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Flexural and Morphological Properties of Epoxy/Glass Fibre/Silane-Treated Organo-montmorillonite Composites

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Abstract: *Organo-montmorillonite (OMMT) was treated with 3-aminopropyltrimethoxysilane. Epoxy (E) composites reinforced with glass fibber (GF) and OMMT were prepared with the hand-lay up technique. The flexural properties of the E/GF/OMMT composites were characterised by the three-point bending flexural test. The flexural modulus and strength of the E/GF composites were improved by the addition of silane-treated OMMT. The exfoliation of the OMMT in the E was studied using X-ray diffraction (XRD). It was found that the OMMT silicate layers were exfoliated successfully in the E matrix. The flexural fractured surface morphology of the E/GF/OMMT composites was investigated using scanning electron microscopy (SEM). It is interesting to note that parts of the silane-treated OMMT also adhered to the GF, which can promote better interfacial interaction and wettability between the E and GF.*

Keywords: silane coupling agent, exfoliated epoxy nanocomposites, organo-montmorillonite

Abstrak: *Organo-montmorillonit (OMMT) telah dirawat dengan 3-amino-propiltrimetoksisilana. Komposit epoksi (E) diperkuatkan gentian kaca (GF) dan OMMT telah disediakan dengan menggunakan teknik 'hand-lay up'. Sifat-sifat pelenturan bagi komposit E/GF/OMMT telah dicirikan dengan ujian pelenturan tiga titik. Modulus dan kekuatan pelenturan bagi komposit E/GF telah dipertingkat dengan penambahan OMMT-dirawatkan silana. Kebolehan eksfoliasi bagi OMMT dalam E telah dikaji dengan menggunakan pembelauan sinar-X (XRD). Adalah didapati bahawa lapisan silikat OMMT telah berjaya dieksfoliasikan dalam E. Morfologi permukaan peretakan akibat pelenturan bagi komposit E/GF/OMMT telah diselidik dengan menggunakan mikroskopi elektron penskanan (SEM). Yang menarik, didapati bahawa sebahagian OMMT-dirawatkan silana melekat di permukaan GF, yang boleh memberikan interaksi antara fasa dan keboleh-pembasahan yang lebih baik antara E dengan GF.*

Kata kunci: agen pengkupelan silana, nanokomposit epoksi tereksfoliasi, organo-montmorillonit

1. INTRODUCTION

Epoxy (E) resins are increasingly used as matrixes in composite materials in many applications, such as aerospace, automotive, structure application, shipbuilding and electronic devices, because of their low creep, good adhesion to many substrates and high strength, low viscosity, and low shrinkage during curing.[1] In addition, E resin can be used in both laminating and moulding techniques to produce fibre-reinforced composites with greater mechanical strength, chemical resistance, and electronic insulating properties. Recently, there has been great interest in E-nanofiller composites. Among the E-inorganic nanocomposites, the use of layered silicates [e.g., montmorillonite (MMT)] is popular because clay has a high aspect ratio, plate morphology, natural availability, and unique intercalation ability.

There are few works reported on E/fibre/clay ternary nanocomposites.[2–8] According to Xu and Hoa,[2] carbon fibre reinforced E/clay nanocomposites were manufactured with a hot melt lay-up plus autoclave process. Siddiqui *et al.*[3] investigated the mechanical properties and fracture behaviour of nanocomposites and carbon fibre composites (CFRPs) that contained organoclay in the E matrix. Bozkurt *et al.*[4] reported that the flexural properties of non-crimp glass fibre (GF) reinforced E laminates were improved by adding clay because of the improved interface between the GF and E. According to Lin *et al.*,[5] layered silicate/GF/E hybrid nanocomposites were successfully prepared using a vacuum-assisted resin transfer moulding (VARTM) process. Miyagawa *et al.*[6] studied the mechanical and thermo-physical properties of bio-based E nanocomposites reinforced with organo-MMT (OMMT) clay and polyacrylonitrile (PAN)-based carbon fibres. It was demonstrated that the clay nanoplatelets were dispersed homogeneously and completely exfoliated into the E matrix with a sonication technique. Our previous works on E/GF/OMMT nanocomposites found that the combination of GF and OMMT could provide a synergistic effect on the mechanical and thermal properties and water absorption resistance of E.[7, 8]

In nature, MMT is likely to stack among the layers via the Van der Waals forces. In addition, the hydrophilic nature of the clay could lead to incompatibility with most hydrophobic polymeric materials. Thus, chemical modification on the clay or polymer resin or both has been carried out to enhance the interaction between the clay and the polymer.[9] The surface of the MMT is commonly modified with a cation exchange technique to expand the basal spacing and make the layered silicate compatible with most hydrophobic polymer matrixes.[10] Modification of the hydrophilic clay surface was also carried out using a silane coupling agent. According to Dean *et al.*,[11] the inter-gallery spacing of 3-(acryloxy)propyldimethylmethoxysilane (APDMMS) modified MMT was increased effectively. Ha *et al.*[12] demonstrated that the tensile strength and elastic modulus of 3-aminopropyltriethoxysilane (3-APS) modified MMT/E nanocomposites are higher than those of unmodified MMT/E. Ha *et al.*[13] also reported that modifying MMT using APS causes expansion in the interlayer galleries, which improves the dispersion of MMT into the E matrix. According to Wang *et al.*,[14] improvements in the modulus and fracture toughness of E were achieved by incorporating silane-modified clay. Wang *et al.*[15] reported that the E/crude clay nanocomposites were produced with a slurry compounding approach. It was found that only 5 wt% of silane modifier is required to facilitate the dispersion and exfoliation of clay in an E matrix. According to Di Gianni *et al.*,[16] among the many modification reactions, the silanisation reaction uses alkoxysilanes and exploits the -OH reactive sites of the MMT structure. In this research, we investigate the mechanical and morphological properties of E/GF/3-aminopropyltrimethoxysilane-treated OMMT nanocomposites.

2. EXPERIMENTAL

2.1 Materials

The E used in this study was diglycidyl ether bisphenol A (DGEBA) [DER 331] provided by Dow Chemical Sdn. Bhd. (Malaysia). The curing agent, cycloaliphatic amine hardener HY2964, was purchased from Ciba Geigy (Switzerland). The GF was in the form of a chopped strand mat (CSM). The OMMT (Nanomer 1.30E) was supplied by Nanocor, USA. The 3-aminopropyltrimethoxysilane with a molecular weight of 179.29 was supplied by Fluka (Switzerland). The surface modification of OMMT using a silane coupling agent was carried out as follows: a 205.8g ethanol solution (95% ethanol and 5% water) was stirred before 10.8 ml of silane coupling agent was added. The mixture was then stirred for 5 hours using a mechanical stirrer. Next, the mixture was filtered and dried for 4 hours. The amount of 3-aminopropyltrimethoxysilane required for OMMT treatment was calculated using equation (1):

$$\text{Amount of silane coupling agent} = (m_f \text{ x } SA_f)/CA_{sca} \tag{1}$$

where m_f = amount of filler
SA_f = surface area of filler
CA_{sca} = minimum coating area of silane coupling agent.

2.2 Sample Preparation

The ratio between DGEBA and hardener was 10:6 by weight. Then, 3 wt% of OMMT was added to the DGEBA resin. The mixture was then stirred using a mechanical stirrer at 100 rpm. The stirring process continued until all the OMMT powder was dispersed well in the E resin (about 10 min). Next, the hardener was added into the mixture and the stirring process continued for 10 min. Four plies (17 x 17 cm^2) of CSM were cut. The details of the hand-lay up process have been reported elsewhere.[7] The E/GF/OMMT laminate samples were placed in an oven for complete curing at 100°C for 60 min. The cured E/GF/OMMT specimens were then cut into the proper geometry (flexural beam) according to ASTM D790.[17]

2.3 Materials' Characterisation

2.3.1 X-ray diffraction (XRD)

The X-ray diffraction (XRD) was performed with a diffractomer (Siemens D5000, Germany). The XRD measurements were made directly from OMMT powders. For the E composites, the measurements were carried out on bars. The X-ray beam equipped with CuK_α radiation was operated at 40 kV. The scan rate and step size were 1^o min^{-1} and 0.02^o, respectively. The diffraction patterns were collected from 1^o to 10^o. The d-spacing was calculated using Bragg's Equation ($n\lambda = 2dsin\theta$).

2.3.2 Flexural tests

Flexural testing of the E composite was performed according to ASTM D790[17] with an Instron 3366 (USA) machine equipped with a three-point bending rig. The crosshead speed was set to 15 mm min^{-1}. The specimen size was 150 x 12.7 x 3.2 mm (length x width x thickness). The flexural modulus and strength of the E composites were determined.

2.3.3 Field emission scanning electron microscopy (FESEM)

The fractured surface of the E/GF/OMMT composites was investigated using field emission scanning electron microscopy (FESEM, Supra 35VP-24-58) at an acceleration voltage of 15 kV. The fractured surface of the samples was sputter-coated with a thin gold-palladium layer in vacuum chamber for conductivity before examination.

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction

Figure 1 shows the XRD patterns of the OMMT and E/GF/OMMT nanocomposite. The OMMT patterns reveals a characteristic peak (d_{001}) at $2\theta = 3.45^o$. Note that the characteristic peak of silane-treated OMMT had a lower 2θ value, which indicates that the interlayer spacing increases because of the 3-aminopropyltrimethoxysilane. These results are in agreement with those reported by Ha *et al.*,[13] Wang *et al.*,[15] and Di Gianni *et al.*[16] It was found that the silane coupling agent can produce good dispersion, intercalation and exfoliation of MMT in the E matrix. According to Bozkurt *et al.*,[4] the intergallery spacing of the layered clay increased with the use of surface treatment. Ha *et al.*[12] reported that the d-spacing between silicate layers increased more than 55% by modifying the MMT with 3-APS. It is believed that the silane coupling agent forms intermolecular hydrogen bonds instead of covalent bonds with the clay surface, which is attributed to the affinity and interaction between the silane coupling agent and the MMT. The XRD traces of E/GF/silane-OMMT nanocomposites do not show the characteristic basal reflection of the OMMT, which likely reflects the fact that the silane-treated OMMT was exfoliated in the E matrix.

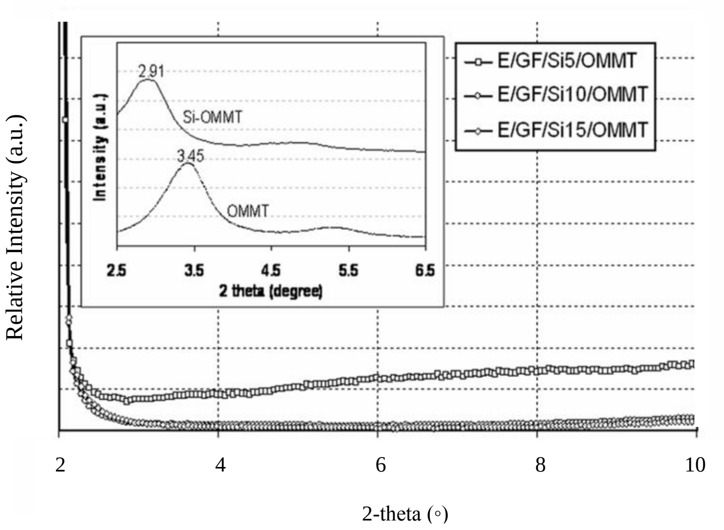

Figure 1: XRD spectra of OMMT and the E/GF/OMMT composite.

3.2 Flexural Properties

The effects of silane-treated OMMT loading on the flexural modulus of E/GF composites are presented in Figure 2. The incorporation of silane-treated OMMT increases the stiffness of the E/GF composites significantly. The flexural modulus of E/GF/OMMT is 4.41 GPa. Note that the flexural modulus increased significantly as the loading of silane-treated OMMT increased. In addition the flexural modulus of E/GF/Si-15/OMMT is approximately 4.98 GPa, which is an increase of 13%. This result is due to the exfoliation of silicate layers in the E matrix. The improvement in modulus could also be attributed to the high aspect ratio, contact surface and reinforcing effects of the silane-treated OMMT. According to Siddiqui *et al*.,[3] the organoclay significantly enhances the flexural modulus of E composites, and the improvement of the flexural modulus was at the expense of a reduction in flexural strength. Wang *et al*.[14] reported that the storage modulus, Young's modulus and fracture toughness of E improved when silane modified clay was incorporated. Figure 3 shows the effects of silane-treated OMMT on the flexural strength of E/GF composites. It is interesting to note that the flexural strength of E/GF/silane-treated OMMT composites is higher than that of E/GF composites. Comparing the flexural strength of E/GF/OMMT (200.4 MPa) and E/GF/Si-15/OMMT (220.4 MPa), the improvement is about 10%, which is attributed to the improved interfacial interaction between GF and silane-treated OMMT. Xu and Hoa[2] reported that adding 2 phr nanoclay enhanced the flexural strength of carbon/E composites by about 38%. According to Ha *et al*.,[12] both the elastic modulus and strength of surface-modified MMT/E nanocomposites increase as the concentration of clay increases, which is attributed to the increased exfoliation of clays and the improved interfacial strength that results from the surface modification.

3.3 Morphological Properties

Figure 4(a–c) display the FESEM micrographs taken from the flexural fractured surface of E/GF, E/GF/OMMT and E/GF/silane-treated OMMT composites, respectively. It can be observed that the GF surface of E/GF/silane-treated OMMT is relatively rough and likely coated with a layer of silane-treated OMMT. This result may be indicative of the improved interfacial interaction between GF and modified OMMT; there is significant improvement in the flexural modulus and strength of the E/GF composites with the addition of silane-treated OMMT. According to Lin *et al*.,[5] the clays were dispersed between both the bundles of GF and within the interstices of the fibre filament.

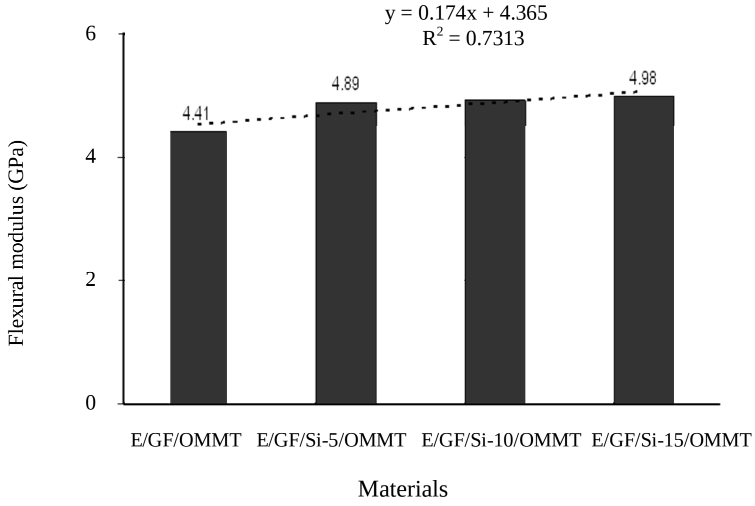

Figure 2: Effects of silane-treated OMMT on the flexural modulus of E/GF composites.

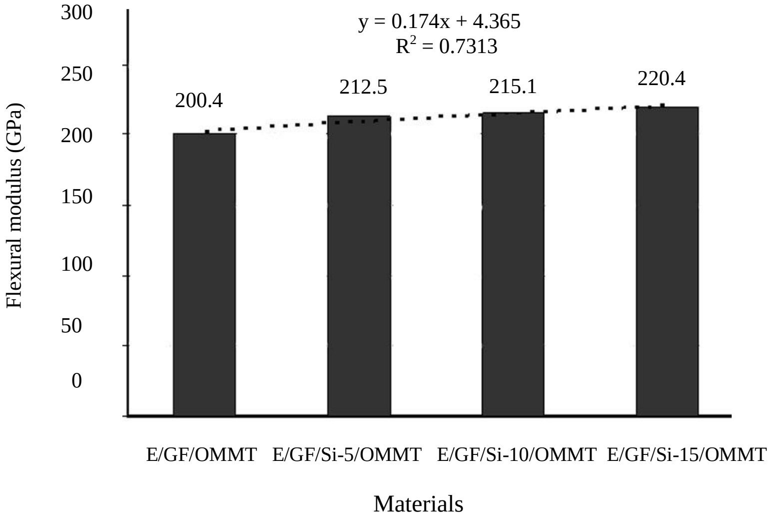

Figure 3: Effects of silane-treated OMMT on the flexural strength of E/GF composites.

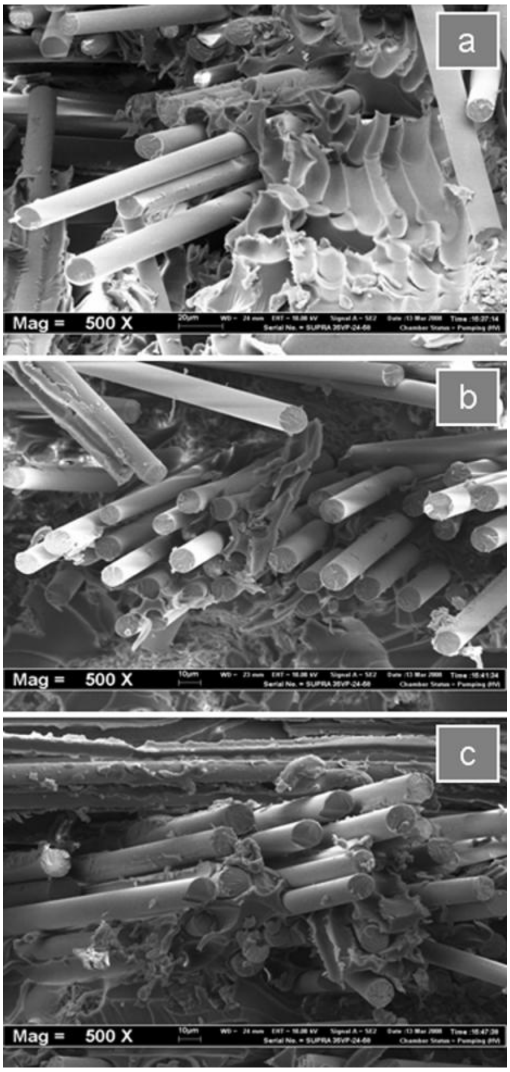

Figure 4: FESEM micrographs taken from the flexural fractured surface of (a) E/GF composites, (b) E/GF/OMMT composites and (c) E/GF/silane-treated OMMT composites.

4. CONCLUSION

The OMMT modification by the silane coupling agent can further expand the d-spacing of the OMMT, which could favour the intercalation and exfoliation of silane-treated OMMT in the E matrix. It is also believe that the GF and silane-treated OMMT may interact, which consequently enhances the flexural modulus and strength of the E/GF composites.

5. ACKNOWLEDGEMENT

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