of urea. The composite reached 12% of water solubility in 24 hours, increasing slowly to 14% in 3 days and finally achieved 25% after 7 days. This result implies that the composite could last for a reasonable length of service time in static aquatic conditions. The release behaviour of urea was examined and was found that the entrapped urea could diffuse out from the polymer matrix into the soil through the water medium. The composite that contains 10-wt% of urea released 25% of the urea content in the first hour. The urea content in the water increased to 36% after 10 hours, while a total of 57% of the urea was released into the water after 24 hours.

The nutrients release rate of these composite is less likely to conform to the standard published by the International Fertilizer Industry Association. Therefore, cross-linking agent was introduced in certain amount to reduce the moisture permeability of the polymers. In this study, MDI was selected. The results show that incorporation of MDI



successfully enhanced the thermal stability and improved the water barrier property of the composites. Such enhancement effect increases with increased MDI loading. The FTIR study confirmed that the cross-linking in the composites was formed and a positive relation among cross-linking, water diffusion, and thermal stability has found.

One of the most important properties of biodegradable mulches is their biodegradability. The biodegradable behaviours of cross-linked and uncross-linked PVA/KF composites as mulches were studied by using soil burial method in flower pot. Experimental data showed that the biodegradation of PVA/KF composites had resulted in weight loss, cracks, chemical changes, and fungal appearance in soil burial for 28 days. The weight loss of PVA/KF composite increased from 18% in 7 days, and to 50% after 28 days. On the other hand, the weight loss of MDI cross-linked PKV/KF composite increased at a much slower rate, from 7% in 7 days, to 14% after 28 days of biodegradation. The results showed that the introduction of cross-linking can slow down the degradation rate.

The composites were also tested in small garden plot after the biodegradation study. The long beans plants were healthy and strong under the protection of PVA/kenaf fibre mulches. The plant height was also comparable to the plants where PE films were adopted. These biodegradable composite mulches could retain the soil moisture better than the PE films. The implementation of PVA helps the mulches to remain intact with soil. From time to time, these PVA/KF based mulches would degrade into soil with a consequent positive environmental impact. These results showed that the materials have short service time, sufficient to protect the seedlings for 15-30 days.

Overall, PVA/KF based biodegradable composites seem to be very promising mulches. With good control released property, the composites are suitable carrier materials for urea. Incorporation of MDI allows the composites to be employed at high temperature and humidity areas. In field trial, these biodegradable mulches were able to

achieve similar plant performance as the traditional mulching method, PE films. With good biodegradability, no undesirable accumulation of plastic residues would occur in field, remaining kenaf fibres as a natural fertilizer for seedlings. These composites do not create any disposal problem and could be promising alternative materials for the replacement of PE films on crop production. They make the daily work easier for farmers compare to conventional plastic films. The use of these environmentally friendly mulches implies a drastic reduction in man labour and disposal cost.

## **5.2 Suggestions for future works**

The current study has raised several questions for the focus of new research. Kenaf fibre has shown its feasibility to combine with PVA. Future research should be conducted to determine the other pairing of PVA with natural fibre or agro-waste such as palm fibre, coconut coir, wheat straws and so on. Different combinations should be tested for multiple times with different crops, in different climate regimes, seasonal, geographical locations. Different irrigation techniques and frequencies should be assessed to determine their influence on the biodegradation of mulches. Apart from mulches, these composite materials could be developed into other products such as horticulture containers or as carrier mats for fertilizer, herbicides and pesticides.

Additionally, further research should be conducted to determine the best thickness of mulches for optimal crops production. The mulch thickness is an important consideration because it may influence the crop yields, moisture loss, weed management and their own lifespan (degradation time). Previous studies have reported varying level of mulches thickness, which the threshold may be vary among the mulch types, soil types, materials used etc. Moreover, mulches applied in the field experienced varying degrees of decomposition or degradation throughout the year, resulting in varying level of mulch

thickness. It may be necessary to reapply the mulches from time to time in order to maintain sufficient thickness for optimal weed control, minimal moisture loss good and marketable crop yields.

The organic agriculture system is expanding rapidly in these recent years. There is an increasing number of farmers are adopting this system to lower input costs, conserve non-renewable resources, and capture high-value markets to increase farm income. Since such system has attracted great attention, it is important to evaluate whether these mulches is suitable for organic plantation in spring, summer and autumn seasons. Field research should be conducted across a wide range of conditions to verify these mulches do not detriment the agro-ecosystem, as it can decompose completely in soil. It is known that PVA is a synthetic polymer based on non-renewable resources which meet specific biodegradability standards. More studies are needed to evaluate the impacts of any residual materials from biodegradation to the environment. This is essential to confirm these mulches match a defined set of organic standards before it is permitted in organic agriculture system.

After implementation of biodegradable mulches, it is important to determine the impact of biodegradable mulches to soil biological and chemical properties. When biodegradable plastic mulches are ploughed and/or left to degrade in field, it is expected that the mulches will increase the percentage of organic matter due to the high kenaf content in it. The higher the percentage of organic matter will lead to better soil structure, improving water holding capacity of soil, reducing aggregation especially in heavy clay soils (McMillen, 2013). In addition, there should be no formation of any toxic residues or harmful substances. In this study, the soil quality during and after degradation of biodegradable mulches are unclear. The influence of these specific bacteria that decompose the mulches to the soil bacteria community is remained unknown. When high amount of biodegradable mulches were left in field, it is worried that these specific

bacteria may destroys the soil bacteria community structure. Evaluation of soil is to confirm the soil is safe and healthy for the subsequent plantation.

Lastly, a sociological study should be conducted to evaluate the farmers' perceptions about these biodegradable mulches and their attitudes toward the adoption of these mulches in their garden or field. This is also an opportunity to introduce biodegradable mulches to the participants and receive their knowledge, opinions and attitudes about the mulches. Any barriers to adoption of biodegradable mulches can be recorded and used to improve the mulches in further study.

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## REFERENCES

- Abdulkhani, A., Hojati Marvast, E., Ashori, A., Hamzeh, Y. and Karimi, A.N. (2013). Preparation of cellulose/polyvinyl alcohol biocomposite films using 1-n-butyl-3-methylimidazolium chloride. *International Journal of Biological Macromolecules*, 62, 379–386.
- Akil, H. M., Omar, M. F., Mazuki, A. A. M., Safiee, S., Ishak, Z. A. M. and Abu Bakar, A. (2011). Kenaf fiber reinforced composites: a review. *Materials & Design*, 32(8): 4107-4121.
- Anderson, D. F., Garisto, M. A., Bourrut, J. C., Schonbeck, M. W., Jaye, R., Wurzberger, A. and DeGregorio, R. (1995). Evaluation of a paper mulch made from recycled materials as an alternative to plastic film mulch for vegetables. *Journal of Sustainable Agriculture*, 7(1): 39–61.
- Andrady, A. L. (2003). *Plastics and the Environment*. New Jersey: John Wiley & Sons.
- Chiellini, E., Corti, A., D'Antone, S., Ilieva, V. I., Magni, S., Miele, S. and Pampana, S. (2003). Liquid mulch based on poly(vinyl alcohol). PVA-soil interaction. *Macromolecular Symposia*, 197(1): 133-142.
- ASTM D883-12, (2012). *Standard Terminology Relating to Plastics*. U.S.: ASTM International.
- Awal, A., Rana, M. and Sain, M. (2015). Thermorheological and mechanical properties of cellulose reinforced PLA bio-composites. *Mechanics of Materials*, 80, 87–95.
- Azwa, Z. N., Yousif, B. F., Manalo, A.C. and Karunasena, W. A. (2013). Review on the degradability of polymeric composites based on natural fibres. *Materials and Design*, 47, 424–442.
- Bayerl, T., Geith, M., Somashekar, A.A. and Bhattacharyya, D. (2014). Influence of fibre architecture on the biodegradability of FLAX/PLA composites. *International Biodeterioration & Biodegradation*, 96, 18–25.
- Brooks, T. W. (1996). *Method and apparatus for recycling previously used agricultural plastic film mulch*. Retrieved from <http://www.google.com/patents/US5510076>
- Céline, A., Fréour, S., Jacquemin, F. and Casari, P. (2014). The hygroscopic behavior of plant fibers: a review. *Frontiers in Chemistry*, 1, 1-12.
- Cerpakovska, D. and Kalnins, M. (2012). Barrier and sorption properties of porous poly(vinyl alcohol)–cellulose fibre composites. *Proceedings of the Estonian Academy of Sciences* 61, 178–184.

- Chao, K. P., Chow, J. D., Chai, W. L. and Hong, G. M. (2012). Estimation of resistance of starch/polyvinyl alcohol blends to permeation by organic solvents. *Carbohydrate Polymers*, 89, 432–437.
- Chiellini, E., Cinelli, P., Corti, A. and Kenawy, E. R. (2001). Composite films based on waste gelatin: thermal–mechanical properties and biodegradation testing. *Polymer Degradation and Stability*, 73, 549–555.
- Chiellini, E., Cinelli, P., Magni, S., Miele, S. and Palla, C. (2008). Fluid biomulching based on poly(vinyl alcohol) and fillers from renewable resources. *Journal of Applied Polymer Science*, 108, 295-301.
- Chiellini, E., Corti, A., D’Antone, S. and Solaro, R. (2003). Biodegradation of Poly (vinyl alcohol) based materials. *Progress in Polymer Science*, 28, 963 – 1014.
- Chuah, T. G., Wan Azlina, A. G. K., Robiah, Y. and Omar, R. (2006). Biomass as the renewable energy sources in Malaysia: an overview. *International Journal of Green Energy*, 3, 323-346.
- Cinelli, P., Chiellini, E., Gordon, S. H. and Imam, S. H. (2003). Characteristics and degradation of hybrid composite films prepared from PVA, starch and lignocellulosics. *Macromolecular Symposia*, 197, 143-155.
- Cinelli, P., Chiellini, E., Lawton, J. W. and Imam, S. H. (2006a). Properties of injection molded composites containing corn fiber and poly(vinyl alcohol). *Journal of Polymer Research*, 13, 107-113.
- Cinelli, P., Chiellini, E., Lawton, J. W. and Imam, S. H. (2006b). Foamed articles based on potato starch, corn fibers and poly(vinyl alcohol). *Polymer Degradation and Stability* 91, 1147–1155.
- Clarke, S. P. (1996). *Recycling Farm Plastic Films*. Retrieved from <http://www.omafra.gov.on.ca/english/engineer/facts/95-019.htm>
- Clift, M. J. D., Foster, E. J., Vanhecke, D., Struder, D., Wick, P., Gehr, P., Rutishauser, B. R. and Weder, C. (2011). Investigating the Interaction of Cellulose Nanofibers Derived from Cotton with a Sophisticated 3D Human Lung Cell Coculture. *Biomacromolecules*, 12, 3666–3673.
- Corbin, A., Miles, C., Cowan, J., Hayes, D., Dorgan, J. and Inglis, D. (2013a). *Using biodegradable plastics as agricultural mulches*. Retrieved from <http://cru.cahe.wsu.edu/CEPublications/FS103E/FS103E.pdf>
- Corbin, A., Miles, C., Cowan, J., Hayes, D., Moore-Kucera, J. and Inglis, D. (2013b). Current and future prospects for biodegradable plastic mulch in certified organic production systems. Retrieved from <http://www.extension.org/pages/67951/current-and-future-prospects-for-biodegradable-plastic-mulch-in-certified-organic-production-systems#.VW5x0kq1eM8>

- Corradini, E., Marconcini, J. M., Agnelli, J. A. M. and Mattoso, L. H. C. (2011). Thermoplastic blends of corn gluten meal/starch (CGM/Starch) and corn gluten meal/polyvinyl alcohol and corn gluten meal/poly (hydroxybutyrate-co-hydroxyvalerate) (CGM/PHB-V). *Carbohydrate Polymers*, 83, 959-965.
- Costa, L. M. M., Olyveira, G. M. D., Cherian, B. M., Leao, A. L., Souza, S. F. D. and Ferreira, M. (2013). Bionanocomposites from electrospun PVA/pineapple nanofibers/*Stryphnodendron adstringens* bark extract for medical applications. *Industrial Crops and Products*, 41, 198-202
- Dane, J. H. and Topp, G. C. (2002). *Methods of soil analysis, Part 4 – Physical methods*. U.S.: Soil Science Society of America.
- Debiagi, F., Kobayashi, R. K. T., Nakazato, G., Panagio, L. A. and Mali, S. (2014). Biodegradable active packaging based on cassava bagasse, polyvinyl alcohol and essential oils. *Industrial Crops and Products*, 52, 664–670.
- DeMerlis, C. C. and Schonerker, D. R. (2003). Review of the oral toxicity of polyvinyl alcohol (PVA). *Food and Chemical Toxicology*, 41, 319-326.
- Dittenber, D. B. and GangaRao, H. V. S. (2012). Critical review of recent publications on use of natural composites in infrastructure. *Composites Part A: Applied Science and Manufacturing*, 43, 1419–1429.
- Dockery, D. W. and Pope, C. A. (1994). Acute respiratory effects of particulate air pollution. *Annual Review of Public Health*, 15: 107–132.
- Dufresne, A. (2013). Nanocellulose: a new ageless bionanomaterial. *Materials Today*, 16, 220-227.
- El-Salmawi, K. M. (2007). Application of polyvinyl alcohol (PVA)/carboxymethyl cellulose (CMC) hydrogel produced by conventional crosslinking or by freezing and thawing. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, 44, 619-624.
- Finkenstadt, V. L. and Tisserat, B. (2010). Poly(lactic acid) and Osage Orange wood fiber composites for agricultural mulch films. *Industrial Crops and Products*, 31, 316–320.
- Goldberger, J. R., Jones, R. E., Miles, C. A., Wallace, R. W. and Inglis, D. A., (2013). Barriers and bridges to the adoption of biodegradable plastic mulches for US specialty crop production. *Renewable Agriculture and Food Systems*, 30, 143-153.
- Goldschmidt, A. and Streitberger, H. J. (2003). *BASF Handbook on Basics of Coating Technology*. Hannover: Vincentz Network.
- Gonzalez, J. S., Luduena, L. N., Ponce, A. and Alvarez, V. A. (2014). Poly(vinyl alcohol)/cellulose nanowhiskers nanocomposite hydrogels for potential wound dressings. *Materials Science and Engineering: C*, 34, 54–61.

- Goswami, B. C., Anandjiwala, R. D. and Hall, D. M. (2004). *Textile Sizing*. (1<sup>st</sup> ed.). New York: Marcel Dekker, Inc.
- Hajnalka, H., Racz, I. and Anandjiwala, R. D. (2008). Development of HEMP fibre reinforced polypropylene composites. *Journal of Thermoplastic Composite Materials*, 21, 165–74.
- Halley, P., Rutgers, R., Coombs, S., Kettels, J., Gralton, J., Christie, G., Jenkins, M., Beh, H., Griffin, K., Jayasekara, R. and Lonergan, G. (2001). Developing Biodegradable Mulch Films from Starch-Based Polymers. *Starch*, 53, 362–367.
- Han, J., Lei, T. and Wu, Q. (2013). Facile preparation of mouldable polyvinyl alcohol-borax hydrogels reinforced by well-dispersed cellulose nanoparticles: physical, viscoelastic and mechanical properties. *Cellulose*, 20, 2947-2958.
- Hayes, D. G., Dharmalingam, S., Wadsworth, L. C., Leonas, K. K., Miles C. A. and Inglis, D. A. (2012). Biodegradable Agricultural Mulches Derived from Biopolymers. In K. Khemani & C. Scholz (Eds.), *Degradable Polymers and Materials, Principles and Practice*, (pp. 201-223). U.S.: American Chemical Society.
- Holloway, J. L., Lowman, A. M. and Palmese, G. R. (2010). Mechanical evaluation of poly(vinyl alcohol)-based fibrous composites as biomaterials for meniscal tissue replacement. *Acta Biomaterialia*, 6, 4716–4724.
- Hong, Y. C., Lee, J. T., Kim, H., Ha, E. H., Schwartz, J. and Christiani, D. C. (2002). Effects of air pollutants on acute stroke mortality. *Environmental Health Perspectives*, 110(2): 187–191.
- Imam, S. H., Cinelli, P., Gordon, S. H. and Chiellini, E. (2005). Characterization of Biodegradable Composite films prepared from blends of poly(vinyl alcohol), cornstarch, and lignocellulosic fiber. *Journal of Polymers and the Environment*, 13, 47-55.
- Immirzi, B., Santagata, G., Vox, G. and Schettini, E. (2009). Preparation, characterisation and field-testing of a biodegradable sodium alginate-based spray mulch. *Biosystems Engineering* 102, 461 – 472.
- Jandas, P. J., Mohanty, S., Nayak, S. K. (2013). Sustainability, Compostability, and Specific Microbial Activity on Agricultural Mulch Films Prepared from Poly(lactic acid). *Industrial & Engineering Chemistry Research*, 52, 17714-17724.
- Jayasekara, R., Harding, I., Bowater, I., Christie, G. B. Y. and Lonergan, G. T. (2004). Preparation, surface modification and characterisation of solution cast starch PVA blended films. *Polymer Testing*, 23, 17–27.
- Kalapakdee, A., and Amornsakchai, T. (2014). Mechanical properties of preferentially aligned short pineapple leaf fiber reinforced thermoplastic elastomer: Effects of fiber content and matrix orientation. *Polymer Testing*, 37, 36-44.



- Kapanen, A., Schettini, E., Vox, G. and Itavaara, M. (2008). Performance and Environmental Impact of Biodegradable Films in Agriculture: A Field Study on Protected Cultivation. *Journal of Polymers and the Environment*, 16, 109-122.
- Kasirajan, S. and Ngouajio, M. (2012). Polyethylene and biodegradable mulches for agricultural applications: a review. *Agronomy for Sustainable Development*, 32, 501–529.
- Kim, S. J., Moon, J. B., Kim G. H. and Ha, C. S. (2008). Mechanical properties of polypropylene/natural fiber composites: Comparison of wood fiber and cotton fiber. *Polymer Testing*, 27, 801-806.
- Kinnersley, A. M., Scott, T. C., Yopp, J. H. and Whitten, G. H. (1990). Promotion of plant growth by polymers of lactic acid. *Plant Growth Regulation*, 9, 137–146.
- Kitamoto, H. K., Shinozaki, Y., Cao, X., Morita, T., Konishi, M., Tago, K., Kajiwara, H., Koitabashi, M., Yoshida, S., Watanabe, T., Yamashita, Y. S., Kambe, T. N. and Tsushima, S. (2011). Phyllosphere yeasts rapidly break down biodegradable plastics. *AMB Express*, 1:44.
- Kotrba, R. (2008, April). What to do with the remnants of a plastic culture. *Biomass*. Retrieved from [http://www.biomassmagazine.com/article.jsp?article\\_id=1532](http://www.biomassmagazine.com/article.jsp?article_id=1532)
- Kovacs, T., Naish, V., O'Connor, B., Blaise, C., Gagné, F., Hall, L., Trudeau, V. and Martel, P., (2010). An ecotoxicological characterization of nanocrystalline cellulose (NCC). *Nanotoxicology*, 4, 255-270.
- Kumar, A., Negi, Y. S., Choudhary, V. and Bhardwaj, N. K. (2014). Effect of modified cellulose nanocrystals on microstructural and mechanical properties of polyvinyl alcohol/ovalbumin biocomposite scaffolds. *Materials Letters*, 129, 61–64.
- Laboulfie F., Hemati, M., Lamure, A. and Diguët, S. (2013). Effect of the plasticizer on permeability, mechanical resistance and thermal behaviour of composite coating films. *Powder Technology*, 238, 14-19.
- Lamont, W. (2004). *Production of vegetables, strawberries and cut flowers using plasticulture*. New York: Natural Resources, Agriculture and Engineering Service (NRAES).
- Lee, T. S., Rahman, W. A. W. A., Rahmat, A. R. and Mokhtar, M. (2011). Determination of thermal stability and activation energy of polyvinyl alcohol–cassava starch blends. *Carbohydrate Polymers*, 83, 303–305.
- Levitan, L. and Barro, A. (2003). Recycling agricultural plastics in New York State. Retrieved from <http://cwmi.css.cornell.edu/recyclingagplastics.pdf>
- Lin, C. C., Lee, L. T. and Hsu, L. J. (2014). Degradation of polyvinyl alcohol in aqueous solutions using UV-365 nm/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> process. *International Journal of Environmental Science and Technology*, 11, 831–838.

- Madbouly, S. A., Schrader, J. A., Srinivasan, G., Liu, K., McCabe, K. G., Grewell, D., Graves, W. R. and Kessler, M. R. (2014). Biodegradation behaviour of bacterial-based polyhydroxyalkanoate (PHA) and DDGS composites. *Green Chemistry*, *16*, 1911-1920.
- Maiti, S., Ray, D., Mitra, D. and Mukhopadhyay, A. (2013). Isolation and characterisation of starch/polyvinyl alcohol degrading fungi from aerobic compost environment. *International Biodeterioration & Biodegradation*, *82*, 9-12.
- Majumdar, S. and Adhikari, B. (2005). Polyvinyl alcohol-cellulose composite: a taste sensing material. *Bulletin of Materials Science*, *28*, 703-712.
- Maran, J. P., Sivakumar, V., Thirugnanasambandham, K. and Sridhar, R. (2014). Degradation behavior of biocomposites based on cassava starch buried under indoor soil conditions. *Carbohydrate Polymers*, *101*, 20-28.
- Mathew, A. P., Oksman, K. and Sain, M. (2005) Mechanical properties of biodegradable composites from polylactic acid (PLA) and microcrystalline cellulose (MCC). *Journal of Applied Polymer Science*, *97*, 2014-2025.
- McMillen, M. (2013). *The effect of mulch type and thickness on the soil surface evaporation rate* (Degree's thesis). Retrieved from <http://digitalcommons.calpoly.edu/hcssp/22/>
- Michael and Irene Ash. (2004). *Handbook of Green Chemical*. (2<sup>nd</sup> ed.). USA: Synapse Information Resources, Inc.
- Mihrianyan, A. (2013). Viscoelastic properties of cross-linked polyvinyl alcohol and surface-oxidized cellulose whisker hydrogels. *Cellulose*, *20*, 1369-1376.
- Miles, C., Beus, C., Corbin, A., Wallace, R., Saez, H., Walters, T., Leonas, K., Brodhagen, M., Hayes, D. and Inglis, D. (2009). Research and extension priorities to ensure adaptation of high tunnels and biodegradable plastic mulch in the United States. Retrieved from <http://mtvernon.wsu.edu/hightunnels/Content/Miles-et-al-key-informant-survey-paper.pdf>
- Mohanty, J. R., Das, S. N., Das, H. C., Mahanta, T. K. and Ghadei, S. B. (2014). Solid Particle Erosion of Date Palm Leaf Fiber Reinforced Polyvinyl Alcohol Composites. *Advances in Tribology*, *2014*, 8 pages, doi:10.1155/2014/293953
- Mohanty, J. R., Das, S. N., Das, H. C. and Swain, S. K. (2013). Effective mechanical properties of polyvinylalcohol biocomposites with reinforcement of date palm leaf fibers. *Polymer Composites*, *34*, 959-966.
- Monti, A. and Alexopoulou, E. (2013). *Kenaf: A Multi-Purpose Crop for Several Industrial Applications: New insights from the Biokenaf Project*, London: Springer Verlag.

- Moreno, M. M. and Moreno, A. (2008). Effect of different biodegradable and polyethylene mulches on soil properties and production in a tomato crop. *Scientia Horticulturae*, 116(3): 256-263.
- Mwaikambo, L. Y. and Bisanda, E. T. N. (1999). The performance of cotton–kapok fabric–polyester composites. *Polymer. Test.ing*, 18, 181-198.
- Narayan, R., 2010. Misleading claims and misuse proliferate in the nascent. *Bioplastics Magazine*, 5. Retrieved from [http://www.bioplasticsmagazine.com/bioplasticsmagazine-wAssets/docs/article/1001\\_p38\\_bioplasticsMAGAZINE.pdf](http://www.bioplasticsmagazine.com/bioplasticsmagazine-wAssets/docs/article/1001_p38_bioplasticsMAGAZINE.pdf)
- Ni, H., Zeng, S., Wu, J., Cheng, X., Luo, T., Wang, W., Zeng, W. and Chen, Y. (2012). Cellulose nanowhiskers: Preparation, characterization and cytotoxicity evaluation. *Bio-Medical Materials and Engineering*, 22, 121–127.
- Nickerson, R. (1973). Polyvinyl alcohol adhesive composition with high wet tack containing a boron compound and a cis 1,2-polyol compound. Retrieved from <http://www.google.com/patents/US3720633>
- Niu Y and Li H (2012). Controlled release of urea encapsulated by starch-g-poly(vinyl acetate). *Industrial & Engineering Chemistry Research*, 51, 12173-12177.
- Odian, G.C. (2004). *Principles of Polymerization*. (4th ed.). New Jersey: John Wiley & Sons, Inc.
- Ooi, Z. X., Ismail, H., Abu Bakar, A. and Abdul Aziz, N. A. (2012). Properties of the crosslinked plasticized biodegradable poly(vinylalcohol)/rambutan skin waste flour blends. *Journal of Applied Polymer Science*, 125, 1127-1135.
- Ozaki, S. K., Monteiro, M. B. B., Yano, H., Imamura, Y. and Souza, M. F. (2005). Biodegradable composites from waste wood and poly(vinyl alcohol). *Polymer Degradation and Stability*, 87, 293–299.
- Pang, J., Liu, X., Zhang, X., Wu, Y. and Sun, R. (2013). Fabrication of Cellulose Film with Enhanced Mechanical Properties in Ionic Liquid 1-Allyl-3-methylimidazolium Chloride (AmimCl). *Materials*, 6, 1270-1284.
- Qiu, K., and Netravali, A. N. (2012). Fabrication and characterization of biodegradable composites based on microfibrillated cellulose and polyvinyl alcohol. *Composites Science and Technology*, 72, 1588–1594.
- Qiu, K., and Netravali, A. N. (2013). A composting study of membrane-like polyvinyl alcohol based resins and nanocomposites. *Journal of Polymers and the Environment*, 21, 658-674.
- Rahman, M. M., Afrin, S. and Haque, P. (2014). Characterization of crystalline cellulose of jute reinforced poly(vinyl alcohol) (PVA) biocomposite film for potential biomedical applications. *Progress in Biomaterials*, 3, 1-9.

- Rahman, W. A. W. A., Lee T. S., Rahmat, A. R. and Samad, A. A. (2010). Thermal behaviour and interactions of cassava starch filled with glycerol plasticized polyvinyl alcohol blends. *Carbohydrate Polymers*, 81, 805–810.
- Ramakrishna, A., Tam, H. M., Wani, S. P. and Long. T. D. (2006). Effect of mulch on soil temperature, moisture, weed infestation and yield of groundnut in northern Vietnam. *Field Crops Research*, 95, 115-125.
- Ramaraj, B. (2007). Crosslinked poly(vinyl alcohol) and starch composite films. II. Physicomechanical, thermal properties and swelling studies. *Journal of Applied Polymer Science*, 103, 909-916.
- Rolando, T. E. (1998). *Solvent-Free Adhesives*. Shawbury: Rapra Technology Ltd.
- Rosa, S. M. L., Rehman, N., Miranda, M. I. G. D., Nachtigall, S. M. B. and Bica, C. I. D. (2012). Chlorine-free extraction of cellulose from rice husk and whisker isolation. *Carbohydrate Polymers*, 87, 1131– 1138.
- Sarasa, J., Gracia, J. M. and Javierre, C. (2009). Study of the biodegradation of a bioplastic material waste. *Bioresource Technology*, 100, 3764–3768.
- Sartore, L., Vox, G. and Schettini, E. (2013). Preparation and Performance of Novel Biodegradable Polymeric Materials Based on Hydrolyzed Proteins for Agricultural Application. *Journal of Polymers and the Environment*, 21, 718–725.
- Shi, L., Ao, L., Kang, H. and Su, H. (2012). Evaluation of Biodegradable Films Made of Waste Mycelium and Poly(Vinyl Alcohol) on the Yield of Pak-Choi. *Journal of Polymers and the Environment*, 20, 492-500.
- Shogren, R. L. (1999). Preparation and characterization of a biodegradable mulch: paper coated with polymerized vegetable oils. *Journal of Applied Polymer Science*, 73(11): 921–967.
- Shogren, R. L. (2000). Biodegradable mulches from renewable resources. *Journal of Sustainable Agriculture*, 16(4): 33–47.
- Shrefler, J. and Brandenberger, L. (1991). *Use of plastic mulch and row covers in vegetable production*. Retrieved from <http://pods.dasn.okstate.edu/docushare/dsweb/Get/Document-1099/F-6034%20web.pdf>
- Spoljaric, S., Salminen, A, Luong, N. D. and Seppala, J. (2014). Stable, self-healing hydrogels from nanofibrillated cellulose, poly(vinyl alcohol) and borax via reversible crosslinking. *European Polymer Journal*, 56, 105–117.
- Toh W. Y., Rahman, W. A. W. A. and Lee, T. S. (2011). Properties and morphology of poly(vinyl alcohol) blends with sago pith bio-filler as biodegradable composites. *Journal of Vinyl and Additive Technology*, 17, 184–189.

- Vartiainen, J., Pöhler, T., Sirola, K., Pylkkänen, L., Alenius, H., Hokkinen, J., Tapper, U., Lahtinen, P., Kapanen, A., Putkisto, K., Hiekkataipale, P., Eronen, P., Ruokolainen, J. and Laukkanen, A. (2011). Health and environmental safety aspects of friction grinding and spray drying of microfibrillated cellulose. *Cellulose*, 18, 775-786.
- Wang, S., Ren, J., Li, W., Sun, R. and Liu, S. (2014). Properties of polyvinyl alcohol/xylan composite films with citric acid. *Carbohydrate Polymers*, 103, 94–99.
- Warnick, J. P., Chase, C. A., Roskopf, E. N., Simonne, E. H., Scholberg, J. M. (2006). Weed suppression with hydramulch, a biodegradable liquid paper mulch in development. *Renewable Agriculture and Food Systems*, 21, 216–223.
- Wei, L., Liang, S. and McDonald, A. (2015). Thermophysical properties and biodegradation behavior of green composites made from polyhydroxybutyrate and potato peel waste fermentation residue. *Industrial Crops and Products*, 69, 91–103.
- Xu, X., Yang, Y. Q., Xing, Y. Y., Yang, J. F. and Wang, S. F. (2013). Properties of novel polyvinyl alcohol/cellulose nanocrystals/silver nanoparticles blend membranes. *Carbohydrate Polymers*, 98, 1573–1577.
- Yip, H. L., Shaaban, A., Mitan, N. M. M., Dimin, M. F., Mohamad, N., Hamid, N. and Sian, M. S. (2013). Characterization of urea encapsulated by biodegradable starch-PVA-glycerol. *Journal of Polymers and the Environment*, 21, 1083-1087.
- Yu, T., Jiang, N. and Li, Y. (2014). Study on short ramie fiber/poly(lactic acid) composites compatibilized by maleic anhydride. *Composites Part A: Applied Science and Manufacturing*, 64, 139-146.
- Zhang, L., Zhang, G., Lu, J. and Liang, H. (2013). Preparation and characterization of carboxymethyl cellulose/polyvinyl alcohol blend film as a potential coating material. *Polymer-Plastics Technology and Engineering*, 52, 163-167.
- Zheng, Q., Cai, Z. and Gong, S. (2014). Green synthesis of polyvinyl alcohol (PVA)–cellulose nanofibril (CNF) hybrid aerogels and their use as superabsorbents. *Journal of Materials Chemistry A*, 2, 3110-3118.

## LIST OF PUBLICATION

- Tan, B. K., Ching, Y. C., Gan, S. N. and Rozali, S. (2015). Biodegradable Mulches Based on Poly(vinyl Alcohol), Kenaf Fiber, and Urea. *Bioresources*, 10, 5532-5543.
- Tan, B. K., Ching, Y. C., Gan, S. N., Ramesh, S. and Rahman, M. R. (2014). Water Absorption Properties of Kenaf Fibre–Poly(vinyl alcohol) Composites. *Materials Research Innovations*, 18, 144-146.
- Tan, B. K., Ching, Y. C., Gan, S. N. and Rozali, S. Effect of Diisocyanate on the Properties of Biodegradable Poly(vinyl alcohol)/Kenaf Fibers Mulches. – Under review by *European Polymer Journal*.
- Tan, B. K., Ching, Y. C., Poh, S. C., Abdullah, L. C., and Gan, S. N. A Review of Natural Fiber Reinforced Poly(Vinyl Alcohol) Based Composites: Application and Opportunity. – Under review by *Polymers*.
- Tan, B. K., Ching, Y. C. and Gan, S. N. Novel Environmental Friendly Poly(vinyl alcohol)/Kenaf Fibre Mulches. – Submitted to *Polymer Degradation and Stability*.