CHAPTER 1

INTRODUCTION

1.1 Current Perspectives and Future Prospects of Composite Material: An Overview

A composite material can be defined as heterogeneous mixture of two or more homogeneous phases which have been mixed together. The term composite originally arose when two or more materials were combined in order to develop a useful final product. Nowadays, the term composite is referred to the combination of very strong and stiff fibres with weak matrix which is designed to hold the fibres together. The composite material is developed to achieve high strength and stiffness (due to fibres) and resistance to crack propagation (due to interaction between fibres and matrix). The application of composites was first used in sailing ship which consisted of wood planking on iron frames where the wood covered with copper plates in order to prevent attack of marine organism on the wood [1].

Composites provide almost every aspect of modern materials technology and of everyday life. They depend primarily on the use of strong, stiff fibres to upgrade the performance of traditional bulk materials in construction. Reinforced plastics are the most highly developed class of composite material and an attempt is made to illustrate their wide variety of applications.

Composites material is chosen over traditional material for its good corrosive resistance, greater design flexibility and ability to produce complex parts as well as good electrical and thermal insulating properties. Therefore, composites are widely used in automotive and aircraft parts, industrial storage tank, sport equipment and textile spinning machinery.

In spite of their advantages, fibre reinforced polymer composite however, has a limited performance at high elevated temperatures due to thermal degradation of the polymer matrix. This fact is in line with the study reported by Bowen [2], where they found that most of the fibre reinforced polymer composites (FRPC) lose their strength and stiffness after a long continuous operation in the range of 250˚C-300˚C. Even though there are polymers that high temperature resistance, they are found to be expensive that leads to higher manufacturing cost. Fortunately, with the extensive studies done by researchers recently, both thermoplastic and thermoset have been developed to raise their heat distortion and glass transition temperature, T_g in order to improve composite performance.

1.2 Applications of Fibre Reinforced Polymer Composites (FRPC)

The range of application for polymer matrix composites is very broad and has been now marketed commercially. They include consumer goods, sports equipment, electrical and electronic components as well as construction and building industries. Their use in transportation sector especially, are so wide and common due to their advantages in corrosive resistance, ability to resist impact damage, light weight and most importantly cost saving [2-5].

In general, composite materials are durable and provide flexibility in materials design. The greatest advantages of composites materials are high specific strength and stiffness, as well as light weight. FRPC is ideally used in products and also for strengthening existing structures, which are exposed to extreme environments due to good resistance to heat and corrosion. Recently, civil engineers who are involved in designing the new version of construction have used FRPC as one of the new advanced composite material in order to get the optimum benefit and less poor quality products.

Furthermore, what makes FRPC different from others is its ability to work in severe conditions effectively. Structures such as bridges and columns built that with FRPC have demonstrated exceptional durability and effective resistance against environmental exposure. Architects have also discovered many applications, whereby FRPC can be used; these include structures such as cladding, roofing, flooring and partitions. Recently, both military and civil fields are the main areas that apply these materials in order to improve products quality and reduce cost for maintenance and rehabilitation. In fact, the demands for these industries have been the main force in improving the development of composites materials [3].

1.3 Research Background

A great number of research and development have been done to improve the performance of fibre reinforced polymer composites for variety application in recent years. Glass fibre reinforced polymer composites remain as the largest quantity structural composite material in present use, as they were found widely in building, boat and ship construction, aircraft and automobile structures, chemical plant, and in a wide range of ordinary domestic applications. Glass fibre reinforced polymer composites is also found to be an interesting light weight material for energy conservation [1, 4].

Despite the tremendous advantages that advanced composites have over metals, the ability to absorb energy and resist impact loading is one of the most important criteria that should be considered when designing a component. For FRPC material, it is likely that the impact behaviour will be time dependent, which is dependent on the velocity of the hammer when striking the specimen. It has been shown that, for a glass fibre reinforced polymer composites, the ultimate strength increases linearly as a function of the rate of loading in the fibre direction [5].

Moreover, the simplicity of the process and the relatively low costs make mechanical processing extremely interesting, particularly for short fibre reinforced polymers (SFRP), where the fibre breakage during processing has a lower impact on reinforcing properties than for long fibre reinforced plastics [6].

In addition, short fibres often confer quite synergistic mechanical properties, such as combination of high modulus, strength and toughness. With short, discontinuous fibres of a high-modulus material, the mechanical load is shared between the matrix and the filler, resulting in mechanical properties improvement. With continuous fibres, on the other hand, the fibres carry most of the mechanical load, while the matrix serves to transfer stresses to the load bearing fibres and to protect them against damage [7].

Therefore, the present work focuses on producing short glass fibre reinforced polyamide 6 composites by injection moulding in order to study the performance of FRPC under a variety of environmental and testing conditions. This study provides better understanding in various aspects of mechanical, thermal, dynamic mechanical properties and characterization as well as failure mechanism of short glass fibre reinforced polyamide 6 composites.

1.4 Objectives

Objectives of this research are:

i. to study the effect of glass fibre reinforcement and the water absorption on the mechanical, thermal, and dynamic mechanical properties of composites.

ii. to investigate the effect of strain rate and types of extensometers on the tensile properties of glass fibre reinforced polyamide 6 composites.

iii. to investigate impact resistance behaviour of glass fibre reinforced polyamide 6 composite: effect of specimen's support span, impactor tup velocity, test load and temperature.

iv. to elucidate the failure mechanisms through fracture surfaces of composites by scanning electron microscopy (SEM).

1.5 Scopes

This study covers the basic concept of polymer composite materials, the effect of fibre reinforcement on composite performance, the performance of FRPC behaviour at different environmental and testing conditions as well as their morphology studies.

CHAPTER 2

Literature Review

2.1 Polyamide 6

2.1.1 Introduction

Polyamide (PA), perhaps best known as Nylon® is available in numerous grades but the most commonly used are PA6 and PA6,6 in its unfilled and filled form. Polyamide 6 ($C_6H_{11}NO$) is an important engineering plastic with high melting point (between 200˚C and 300˚C). This semi-crystalline thermoplastic material has a density of 1.14 g/cm^3 and the toughness is approximately 20% higher than polyester and much higher than silk, cotton, wool, Nomex® and Kevlar®. They possess good impact strength, due to the fact that they absorb several percents of water ($\leq$2.5 % wt.) from the atmosphere. The absorbed water in polyamide behaves like plasticizer, which affects materials properties such as strength, stiffness and ductility. This plasticizing effect will interrupt the polymer hydrogen bonding, making it more flexible and increasing the impact strength thus resulting in lower T_g value. Water also results in deterioration of electrical properties [8-9].

Much of the recent growth in polyamide has been found in automotive sector, where polyamide made parts are gradually replacing metals (various steels and light alloys, aluminium and magnesium based), and in some case expensive plastics, including variety of thermosets. It is also widely used in many industrial application including electrical, construction, household, machinery as well as thin films and powder coating. Moreover, a good abrasion resistance and a low friction make them suitable for technical use, such as in bearings and gear wheels. Polyamides are also used for parts that are high wear and tear in nature; it is made into parts used as conveyor rollers, textile, paper and packaging and automotive components.

In addition for many applications, polyamide compositions with improved toughness are required. Quite often polyamides are reinforced with short glass fibres to improve their stiffness and also modifying polyamides with impact modifiers. Such modifiers include low modulus ethylene copolymers containing small amounts of carboxyl or anhydride functionality. Other modifiers include ethylene acid copolymers neutralized with metal cations [7].

2.1.2 Function of Matrix (Polyamide) Phase

There are several functions of polyamide matrix. There are:

- It binds the fibres together and acts as a medium by which an externally applied stress is transmitted and distributed to the fibres.
- To protect individual fibres from surface damage due to mechanical abrasion or chemical reactions with environment.
- The matrix separates the fibres by virtue of its relative softness and plasticity, prevents the propagation of brittle cracks from fibre to fibre, which results in catastrophic failure; in other words, the matrix phase serves as a barrier to crack propagation.

2.2 Fillers

2.2.1 An Overview

It has been established in recent years that incorporation of fillers such as short fibres can significantly improve the mechanical, thermal and barrier properties of the pure polymer matrix. These improvements are achieved through conventional processing techniques without any detrimental effects on processability, appearance, density and ageing performance of the matrix. To enable wider applications for composite materials, it is necessary to increase the fracture toughness so that glass fibre reinforced polymer composites can be employed in high impact and damage-tolerant conditions. Therefore properties such as stiffness and strength can be considerably increased by adding a reinforcing agent to the polymer, particularly glass and/or carbon fibre. As a result, forces the material to fail in brittle manner rather than ductile failure [10-12]. These composites are now being considered for a wide range of applications including packaging, coating, electronics, automotive and aerospace industries.

2.2.2 Types of Reinforcing Fibre

2.2.2.1 Aramid Fibres

Aramid fibres are known as a fibre with high specific tensile strength and relatively low density. In terms of physical appearance, these fibres have a colour of bright golden yellow. Generally, all grades of aramid fibres are particularly good in impact resistance and for anti-ballistic applications, nevertheless aramids with lower modulus grades are widely used.

Although relatively new on the market, the applications of aramid fibres are very broad and not only limited to high performance sector but also used in speciality tyres and production of thermoplastic composites, using a polymer melt, solution, powder, hybrid yarn or fabric. Beside that, these fibres are also used widely in aerospace, structural and transportation sectors both alone and in hybrid composite in combination with other fibres such as carbon [4].

Amornsakschai *et al.* [8] have been used aramid fibre, poly-m-phenylene isophthalamide (Teijin-Conex), to reinforced thermoplastic elastomer, styrene (ethylene butylene) styrene (SEBS). It was found that the modulus at 100 and 300% elongation of the composite increased linearly with increasing fibre loading. On the other hand, tensile strength of the composites decreased as the fibre content was increased. However, tensile strength of the compatibilised composites was found to increase at 5% wt. compatibilizer due to improvement in interfacial adhesion between fibre and matrix.

2.2.3.2 Carbon or Graphite Fibres

Carbon/graphite fibre is produced by controlled oxidization and carbonization of precursors in fibre form. The usual precursors are cellulose, polyacrylonitrile (PAN), lignin and pitch, of which PAN is most commonly used as it has high carbon content (approximately 94% of carbon content). Treatment at temperatures up to 2,600˚C produces a high-strength fibre and increasing the temperature to 3,000˚C produces a high-modulus graphite fibres.

In thermoplastic, carbon fibre is particularly used as a reinforcement of polyamide, where a 30% wt. fibre content will increase flexural strength by about three times, and flexural stiffness may be increased by factor of seven. Electrical properties, friction behaviour and wear resistance may also be improved. The high strength commercially available carbon fibres such as Celion® have increased in both strength and elongation by approximately 50 percent in the past few years [2, 4].

A recent study [10] shows that increases in carbon fibre strength and resin toughness translate into significantly improved composites properties. Wouterson *et al.* [11] showed that introduction of 3% wt. of short carbon fibres in synthetic foam, caused an increased in fracture toughness, K_c and energy release rate, G_c, by 95% and 90% respectively, indicating the potent toughnening potential for short carbon fibres in synthetic foam systems.

On the other hand, Wan *et al*. [13] reported the moisture absorption process of the carbon fibre-reinforced monomer casting nylon composites is dominated by the matrix material, known as monomer casting nylon. As a result, the moisture contents of the carbon fibre/ monomer casting nylon composites decrease with increasing fibre volume fraction.

2.2.3.3 Glass Fibre

This type of fibre is the most widely used as a reinforcing material, both for thermosetting and thermoplastic composites. It has high tensile strength combined with low extensibility (3.5%) giving exceptional tensile, compression and impact properties, with a relatively high modulus of elasticity and good bend strength. It also has high temperature resistance, good dimensional stability and improves the creep performance considerably. Due to its low moisture absorption, makes it possible to produce mouldings with good electrical properties, even under extreme weather condition [11].

Engineering polymers are often reinforced with glass fibres to obtain increased mechanical stiffness and strength; however, it leads to reduced ductility and impact resistance. In some cases, it is useful to combine reinforcement with rubber toughening to balance end use performance of final product [15].

For the past decades, polyamides have been successfully reinforced by glass fibre, carbon fibre and other inorganic reinforcements [16]. Bader and Collins [17] reported that incorporation of E-glass fibre in polyamide 6 together with silane coupling agent has improved composite stiffness, strength, ductility and toughness. These results is in line with the study by Tjong *et al.* [18] where incorporation of short glass fibre

(SGF) to the polyamide 6,6 hybrid composites toughened with maleated styrene-ethylene butylene-styrene (SEBS-g-MA) at 80/20 blend improves both the tensile strength and stiffness substantially at the expense of its tensile ductility. Recently, it has also been reported [19, 20] that the glass fibres, as well as the amount added, can increase the crystallization rate and consequently affect the microstructure of the base polymers.

There are several types of glass:

- A-glass (for alkali) is the original type of glass fibre. This is a high-alkali-content material, with a chemical composition similar to that of window glass.
- C-glass (for chemical) is a grade with improved resistance to chemical attack, mainly used for surface tissue.
- D-glass has particularly good dielectric characteristic and used widely in electronics industry.
- E-glass (for electrical) is a calcium alumino-borosilicate composition, for low alkali content and stronger than A-glass. It has good tensile and compressive strength and stiffness, good electrical properties and relatively low cost, but low impact resistance
- R- & S- glasses have a different chemical composition, giving a higher tensile strength and modulus, and better wet strength retention. They were developed to meet the demand for higher technical performance from the aerospace and defence industries.

2.3 Fibre Reinforced Polymer Composites (FRPC)

2.3.1 Introduction

Many of our modern technologies require materials with unusual combinations of properties that cannot be met by the conventional metal alloys, ceramics, and polymeric materials. This is true especially for materials that are required for aerospace, underwater and transportation applications. For an example, aircraft engineers are increasingly searching for structural material that have low densities, strong, stiff, high impact resistance and are not easily corroded. Thus, fibre reinforced polymer composites are designed with high strength and/or stiffness as well as light weight in order to meet the nowadays applications.

In order to get the greatest improvement in composite toughness, reinforcement with short fibres is very important for both thermoplastic and thermoset materials. Fibres, particularly long and continuous, provide the stiffest and strongest reinforcing materials and for this reason they are the most commonly used reinforcing agent. The introduction of fibres into the matrix induces directionality (or anisotropy) to the material and for this reason the properties of the FRPC are therefore highly dependent on the alignment of the fibres [21]. In some cases, toughness is enhanced but in others where tougher resins are used, impact strength may be reduced, especially with shorter glass fibre [22]. Currently, it is now possible to obtain commercially almost any thermoplastic resin reinforced with glass fibre.

2.3.2 Interfacial Adhesion and Compatibility Between Particles and Matrix

It is well known in fibre reinforced polymer composite materials, the adhesion between fibres and matrix is compulsory and highly desirable. If the adhesion is good, the stress is transferred between the load-carrying fibres over the matrix efficiently, resulting in the strong and stiff material. Nevertheless, if the interfacial bond is too strong, the composite may be too brittle and make the material more notches sensitive [24]. The interfacial bond strength may be controlled by coupling agents which are designed not only to improve the bonding, but also to enhance strength retention under extreme environmental conditions. This statement is in line with the study reported by Bader *et al*. [17] who claim that by introducing silane coupling agent into polyamide 6 reinforced glass fibre composite, the strength, ductility and toughness shows an improvement compared to untreated composites. On the other hand, Shiqiang *et al.* [24] found that the surface treatment and sizing improve the fibre-matrix adhesion substantially since there is a clear increment of the fibre fragment number after the fibre was treated and sized. Fibre fragmentation is a phenomenon that sensitive to the level of fibre/matrix interfacial adhesion.

It is well known that improvement in mechanical properties may be achieved by incorporation of short glass fibres into thermoplastic. Akkaoui *et al*. [25] in their study observed a significant reduction in percent elongation values with the addition of the glass mat as a reinforcement agent. This is due to good adhesion between the matrix and the glass mat in which the load is transferred from matrix to glass mat efficiently. Nonetheless, it is also found that the interfacial influence of fibre matrix adhesion may vary from one composite system to another due to the variation in the properties of fibres and matrix, the ability to transfer stresses across the fibre-matrix interface as well as the degree of the influence as the fibre volume fraction is changed [26-28].

The reduction in mechanical properties caused by moisture intake was reported by many researchers for various composite systems [18–20]. Almgren *et al*. [23] in their study state that interfacial stress transfer becomes less efficient when moisture is adsorbed at the interface which results in relative stress redistribution from the fibres to the matrix. With less efficient interfacial stress transfer, a larger part of the load is carried by the matrix. Vlasveld *et al.* [29] also agree with the statement that moisture will reduced the level of interfacial bonding due to interference of the water molecules with the bonding between sizing and polyamide. Bergeret *et al*. [30] on the other hand, confirmed through scanning electron microscopy observations showed that hygrothermal ageing reduced the effectiveness of the interfacial bonds between glass fibre reinforced thermoplastic composites and reduction in ultimate stress to failure and impact strength is based on the nature of the matrix.

Generally, the interfacial adhesion and matrix shear yield strength can be described through morphology of the pull out fibres on the fracture surface. Fu *et al.* [28] reported the fracture surface morphology of short fibre reinforced thermoplastic indicate that the composite strength increases with rubber content due to the enhanced interfacial adhesion. Several researchers [17,31] also reported that the condition of the pulled out fibre surfaces is generally considered indicative of the strength of the fibre matrix interfacial bond, where ‘clean’ fibres indicating poor bonding and ‘dirty’ fibres indicating strong bond.

2.4 Mechanical Properties

2.4.1 Tensile Test

Tensile tests are done to determine the modulus, yield strength, and elongation at break. Tensile strength is the maximum tensile stress in which a material is capable of developing. It is calculated from the maximum load carried during a tensile test and the original cross-sectional area of the specimen. In order to provide high accuracy in strain measurement, an extensometer is used in order to measuring changes in linear dimensions. It is also known as strain gauge. Wouterson *et al.* [11] and Laura *et al.* [32] in their study were found to use clip-on strain gauge to record the tensile strain and determine Young's modulus accurately.

The strength of fibres is normally measured by tensile testing at gauge lengths of 6 mm upward [27]. One of the main reasons for utilizing tensile testing is the sensitivity of brittle reinforcement fibres to surface damage. In order to understand the contribution of fibre strength to composite performance, strength measurement at gauge length which representative the composite reinforcement length is highly needed.

Previous studies [28, 33] show that the composite tensile strength increases with fibre loading. Therefore, the increase of fibre volume fraction would lead to lower average fibre length due to higher viscous forces exerting on fibres. On the other hand, as fibre volume fractions increases, fibre-fibre interaction would also result in more to fibre length damage. In addition, the tensile strength of short fibre reinforced thermoplastic composites increased with both fibre-matrix interfacial strength and mean fibre length. It was also found that processing parameters such as pressure application time and moulding temperature have a significant influence to the tensile behaviour of neat PA6 and PA6/Glass Mat composites as reported by Akkaoui and Bayram. [25].

The loss in modulus and yield strength can be completely reversed by addition of glass fibres. In fact, the stiffness and strength of the glass fibre reinforced rubber-toughened material can be much higher than neat polyamide 6 if a sufficient amount of glass fibre is used as reported by Laura *et al.* [32]. Akkaoui and Bayram [25] in their study also reported a reduction in percent elongation with the addition of the reinforcement agent, glass mat compared to neat polyamide due to good adhesion between the matrix and glass mat. This result in efficient load transferred from matrix to glass mat.

It is well known that the environmental conditions have a significant effect on the tensile properties of composites. For hydrophilic materials, moisture is found to reduce stiffness and increase creep through a plasticization effect. This result in free volume increment as moisture is introduced to a polymer. Logically, when water diffuses into a fibre, water molecules may interrupt the original hydrogen bonds between the polymeric molecules of the fibre. This leading to temporary reduction in the material's rigidity and therefore the increment in deformation is observed. [34].

Dhakal *et al*. [35] observed a reduction in ultimate tensile strength but then stabilised as water content increased. The increase in failure strain upon exposure of the samples to a wet environment can be attributed to the plasticization of composites cause by moisture absorption. Thus, further improvement in fibre volume fraction should decrease the moisture content of the composites as reported by Wan *et al.* [13].

In the case where the fibres run from end to end of a long sample, the two components will be constrained to deform equally, provided the fibre/matrix bonding is good. Then the load carried by the composite as a whole will be distributed between them in proportion of their relative cross-sectional areas. Any stress on the composite is therefore given by:

$$\sigma = \sigma_f V_f + \sigma_m (1 - V_f) \tag{2.1}$$

Where σ_f and σ_m is the strength of the fibre and matrix respectively and V_f is the fibre volume fraction. The relationship will hold until failure, which will occur at the failure strain of one of the phases. In carbon fibre reinforced plastics, usually the fibres that fail first, and in glass reinforced plastic it is often the matrix. σ_f is usually taken to represent the failure stress of the fibres, and if the stress carried by the matrix at the fibre failure strain is termed σ_m' the ultimate tensile strength of the composite, σ_c, is then simply:

$$\sigma_c = \sigma_f V_f + \sigma_m'(1 - V_f) \tag{2.2}$$

This rule of mixture, Equation (2.2) is strictly valid only for composites in which fibres and matrix have identical Poisson's Ratio and equation usually gives a good estimation of composite strength.

2.4.2 Impact Test

Nowadays there has been increasing interest in instrumented impact-testing machines especially in industrial laboratories. For many years, Charpy and Izod tests [36] have been commonly used to evaluate the impact resistance of polymers and their composites due to their simplicity. Most of the impact investigations into impact behaviour have been concerned with pendulum impact tests. Unfortunately, impact pendulum tests give results that are very sensitive to sample dimension and difficult to relate with service condition. Therefore, instrumented drop weight impact tests are widely used among the different types of impact tests due to its capability of testing materials at a wide range of velocities [4].

The impact resistance can be defined as the ability of a material and its structure to survive impact induced damages during an impact event. The impact performance of composite materials depends upon many factors, including the nature of the fibre, matrix, interface, geometry and testing conditions [37]. Matrix ductility, fibre type and content, as well as void content of the composites are the main structural parameters which affect the impact behaviour significantly [38]. Basically, under impact loading materials tend to behave in a brittle manner before fracture.

The main reason for doing impact testing upon glassy polymers is to study ductile/brittle transition which is accompanied by sudden drop in impact strength. This transition obviously has important implications for the use of glassy thermoplastic in engineering applications and in determining its impact failure process [4, 37]. A transition from ductile to brittle failure is possible by modifications to the testing conditions such as reducing the testing temperature [39]. Pitman *et al.* [40] study the effect of annealing and reducing the test temperature in which both raise the yield stress and cause brittle fracture. Lowering the molar mass of the polymer causes a reduction in the craze stress, making crazing easier and leading to brittle behaviour. Meanwhile, by adding plasticiser a reduction in yield stress was observed resulting in ductile behaviour [41]. However, Zhang *et al.* [37] report the fracture behaviour and mechanism of the laminate composites at low and high temperature levels are complicated when compared with those of the composite at room temperature.

A few studies [6, 38, 49, 50] have focused on the effect of temperature on the impact response of polymer matrix composites. It was found the impact fracture energy of semicrystalline polymers is generally found to drop as the temperature is reduced and depend upon the fabrication conditions of the polymer [42]. Another alternative method of measuring the composite's impact resistance is to subject the laminate to low energy impact and then determine the amount of damage incurred. The low energy impact was obtained by reducing the drop weight and impact velocity [10]. Short *et al.* [43] showed that low velocity impact of fibre reinforced thermoplastic composites cause a pattern of damage consisting in general of delamination, fibre breakage and matrix cracking. They explained that such damage is accidental and may go unnoticed; therefore, composites must be designed assuming impact damage exists. Sugun and Rao [44] used repeated drop tests with final delamination area maps to understand the impact damage tolerance of polymer composites. Their results showed that repeated drop weight impact tests provide a very good understanding of the impact damage tolerance of polymer composites, and help to rank them on this basis.

2.4.3 Fracture Toughness

Over recent years there has been a tremendous upsurge in interest in the fracture behaviour of polymers. One reason for this is the increasing use of polymers in structural engineering applications, since in such circumstances it is essential to have as complete understanding on the polymer's fracture behaviour. A great deal of effort has been expanded into methods of toughening polymers and increasing the fracture energy. It is therefore possible to increase the toughness of polymers by modifying the material rather than changing the specimen geometry. For example, toughening polymer is possible by incorporating a soft rubbery phase into a brittle polymer a technique known as rubber toughening. This is proven by Young and Paul [15] that reported rubber particles appropriately dispersed within a neat polyamide 6 matrix increase toughness via cavitation that eventually allows the matrix to dissipate more energy.

Impact test results provide the values of fracture energy (W) and peak load (P). Fracture energy or work of fracture can be define as total work required to fracture the sample, per unit area of new surface produced or the total amount of energy dissipated during crack growth [4]. The relationship between W and the critical strain energy release rate (G_c) and specimen geometry function ($BD\Phi$) is given by:

$$W = G_c BD\Phi \tag{2.3}$$

where B and D are the width and depth of the specimen, respectively. A correction factor, Φ is given by:

$$\Phi = \frac{1}{2}(\frac{a}{D}) + \frac{1}{18\pi}(\frac{S}{D})\frac{1}{(a/D)}$$

(2.4)

where a and S are notch depth (or crack length) and span of the specimens, respectively.

A plot of W against BDΦ produced a straight line, where its slope is equal to the G_c of the materials. G_c is a total energy absorbed by test specimen divided by its net cross section area and is used to measure of the energy necessary for crack initiation.

To increase the toughness, it is therefore necessary to ensure that the volume in which these or other energy dissipating mechanisms occur is sufficiently large whilst at the same time limiting the growth and breakdown of voids and crazes to prevent premature crack initiation. The inclusion of short fibres of glass or carbon into plastics may also increase composites toughness [42]. Hardy [47] has studied the fracture behaviour of a range of injection moulded glass acetal composites with various glass surface finishes. He concluded that critical stress intensity factor, K_c was a linear function of the contribution of the fibre reinforcement to the tensile strength but independently to the amount and length of the fibres as well as the nature of fibre finish.

By definition, fracture toughness is measurement of a material's resistance to brittle fracture when a crack is present [48]. A tough material requires a great deal of work, while a brittle material requires little [49]. In Equation 2.5, the parameter K_c is termed the critical stress intensity factor; it provides a specification of the stress distribution around a crack. The stress intensity factor is related to the applied stress and the crack length by the following equation:

$$K_c = Y\sigma\sqrt{a} \qquad (2.5)$$

Here Y is a constant related to the sample's geometry, *a* is a crack length σ is the stress applied to the material. A plot of σY against $1/\sqrt{a}$ will give a straight line where K_c values was taken from the graph slope. K_c provides a measure of material toughness K has the unusual units of MPa $\sqrt{m}$. The method of G_c and K_c determination has been employed by Carling and Williams [14] in most of their work.

The values of impact energy are given by the instrumented impact tester, whereas the impact strength values were calculated. The calculation of impact energy and impact strength was done using a formula:

$$\text{Impact energy (J)} = \text{mgh x } \frac{1}{2}\text{mv}^2 \tag{2.6}$$

where m is the mass of tup (kg), g is the gravitational constant (9.8 ms^{-2}), h is the height of tup (m), and v is the velocity of tup (m/s):

$$\text{Impact strength (kJm}^2\text{)} = \frac{\text{impact energy}}{\text{thickness x width}} \tag{2.7}$$

The strength and toughness of a composite depends on the shape and size of the filler, the amount which is compounded with the matrix, the bonding between the filler and the matrix as well as the toughness of the matrix and filler. In fact, modifying the adhesion between the filler and the resin can have a strong effect on the fracture energy as proven by Richardson [4]. Turner [50] has also shown that the fracture toughness of a wide range composites based on polyesters, epoxies and rigid polyethylenes reinforced with E-glass mat is a linear function of the weight fraction of glass and independent of the fracture toughness of the resin. This is clearly an important result for designers in glass fibre reinforced thermoplastic materials.

In some cases, as the filler volume fraction is varied, the fracture energy increases until at some critical volume fraction it begins to decrease again. This is consistent with the result by Bader *et al.* [51] that shown how the impact energy of various types of carbon fibre reinforced plastic depends on fibre volume fraction. They showed that the stronger carbon fibres give much tougher composites, due to greater stored elastic energy.

In addition, the fracture energy of aligned composites can be strongly affected by both the presence of voids and by environmental attack. Richardson [4] reported that 5 vol.% of voids reduces the Charpy impact energy of type 1 carbon fibre reinforced polymer by 30% for cracks propagating normal to fibres and by 50% for cracks travelling parallel with the fibres. Expose the same material to steam reduced the fracture energy of untreated fibre composites by 14% and that of commercially treated fibre composites by 44%. As we have already indicated, the effect of using a coupling agent on the toughness of glass fibre reinforced polymer is to reduce fracture energy considerably. The silane coating does however help a glass fibre reinforced polymer composite to resist degradation when exposed to water [52].

2.5 Testing Condition Effect on Composite Properties

2.5.1 Tensile Properties

The rate at which a test is performed can have a significant effect on tensile properties. Strain rate represents how quickly the strain in the gauge length is changing with respect to time. Usually, materials that are sensitive to strain rates exhibit higher tensile strengths and lower elongations at faster speeds. However, for certain materials, the tensile strength is not heavily affected by strain rate. For example, tensile properties for plastics, polymers and steels are very sensitive to testing rates, but aluminium alloys exhibit little sensitivity.

In addition, accurate strain measurements are required for most mechanical properties studies of composite materials. Thus, suitable extensometer is necessary in measuring engineering strain and modulus by measure the actual elongation between two given points on the sample. To make direct measurement of engineering strain, an extensometer was mounted at the mid-length of the specimen and is used to measure the displacement within the gauge length. An advantage of this extensometer is its ability to maintain a high degree of accuracy over long periods of use.

Zhou and Mallick [53] used a 25 mm strain gauge extensometer to measure axial strain in glass fibre/polyamide 6,6 composite for accurate strain and modulus measurement. The tests were conducted at 0.05, 0.5, and 5 min^{-1} strain rates at room temperature. The results showed that, both tensile strength and tensile modulus increased with increasing strain rate. The failure strain however was not affected much by strain rate in the strain rate range used in this study. This result proved that glass fibre/ polyamide 6,6 is a strain rate sensitive material.

The same trend was also reported by Mitsugu *et al.* [54] in their study of glass fibre composite with polyamide-6 matrix. They observed superior tensile performance as strain rate increased up to 1 x 10 s^{-1} and then slightly decreased at higher strain rates (>1 x 10 s^{-1}).

On the other hand, Shi *et al.* [55] divided the effect of temperature on yield strength and ultimate tensile strength into three aspects: low temperature, intermediate temperature, and high temperature. Below T_g, 40 to 75˚C, the epoxy matrix is in the glassy state. The matrix strength of the cross-links decreases with increasing temperature. Therefore, the yield strength and ultimate tensile strength reduce with increasing testing temperature. When the temperature is increased to 100˚C, (at T_g) the material is in the transition from the glassy state to the rubbery state. The Young's modulus then decreases sharply in the temperature range of 100–125˚C. When the temperature is increased further and reaches 150˚C, the material is in the rubbery state, the Young's modulus then presents the weakest dependence on temperature in the temperature range of 150–240˚C.

2.5.2 Impact Properties

The impact property of a material is its capacity to absorb and dissipate energies under impact or shock loading. Generally, the neat resin has very low impact resistance. However, reinforcement with glass fibre increases its impact strength significantly. In general, composite impact energy level depends on several factors such as nature of the component, geometry, fibre arrangement and fibre matrix interface. The matrix fracture, fibre matrix de-bonding and fibre pullout are important failure modes observed in the fibre composites due to impact loading. The load is transferred through shear, and when the shear force exceeds the fibre matrix interaction force, the fibre matrix de-bonding takes place. Fibre fracture will be predominating when the stress level exceeds the fibre stress, and then the fractured fibres are pulled out from the matrix.

It is well known that the specimen's length, width and thickness, and whether the specimen is unnotched or notched and, if notched, the depth and sharpness of the notch, plays an important role in determining impact behaviour. For example, increasing the length of a Charpy specimen decreases the strain-rate and this may result in higher impact strength. Moreover, the thickness of the specimen in a flexed-beam test may have a drastic effect on the impact strength. Some polymers exhibit a ductile failure and possess high impact strength when the specimen is relatively narrow but undergo a transition to brittle fracture, accompanied by low impact strength, as the thickness is increased [42].

Levay *et al*. [56] in their study investigate the influence of testing conditions such as loading rate, crack length, mechanical damping on the fracture mechanic characteristic of a short glass fibre reinforced polyamide. They found that the material with 16% fibre volume fraction reinforcement has the highest toughness both for fracture toughness and strain rate values. However, the fracture toughness is reducing with increment in the relative crack length.

Kang and Kim [60] in their study on impact behaviour of Kevlar fibre reinforced composites found that, at low velocity impacts, bending deformation and delamination are the major energy absorption mechanisms. By contrast, under high velocity impact, global deformation, fibre breakage, delamination and shear-out are the factor in contributing energy absorption mechanisms.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

The materials used in this study were Technyl® C216 NAT (unreinforced polyamide-6) and Technyl® C216 V30 NAT (short glass fibre reinforced polyamide 6 composites, 16% V_f). To condition the sample, sodium hydrogen sulphate, $NaHSO_4$ and silica gel were used.

3.2 Preparation of Specimens

For the preparation of specimen with different fibre volume fraction, appropriate amounts of both filled and unfilled PA6 matrix were dried at 90°C for 6-7 hours in a vacuum oven to remove the absorbed water before being injection moulded into a single gated four cavities which consist of two tensile specimens and two impact specimens. The dimensions of dumb-bell shaped tensile test pieces were in accordance with the ASTM Standard D638-80, type 1 [62].

In this study, neat PA6 and four batches of composites with different fibre volume fractions were prepared. The blends were shaken together in a plastic bag of 500 g for each batch for about 10 minutes before feeding them into the hopper and eventually passed through a screw of injection moulding. Details of processing parameter and the list of material batches used in this study are specified in Tables 3.1 and 3.2 respectively.

Table 3.1: Temperature settings on automatic injection moulding machine model Boy® 50M.

Processing parameter	Unit	Glass fibre composite
Temperature setting:	°C	
Rear		220
Centre		225
Front		230
Nozzle		235
Screw speed	RPM	40-50
Pressure	bar	100-170
Cooling time	seconds	30
Mould temperature	°C	80

Table 3.2: Specimens code and description.

Specimen	V_f	Description
SG00	0.00	Technyl® C216, used as received.
SG02	0.02	Technyl ® C216 V30, diluted with PA6 matrix.
SG05	0.05	Technyl ® C216 V30, diluted with PA6 matrix.
SG08	0.08	Technyl ® C216 V30, diluted with PA6 matrix.
SG10	0.10	Technyl ® C216 V30, diluted with PA6 matrix.
SG16	0.16	Technyl ® C216 V30, used as received.

3.3 Determination of Fibre Volume Fraction (V_f)

For the determination of fibre volume fraction, V_f, samples from the central portion of injection moulded tensile test piece were cut and the polymer matrix was removed by heating a composite specimen in a muffle furnace at a temperature of up to 600˚C for a period of about 7-8 hours. Fibres were then weighted [63].

3.4 Determination of Fibre Length Distribution (FLD)

In this study, the isolation of the fibres from the composite material is done by burning the matrix at 600ºC in a muffle furnace for 7-8 hours. The fibres were then dispersed in a beaker containing water, glass microscope slide and a small amount of detergent to reduce surface tension. In order to ensure uniform mixing of fibres, the beaker containing fibres was placed in an ultrasonic water bath for a period of about 2 minutes. The slides with fibres on one side were then dried in an oven. The glass slide were then placed on the observation stage of a Zeiss Primo Star microscope and viewed in dark transmission light with resolution of 4X. A video camera attached to the microscope transmitted live fibre images to the Image Analyser. Dedicated software automatically digitised the fibre image and enhanced the contrast between foreground (fibres) and background. At least 500 fibres were measured and the histogram of percentage of fibre counts (frequency) against fibre length range was plotted.

3.5 Conditioning of Specimens

PA6 is well known to be particularly affected by moisture that eventually affects the mechanical performance of the final product. Because of that, the mechanical properties at three different environmental conditions were investigated. Therefore, specimens were tested as dry as moulded (DAM), and exposed to 50% RH and wet condition.

The dry as moulded (DAM) specimens were put into desiccators to make sure no water absorption to the samples. Silica gel was used in order to maintain the dryness of the specimens. For wet conditioning, the samples were immersed in the boiling water for at least 24 hours to accelerate the moisture absorption. For 50% RH conditioning, 1.5 kg of sodium hydrogen sulphate was added in 1 litre beaker and stir until it become saturated at room temperature. This saturated solution was then transferred into desiccators where all the specimens were kept in the environment of saturated sodium hydrogen sulphate solution for at least a month [64].

3.6 Thermal Characterisation

3.6.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was used to investigate thermal decomposition behaviour of composite with a TGA6 Thermogravimetric Analyzer (Perkin Elmer, USA.). Tests were done under nitrogen at a scan rate of 20°C/min in a programmed temperature range of 50 to 900°C. A sample of 5 to 10 mg was used for each run. The weight change was recorded as a function of temperature. Derivative peak temperature was taken as the maximum temperature acquired from the differentiation of the weight change as a function of time.

3.6.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry experiments were performed with a Diamond DSC, Perkin Elmer, USA. Each sample was heated and cooled at a scanning rate of 10°C/min under nitrogen atmosphere in order to prevent oxidation. A test sample of 5 to 10 mg was placed in an aluminium capsule and heated and cool back from 0 to 300°C for each run. The melting temperature (T_m), enthalpy (ΔH_m), crystallization temperature (T_c), crystalline enthalpy ($-\Delta H_c$) and crystallinity (χ_c) were determined after the melt-crystallization process. The corresponding glass transition temperature (T_g) based on a second scanning was recorded.

3.7 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical properties of glass fibre reinforced PA6 were analyzed using a dynamic mechanical analyzer in three-point bending mode (Q800, TA Instruments, USA). DMA specimens were cut from injection moulded tensile samples with the dimensions of 55 mm by 13 mm by 3.3 mm. Measurements were conducted over a temperature range of -100ºC to 150ºC at a heating rate of 3ºC/min, at frequency of 1 Hz, and 0.1% strain.

3.8 Mechanical Properties

3.8.1 Tensile Testing

Specimens of both filled and unfilled polyamide were subjected to a tensile test as per ASTM D638, using Instron Universal Testing Machine model 5569 at a constant crosshead speed of 1, 5, 10 and 20 mm/min and a gauge length of 50 mm. The composite modulus was recorded at 0.5% strain. For each test, a minimum of five samples were tested. In this study, two types of extensometer were used which are short travel extensometer (can be extended up to 20%) and long travel extensometer (can be extended up to 500%). The test was conducted at room temperature of about 25˚C.

3.8.2 Impact Testing

The impact tests were carried in an Instron Dynatup 9210 impactor, attached with an environmental chamber. Specimens were notched at the centre on one edge to produce a single edge notch (SEN) impact test specimen. The notch angle was set at 45 degrees. For each batch, specimens were notched with four different notch to depth (a/D) ratios i.e. ≈ 0.1, 0.2, 0.3, and 0.4. The test was conducted in Charpy mode as specified in ASTM D618 [65] where the bar is supported at both ends and struck in the centre. Throughout the test, a support span to depth ratio (S/D) was adjusted and maintained at 4. The V-shape tup, was used for testing. The impact energy was calculated from the area under the diagram of the impact load. Impulse software was used to display and store the impact data. The values reported are the average of at least eight specimens. For specimen tested at different test velocities and test load only specimens for 0%, 8% and 16% V_f was selected because we want to study those parameters at low, in the middle and high fibre content. On the other hand, in temperature testing study, only specimens with highest fibre volume fraction (16% V_f) was selected due to its high strength (160 MPa). The test parameters for impact test were summarized in Table 3.3.

Table 3.3: Impact test parameters for Instron Dynatup 9210.

Test	Height (mm)	Load (kg)	Temperature (˚C)	Impact velocity (ms^{-1})	Support span (mm)	V_f (%)
The effect of specimen's support span.	126	7.648	25	1.55	48 & 60	0, 2, 5, 10, 16
The effect of impactor tup velocity.	40 80 126 200	7.648	25	0.83 1.22 1.55 1.96	60	0, 8, 16
The effect of impact load.	800	6.448 7.648 10.048	25	1.22	60	0, 8, 16
The effect of test temperature.	2000	5.047	33 50 60 70	1.95	60	16

3.9 Fracture Surface Morphology

Field Emission Auger Microprobe, JEOL JAMP-9500F was used to analyze the fractured surfaces of tensile and impact specimens. SEM micrograph was taken at 10 keV acceleration voltages. All specimens were coated with a thin layer of gold to prevent charging effects.