Effects of Hybridization on the Performance of the Epoxy-based Nanocomposites

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ABSTRACT

Epoxy composites were prepared by hybridization of glass fiber and precipitated nano-calcium carbonate (PNCC). The loading of the PNCC was in the range of 2-8 wt%. The mechanical properties of the epoxy/glass fiber/PNCC hybrid composites was determined using flexural and fracture toughness tests. The thermal properties of the epoxy-based nanocomposites was examined using thermogravimetric analyzer. The morphology and dispersion of the PNCC in the epoxy/glass fiber composites was characterized by field emission scanning electron microscopy (FESEM). The epoxy hybrid nanocomposites were subjected to water absorption tests in order to evaluate their retention ability. The mathematical treatment used in analyzing the data was the single free phase model of diffusion, which assumed Fickian diffusion and utilized Fick's second law of diffusion. The enhancement of the mechanical and thermal properties of the epoxy hybrid nanocomposites was influenced by the dispersibility of the PNCC. The kinetics of water absorption of the epoxy hybrid nanocomposites conformed to Fickian law behavior, whereby the initial moisture absorption follows a linear relationship between the percentage gain at any time t and $t^{1/2}$, followed by saturation. It was found that the equilibrium moisture content and the diffusion coefficient are depending on the loading of PNCC and the immersion temperature.

KEYWORDS

nanocomposite, epoxy, coupling agent, hybrid, clay

1. INTRODUCTION

Epoxy resins are versatile thermosetting materials and are widely used as coatings, electronic materials, adhesives, and structural applications. Most cured epoxy resins exhibit excellent mechanical properties, outstanding chemical and corrosion resistance, high thermal stability, and good adhesiveness. There are several approaches have been used to modify the properties of epoxy, which include modification by liquid rubber, addition of inorganic fillers, blending with thermoplastic resin and etc. Recently, nanosize inorganic particles have attracted considerable attention as new additives, because the resulting materials exhibit unique properties. Various nano-size inorganic particles, such as montmorillonite, nano-$CaCO_3$, nano-SiO_2, and nano-Al_2O_3, have been added into the epoxy matrix in order to further improve their performance [1].

The concept of hybridization have been applied in the preparation and manufacturing of epoxy based nanocomposites, for example, epoxy/carbon fiber/clay nanocomposites manufactured through hot melt lay-up autoclave process [2], epoxy/carbon fiber/organoclay nanocomposites [3-4], clay filled non-crimp glass fiber reinforced epoxy laminates [5], layered silicate/glass fiber/epoxy hybrid nanocomposites prepared using vacuum-assisted resin transfer molding process [6], bio-based epoxy nanocomposites reinforced with organo-montmorillonite clay and PAN-based carbon fibers [7], S2-glass/epoxy polymer nanocomposites [8], and epoxy/glass fiber/organo-montmorillonite prepared by hand-lay up technique [9-11].

The performance of the epoxy/fiber/nanofiller hybrid nanocomposites is controlled by its processability, dispersibility of nanofiller, and interaction between the multiphase composites. In this study, different loading (2-8 wt %) of precipitated nano-calcium carbonate (PNCC) was added into epoxy. The effect of the PNCC on the mechanical, thermal, water absorption and morphological properties of epoxy/glass fiber has been investigated. It is believe that the hybridization of glass fiber and filler can give synergistic effects on the performance of epoxy composites.

2. EXPERIMENTAL

2.1 Materials

The epoxy (CP230D) and curing agent (CP2301H) used in this study was supplied by Camel Polymer Sdn.Bhd (Malaysia). The chopped strand mat (CSM) E-glass fiber used in this study was supplied by Saint-Gobain Vetrotex (USA). The specific gravity of the CSM glass fiber is 2.6 with a density of 2540kg/m^3.The nano-calcium carbonate was supplied by Zantat Sdn.Bhd (Malaysia). The particle size of the nano-calcium carbonate is in the range of 40 – 80nm.

2.2 Preparation of Epoxy/Glass Fiber/PNCC Hybrid Nanocomposites

The epoxy/glass fiber/PNCC hybrid composite was prepared by using hand-lay up method. The different loading of PNCC (2-8 wt%) was incorporated into epoxy through sonication process and followed by mechanical stirring process. The epoxy/glass fiber/PNCC mixture was then impregnated into the chopped strand mat glass fiber (4 layers) with the assistance of hand roller to ensure all fibers are wetted and to remove the air bubbles. The laminates were then cured in an oven at 110˚C for 1 hour.

2.3 Characterization of Epoxy Hybrid Composites

2.3.1 Mechanical Properties

Three point bending flexural tests were performed using an Instron 3366 (USA) at ambient temperature according to ASTM D790. The samples geometries are 127 mm x 12.7 mm x 3.2 mm (length x width x thickness). The support span length was set at 50mm. The testing speed was set at 3mm/min.

Single edge notch bending (SENB) test were conducted to obtain the critical stress intensity factor toughness (K_{IC}) of epoxy/glass fiber/PNCC hybrid composites. The samples geometries are 74 mm x 12.5 mm x 3.2 mm (length x width x thickness). The notches was made first by the formation of saw-cut slots having rectangular shape with a width of 1 mm in the mid-section of specimens and then by sharpening with a fresh razor blade. The SENB test was performed using an Instron 3366 machine (USA). The testing speed was set at 10 mm/min. The load–displacement curves were recorded and the maximum loads upon fracture were used to calculate the K_{IC} value. The effects of nano-CaCO3 on the fracture toughness of epoxy/glass fiber hybrid composites were investigated using the critical stress intensity factor toughness (K_{IC}) which is defined by Equation (1).

$$K_{IC} = Y \frac{3PS(a)^{1/2}}{2BW^2} \quad (1)$$

where Y is geometry correction factor, P is the maximum load, S is the length of the span, B is the specimen thickness, W is the specimen width, and a is the total notch length (produced by saw and fresh razor blade). For specific specimen geometry, the geometry correction factor can be determined by the Equation (2).

$$Y = 1.93 - 3.07(a/w) + 14.53(a/w)^2 - 25.11(a/w)^3 + 25.8(a/w)^4 \quad (2)$$

Here, Y is a dimensionless parameter that depends on the crack length and specimen sizes.

2.3.2 Morphological Studies

The fracture surface of flexural specimens of epoxy/glass fiber/PNCC hybrid composites was investigated using Field Emission Scanning Electron Microscopy (Supra 35VP-24-58 FESEM) at an acceleration voltage of 15 kV. The fracture surface was sputter-coated with a thin gold–palladium layer in vacuum chamber for conductivity before examination.

2.3.3 Thermogravimetric analysis (TGA)

The thermal stability of epoxy/glass fiber/PNCC hybrid composites were studied by thermogravimetric analysis (TGA) using Perkin Elmer (TGA 6, USA). The samples were heated from 30˚C to 600°C in a high-purity nitrogen atmosphere with a heating rate of 10˚C/min.

2.3.4 Water Absorption Test

The epoxy hybrid composites specimens were dried at 80°C in a vacuum oven until a constant weight was attained prior to immersion in water baths (Memmert GmbH, Germany) at three different temperatures, i.e. 30, 60 and 90°C, according to ASTM D570. The water absorption tests were performed for 60 days. Weight changes were recorded by periodic removal of the specimen from the water bath. The sample surface was dried and the weight of the sample was measured using a balance (Sartorius AG, Germany) with a precision of 1 mg. The percentage gain at any time t (M_t) as a result of moisture absorption was determined by Equation (3):

$$M_t(\%) = [(W_w - W_d)/W_d] \times 100\% \quad (3)$$

where W_d and W_w denote, respectively, weight of dry material (the initial weight of epoxy hybrid composites specimens prior to exposure to the water absorption) and weight of epoxy hybrid composites specimens after exposure to water absorption. The percentage equilibrium or maximum moisture absorption (M_m) was calculated as an average value of several consecutive measurements that shows no appreciable additional absorption. The weight gain resulting from moisture absorption can be expressed in terms of two parameters, the diffusion coefficient or diffusivity (D), and the maximum moisture content (M_m), as shown in Equation (4).

$$\frac{M_t}{M_m} = 1 - \frac{8}{\pi^2} \exp\left[-\left(\frac{Dt}{h^2}\right)\pi^2\right] \quad (4)$$

where h is the thickness of the sample.

The diffusion coefficient *(D)* was calculated using Equation (5).

$$D = \frac{\pi h^2 (M_2 - M_1)^2}{16 M_m^2 (t_2^{1/2} - t_1^{1/2})} \quad (5)$$

3. RESULTS AND DISCUSSION

3.1 Mechanical properties

The effect of precipitated nano-calcium carbonate (PNCC) on the flexural modulus and flexural strength of epoxy/glass fiber/PNCC hybrid composite is shown in Figure 1 and 2. The flexural modulus for epoxy/glass fiber/PNCC-8wt% hybrid composite is higher than epoxy/glass fiber hybrid composites (c.f. Figure 1). The percentage improvement in flexural modulus of epoxy/glass fiber/PNCC-8wt% is approximately 42.7%. From Figure 2, it can be seen that the flexural strength of epoxy/glass fiber hybrid composites were increased significantly by the incorporation of PNCC. The percentage improvement in flexural strength of epoxy/glass fiber/PNCC-8 wt% is about 35.4%. This is attributed to the homogenous dispersibility and reinforcing-ability of the PNCC in the epoxy/glass fiber composites.

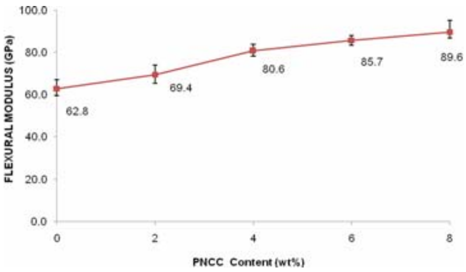

Figure 1: Effects of PNCC on the flexural modulus of epoxy/glass fiber composites.

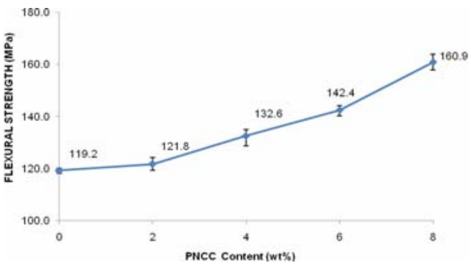

Figure 2: Effects of PNCC on the flexural strength of epoxy/glass fiber composites.

Fracture toughness is a critical mechanical property which characterizes the resistance of a material to crack propagation or to fracture. The K_{IC} values of epoxy/glass fiber/PNCC hybrid composites as a function of nano-$CaCO_3$ content is shown in Figure 3. As can be seen, the fracture toughness of the epoxy/glass fiber/PNCC hybrid composites was increased when nano-$CaCO_3$ loading is increased. The K_{IC} result for epoxy/glass fiber/PNCC-8 wt% was improved about 116.3% compare to epoxy/glass fiber.

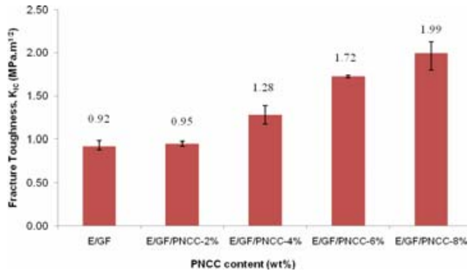

Figure 3: Effects of PNCC on the K_{IC} of epoxy/glass fiber composites

3.2 Morphological properties

The mechanical performance of fiber-reinforced composites is strongly dependent upon the quality of fiber-matrix adhesion. Figure 4a shows the SEM micrographs taken from the flexural fractured surface of epoxy/glass fiber composites without PNCC. From Figure 4a, it can be revealed that there is noticeable gap between glass fiber and epoxy matrix. The interface failure can be due to the lacking of good interfacial bonding between glass fiber and epoxy matrix. This can lead to glass fiber pull out and debonding easily from the epoxy matrix. The flexural fractured surface of the epoxy/glass fiber/PNCC hybrid composites containing 4 wt% PNCC can be seen in Figure 4b. One may observe that the occurrence of fiber pull out and debonding is lesser. In addition, it can be seen that fracture surface of the epoxy/PNCC had been changed to relatively rough. This may indicate that the interaction between the epoxy and fiber became better in the presence of PNCC. Similar observation was reported for epoxy/glass fiber/clay nanocomposites, it is proved that, the presence of the silicate layers at the surface of the glass fibers can improve the interfacial properties between the matrix and the fibers [9].

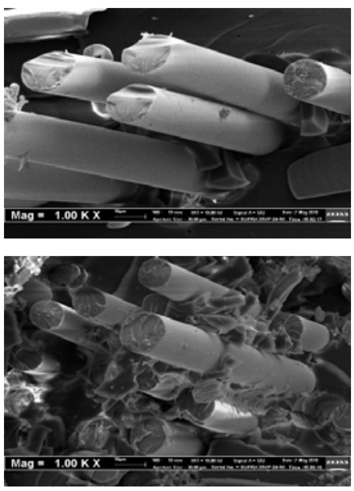

Figure 4: FESEM micrographs taken from the fractured surface of epoxy/glass fiber composites (a), and epoxy/glass fiber/PNCC-4wt% hybrid composites (b).

3.3 Thermal properties

The TGA curves of PNCC fillers, epoxy/glass fiber and epoxy/glass fiber/PNCC hybrid composites are shown in Figure 5. It can be observed that the PNCC, epoxy and epoxy/glass fiber composites displayed single-step degradation process with the initial decomposition temperature at approximately 300˚C. The initial decomposition temperature (T_i) of epoxy/glass fiber and epoxy/glass fiber/PNCC-8 wt% hybrid composites is shifted to higher value than the neat epoxy resin. The TGA result indicates that the addition of PNCC and glass fiber increase the thermal stability of epoxy matrix significantly. This is attributed to the good thermal stability of PNCC and glass fiber.

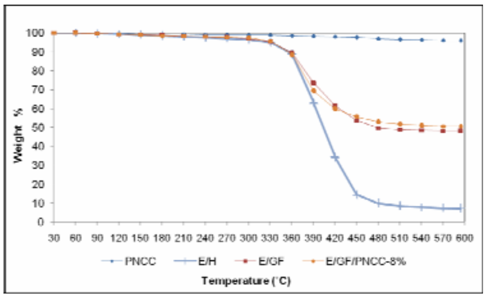

Figure 5: TGA curves of PNCC filler, epoxy and epoxy/glass fiber composites with and without PNCC.

3.4 Water absorption of epoxy hybrid composites

Figure 6 shows the water uptake of epoxy/glass fiber/PNCC hybrid nanocomposites. It can be seen that the water uptake of epoxy increased by the addition of glass fiber and PNCC. This is attributed to the hygroscopicity of the PNCC and the glass fiber. From Figure 6, it can be observed that the water uptake of epoxy/glass fiber/PNCC was reduced as the loading of PNCC increasing.

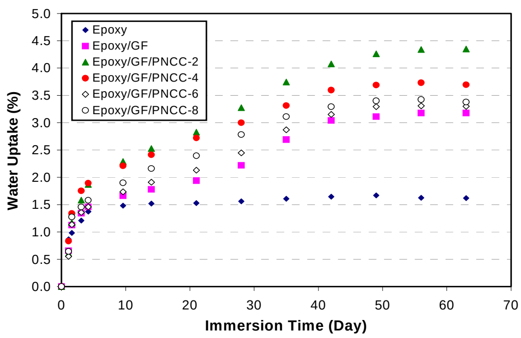

Figure 6: Water uptake of epoxy hybrid nanocomposites.

4. CONCLUSIONS

The flexural properties, fracture toughness and thermal stability of the epoxy/glass fiber were enhanced by the addition of PNCC. However, the addition of PNCC can influence the water absorption of the epoxy hybrid nanocomposites.

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Reference

[1] Isik, I., Yilmazer, U., and Bayram, G. (2003) Impact modified epoxy/montmorillonite nanocomposites: synthesis and characterization. Polymer, 44(20), 6371-6377.

[2] Xu, Y., and Hoa, S.V. (2008) Mechanical properties of carbon fiber reinforced epoxy/clay nanocomposites. Composites Science and Technology, 68(3-4), 854-861.

[3] Siddiqui, N.A., Woo, Ricky S.C., Kim, J.K., Leung, Christopher C.K., and Munir, A. (2007) Mode I interlaminar fracture behavior and mechanical properties of CFRPs with nanoclay-filled epoxy matrix. Composites Part A: Applied Science and Manufacturing, 38(2), 449-460.

[4] Hoa, S. V. and Xu, Y. (2008) Mechanical properties of carbon fiber reinforced epoxy/clay nanocomposites, Composites Science and Technology, 68, 854–861.

[5] Bozkurt, E., Kaya, E., and Tanoğlu, M. (2007) Mechanical and thermal behavior of non-crimp glass fiber reinforced layered clay/epoxy nanocomposites. Composites Science and Technology, 67(15-16), 3394-3403.

[6] Lin, L.Y., Lee, J.H., Hong, C.E., Yoo, G.H., and Advani, Suresh G. (2006) Preparation and characterization of layered silicate/glass fiber/epoxy hybrid nanocomposites via vacuum-assisted resin transfer molding (VARTM). Composites Science and Technology, 66(13), 2116-2125.

[7] Miyagawa, H., Jurek, Robert J., Mohanty Amar, K., Misra, M., and Drzal Lawrence, T. (2006) Biobased epoxy/clay nanocomposites as a new matrix for CFRP. Composites Part A: Applied Science and Manufacturing, 37(1), 54-62.

[8] Haque, A., Shamsuzzoha, M., Hussain, F. and Dean, D. (2003) S2-glass/epoxy polymer nanocomposites: manufacturing, structures, thermal and mechanical properties, Journal of Composite Materials, 37(10), 1821–37.

[9] Mazlan, N., Abu Bakar, A., and Chow, W.S. (2007) Effects of organo-montmorillonite on the mechanical and morphological properties of epoxy/glass fiber composites. Polymer International, 56(4), 512-517.

[10] Chow, W.S. (2007) Water Absorption of Epoxy/Glass Fiber/Organo-Montmorillonite Nanocomposites. Express Polymer Letters, 1(2), 104-108.

[11] Chang, L.N. and Chow, W.S. (2010) Accelerated Weathering on Glass Fiber/Epoxy/Organo-montmorillonite Nanocomposites, Journal of Composite Materials, 44(12), 1421-1434.