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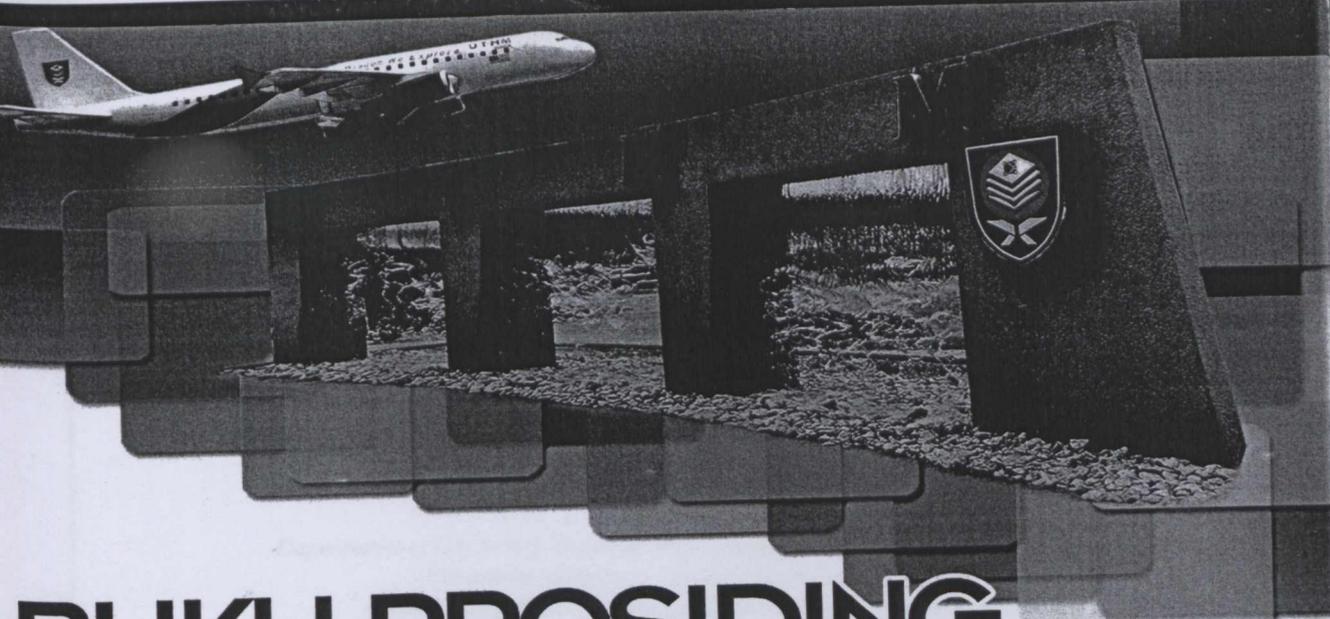
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PLASTICISATION EFFECT ON THERMAL AND TENSILE PROPERTIES OF INJECTION MOULDED SHORT GLASS FIBRE/POLYAMIDE 6,6 COMPOSITES

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Polymer composites of polyamide 6,6 reinforced with short glass fibre were prepared by injection moulding. The composites under different conditions were investigated by thermogravimetric, differential scanning calorimetry, dynamic mechanical and tensile tests. The glass transition temperatures are found to be sensitive to moisture. According to the TGA results, the glass fibre loading in PA 6,6 does have increment effect on the thermal stability of the composites. In contrast, the incorporation of glass fibre and moisture into the PA 6,6 matrix result in a remarkable decrease in degree of crystallinity value. It is found that the incorporation of glass fibre into the polyamide 6,6 gives rise to a significant improvement in tensile modulus and tensile strength. However, fracture strain is reduced. Exposure to different environments from dry to wet conditions has result in a decrease in the strength and modulus for tensile mode, while tensile strain shows an increment from dry to wet conditions.

Keywords: Polymer composites; injection moulding; mechanical properties; thermal analysis; dynamic mechanical analysis.

1. INTRODUCTION

Thermoplastics such as poly(butylenes terephthalate), polypropylene and the polyamides are excellent for use in composite materials in terms of their performance-processability-profitability ratios. The properties of thermoplastic composites result from the combination of the fibre and matrix properties and the ability to transfer stresses across the fibre/matrix interphases [1]. In general, the plastics and their corresponding composites are sensitive to changes in their environment and their mechanical properties may vary widely with conditions.

Most of the polymer composites absorb moisture in humid atmosphere and when immersed in water. The absorption of moisture leads to the degradation of fibre matrix interfacial region and creating poor stress transfer efficiencies resulting in a reduction of mechanical and dimensional properties [2]. In fact, it is generally recognised that the glass fibre-matrix interface is the determining factor of the reinforcement mechanism, especially under wet conditions [3]. The objective of this

work is to investigate the influence of glass as reinforcement in the composites and the effect of conditioning on the mechanical and thermal properties of the composites.

2. EXPERIMENTAL

2.1. Materials and specimen preparation

Materials used for the characterisation were Technyl® A216 and Technyl® A216 V30 composites. For the specimen preparation, a single gated double cavity, impact and tensile [4] standard test bar mould was used in the moulding, using Boy® 50 tonne clamping force injection moulding machine.

For dry specimens, they were kept in the vacuumed desiccators with silica gel immediately after the moulding. For 50% R.H. condition, the specimens were exposed to saturated sodium hydrogen sulphate (NaHSO$_4$) solution environment in the desiccators for at least a month [5]. For wet conditioning, the samples were immersed in the boiling water for at least 24 hours.

2.2. Determination of thermal and dynamic mechanical properties

Thermogravimetric analysis was investigated by using the TGA 6 Thermogravimetric Analyser (Perkin Elmer) at a scan rate of 10°C/min. Differential scanning calorimetry (DSC) experiments were performed with a Diamond DSC (Perkin Elmer) at a scanning rate of 10°C/min under nitrogen atmosphere in order to prevent oxidation.

The dynamic mechanical properties of specimens were analysed with a Dynamic Mechanical Analyser, DMA Q800 (Thermal Analysis Instrument). Test specimens were taken from the middle section of the injection moulded dumb-bell test bar and were subjected to three-point bending mode with a support span of 50 mm. Measurements were conducted over the temperature range of −100°C to 150°C with a heating rate of 3°C/min under a constant frequency of 1.0 Hz.

2.3. Determination of tensile properties.

Tensile tests were carried out using a Universal Testing Machine, Instron 4469 with a constant cross-head speed of 10 mm/min at room temperature of about 25°C. ASTM standard D638-80 [4] was used as a standard in calculating the tensile properties. The composite modulus was recorded at 0.5% strain.

3.   RESULTS AND DISCUSSION

3.1   Thermal properties

Figure 1 shows the TGA curves for all composites in the range of study under wet condition. Gradual weight loss in the temperature range of 50°C to 200°C and 301°C to 799°C indicates the moisture and matrix content, respectively. The $T_{50\%}$ for composites under dry and wet conditions occurs at higher temperature than for matrix. These results suggest that the incorporation of glass fibre into the system has improved the structural destabilisation point of the composites. According to the above results, the glass fibre loading in PA 6,6 does have positive effects on the thermal stability of the composites. The increment of DT_P values of the composites under both conditions compared to neat PA 6,6 also confirms the good thermal stability of these materials [6].
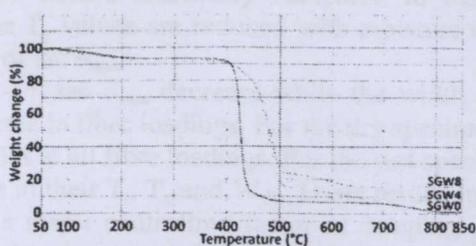
Fig. 1. The TGA thermographs of composites under wet condition.
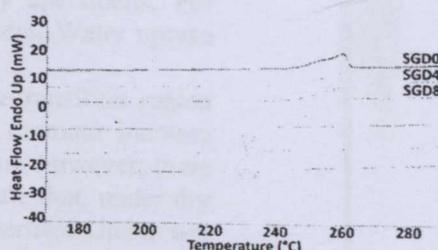
Fig. 2. The DSC thermograms composites under dry condition.

The DSC thermograms allow one to estimate the melting temperature (T_m), crystallisation temperature (T_c), enthalpy of melting (ΔH_m), enthalpy of crystalline $(-\Delta H_m)$, and also degree of crystallinity (X_c) of the composites. In this work, the reference value for the purely crystalline PA 6,6 is taken as 197 J/g (ΔH) [7].

The degree of crystallinity (X_c) is calculated by using the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H} \times 100\%$$

where ΔH_m and ΔH are the enthalpies of composite specimen and purely crystalline PA 6,6 matrix respectively. Incorporation of glass fibres and moisture into the PA 6,6 matrix results in a remarkable decrease in X_c value than pure PA 6,6. This suggests that there is a significant change in the microstructure of the PA 6,6 matrix as a result of the incorporation of glass fibres [8]. The melting peak around 260°C and 253°C could be attributed to the melting of the α-crystalline form (T_m^α) and the thermodynamically unstable γ-crystalline (T_m^γ), respectively [9]. Figure 2 shows that the presence of glass fibre did not produce any effect on the T_m of the composites for both conditions which indicates that the incorporation of glass fibre into the composites does not affect the degree of hydrogen bonding between the polymer chains.

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3.2. Dynamic mechanical analysis (DMA).

Results from dynamic mechanical analyses of the injection moulded composites are given in Figures 3 - 4. For dry specimens, the incorporation of the fibres produces no significant trend in displacement of the α-relaxation peak (T_g). On the other hand, the presence of the glass fibre reduces the magnitude of tan δ_{max} values dramatically. This is believed to be due to the strengthening effect by the fibres. The incorporation of fibres acts as barriers to the mobility of polymer chain, leading to lower degree of molecular motion and hence lower damping characteristics [10]. The same behaviour is observed for composites under wet condition. Water uptake decreases the T_g of pure matrix drastically compared to the dry specimens. For composite specimens, the T_g values are reduced with moisture content. Water uptake also increases the values of tan δ_{max}.

From Figures 3 - 4, tan δ_{max} decrease while the width of α-transition region ($W_{\sqrt{2}}$) increase with increase in fibre loadings. For the dry specimens, dramatic increase in $W_{\sqrt{2}}$ is shown by samples at all fibre loadings. For the wet specimens, however; there are negligible differences in their T_i, T_e and $W_{\sqrt{2}}$. These results indicate that, under dry condition, glass fibre is a major controlling factor in damping properties. Under wet condition, fibre becomes less important and matrix is the controlling factor. It can be seen that the tan δ peaks of α-transition for both unreinforced and reinforced PA 6,6 are shifted to lower values when exposed to humid environment. As humidity acts as a plasticiser, this will induce a further increase in the amorphous chain mobility in the material and hence reduces T_g significantly [11].
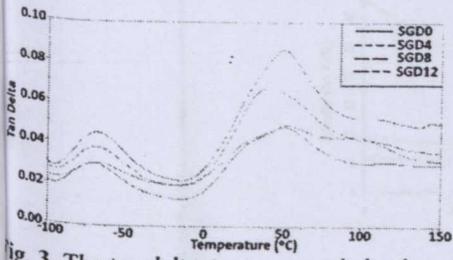
Fig. 3. The tan delta–temperature behaviour of composites under dry condition.
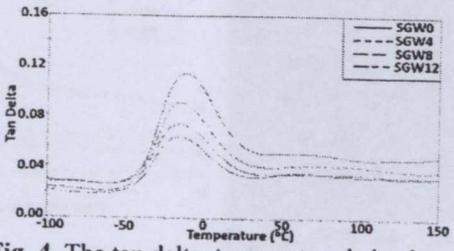
Fig. 4. The tan delta–temperature behaviour of composites under wet condition.

3.3 Tensile properties

Plots of tensile strength, tensile modulus and tensile strain are shown in Figures and 7. The tensile strength and tensile modulus are increased in the order of increasing fibre loading These results confirm that the fibres act as an effective reinforcing agent for PA 6,6, giving rise to a more rigid material [10]. As the volume fraction of fibre reinforcement in composites increases, more fibre-matrix interfacial area is created and the more applied load is transferred to the fibre by the interface [8]. Thus, it is more difficult to break the specimen and hence results in greater tensile strength and tensile modulus. The composites at all fibre loadings at the same condition

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show similar trend. Through the microscopic studies, it can clearly be seen that there is a good fibre-matrix bonding at glass fibre surfaces (Figure 6).
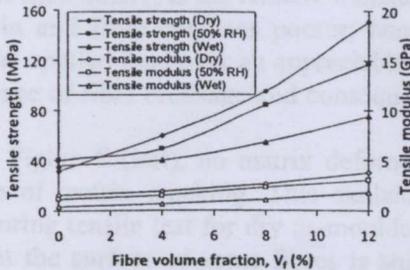
Fig. 5. Tensile strength and tensile modulus of composites under different conditions.
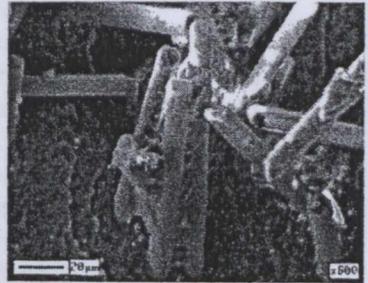
Fig. 6. SEM micrograph taken from tensile fracture surface of composite.

The fracture strain as a function of V_f is shown in Figure 7. The fracture strain decreases with increase in fibre volume fraction. This trend is also reported by Thomason et al. [12] and explained that the stress concentrations at the fibre ends lead to matrix cracking, which ultimately leads to failure when the surrounding matrix and fibres can no longer support the increased load caused by the local failure. Due to the introduction of fibres, the composites become less ductile as the molecular rearrangement does not have time to take place [13].
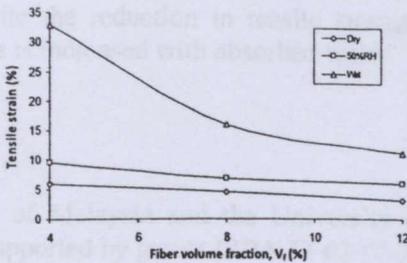
Fig. 7. Tensile strain of composite under different conditions.

Fig. 8. SEM micrograph taken from tensile fracture surface of composite under dry (left) and wet (right) conditions.

At the same fibre loading, samples in wet condition show lowest tensile strength and tensile modulus. The moisture acts as a plasticizer that reduces the entanglement and bonding between molecular chains, therefore increases their volume and mobility. Mohd Ishak et al. [8] have suggested that the absorbed moisture significantly changed the fracture mode from being brittle to a ductile fracture, resulting in reduction of the tensile strength and tensile modulus. On the other hand, the fracture strain of composites increased due to the plasticization of nylon 6,6 caused by

moisture absorption. In the presence of moisture, lubrication effect takes place allowing the polymer chains to slip past each other. As the relative moisture absorbed increases, adhesion between matrix resin and fibre becomes poorer; hence the matrix can no longer effectively distribute the applied load over an appreciable length of the adjacent fibres. Therefore, less occurrence of fibre breakage and consequently, fracture strain of composites increase.

From SEM image in Figure 8 (left), no matrix deformation is observed and there is also some indication of matrix cracking. This explains the extreme brittle behaviour of the composite during tensile test for dry as-moulded specimens. For wet specimens, it can be seen that the surface of some fibres is smooth and there is the matrix yielding which illustrates the physical damage of the interphase and debonding between fibre and matrix.

CONCLUSIONS

The degree of crystallinity of polymer is reduced with incorporation of glass fibre in the composites. The T_g value is not significantly altered by incorporation of glass fibre into the system. However, its value is reduced with moisture content. Tensile strength and tensile modulus are increased with increase in V_f. However, fracture strain of composites under all conditions is decreased in the order of increasing fibre loading. At the same fibre loading, specimen in wet condition showed the lowest tensile strength and tensile modulus. Despite the reduction in tensile strength and tensile modulus, fracture strain of composites is increased with absorbed water.

Acknowledgements

References

[1] Thomason, J. L. (2001). Micromechanical Parameters from Macromechanical Measurements on Glass Reinforced Polyamide 6,6. *Composites Science & Technology* 61: 2007-2016.

[2] Dhakal, H. N.; Zhang, Z. Y.; Richhardson, M. O. W. (2007). Effect of Water Absorption on the Mechanical Properties of Hemp Fibre Reinforced Unsaturated Polyester Composites. *Composites Science & Technology* 67: 1674-1683.

[3] Thomason, J. L. (1995). The Interface Region in Glass Fibre-reinforced Epoxy Resin Composites: 2. Water Absorption, Voids and the Interface. *Composites* 26: 477-485.

[4]   ASTM D638-80. *Standard Test Method for Tensile Properties of Plastics* 35: 228-44.

[5]   ASTM D618-00. *Standard Practice for Conditioning Plastics for Testing* 39-42.

[6]   Lee, S. Y.; Kang, I. A.; Doh, G. H.; Kim, W. J.; Kim, J. S.; Yoon, H. G.; and Wu, Q. (2008). Thermal, Mechanical and Morphological Properties of Polypropylene/Clay/Wood Flour Nanocomposites. *eXPRESS Polymer Letters* 2(2): 78-87.

[7]   Elzein, T.; Brogly, M.; and Schultz, J. (2002). Crystallinity Measurements of Polyamides Adsorbed as Thin Films. *Polymer* 43: 4811-4822.

[8]   Mohd Ishak, Z. A.; Ariffin, A.; and Senawi, R. (2001). Effects of Hygrothermal Aging and a Silane Coupling Agent on the Tensile Properties of Injection Moulded Short Glass Fibre Reinforced Poly(butylenes terephthalate) Composites. *European Polymer Journal* 37: 1635-1647.

[9]   Klata, E.; Van de Velde, K.; and Krucinska, I. (2003). DSC Investigations of Polyamide 6 Hybrid GF/PA 6 Yarns and Composites. *Polymer Testing* 22: 929-937.

[10]   Manchado, M. A. L.; Biagiotti, J.; and Kenny, J. M. (2002). Comparative Study of the Effects of Different Fibres on the Processing and Properties of Polypropylene Matrix Composites. *Journal of Thermoplastic Composite Materials* 15: 337-353.

[11]   Aitken, D.; Burkinshaw, S. M.; Cox, R.; Catherall, J.; Litchfield, R. E.; Price, D. M.; and Todd, N. G. (1991). Determination of the Glass Transition Temperature of Wet Acrylic Fibres using Dynamic Mechanical Analysis. *Journal of Applied Polymer Science: Applied Polymer Symposium* 47:263-269.

[12]   Thomason, J. L.; Vlug, M. A.; Schipper, G.; and Krikort, H. G. L. T. (1996). Influence of Fibre Length and Concentration on the Properties of Glass Fibre-reinforced Polypropylene: Part 3. Strength and Strain at Failure. *Composites: Part A* 27:1075-1084.

[13]   Curtis, P. T.; Bader, M. G.; and Bailey. J. E. (1978). The Stiffness and Strength of a Polyamide Thermoplastic Reinforced with Glass and Carbon Fibres. *Journal of Material Science* 13:377-390.