Mechanical and Thermal Properties of Graphene Oxide Filled Epoxy Nanocomposites
(Sifat Mekanik dan Terma Nanokomposit Epoksi Berpengisi Grafin Oksida)

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ABSTRACT

In this study, graphene oxide (GO) filled epoxy nanocomposites were prepared using hot pressed method. The GO was produced using modified Hummers' method. The produced GO at different compositions (0.1, 0.3 and 0.5 wt%) were mixed with epoxy before the addition of hardener using ultra-sonication. The produced epoxy nanocomposites were characterized in terms of mechanical and thermal properties. The mechanical properties of the nanocomposites were significantly enhanced by the addition of GO. About 50% of increment in the flexural strength of the composite sample filled with 0.3 wt% of GO as compared to the neat epoxy sample. However, only slight improvement in the impact strength of the composite were obtained by adding 0.1 wt% of GO.

Keywords: Epoxy; graphene oxide; mechanical; nanocomposite

ABSTRAK

Dalam kajian ini komposit epoksi berpengisi grafin oksida (GO) disediakan menggunakan kaedah penekanan panas. GO tersebut dihasilkan melalui kaedah Hummers. Penyediaan campuran GO pada komposisi yang berbeza (0.1, 0.3 dan 0.5 wt%) bersama epoksi dilakukan dengan ultrasonik sebelum penambahan agen pengeras. Pencirian sifat mekanik dan terma nanokomposit epoksi dijalankan. Sifat mekanik nanokomposit berjaya dipertingkatkan dengan penambahan GO. Kekuatan lenturan bagi sampel 0.3 wt% GO meningkat sebanyak 50% jika dibandingkan dengan epoksi tanpa pengisi. Walau bagaimanapun, peningkatan yang sedikit telah diperoleh bagi kekuatan impak nanokomposit berpengisi 0.1 wt% GO.

Kata kunci: Epoksi; grafin oksida; mekanik; nanokomposit

INTRODUCTION

Epoxy resin is one of the widely used thermosetting polymers in the production of advanced composites due to its excellent properties, including good dimensional stability, chemical resistance, stiffness and low processing cost (Zhou et al. 2007). However, the scope of use of epoxy is limited because of the brittleness with poor strength and toughness (Montazeri et al. 2010; Zaman et al. 2011). In order to overcome these problems, researchers have incorporated reinforcing filler to strengthen the properties of epoxy resin (Lorenz et al. 2009). Introduction of nanoscale reinforcing fillers into polymeric composite formulations have attracted considerable attention recently. Nanocomposite represents new boundaries in material science, thanks to the changes in reinforcement size from micrometer to nanometer scale (Kueseng et al. 2006; Thostenson et al. 2006). In fact, the nanomaterials in the nanocomposite system is playing an important role for the final properties of the nanocomposites, such as electrical, optical and thermal properties. It can be explained by the high surface to volume ratio of the nanomaterials which well-interact with the polymer matrix and subsequently improved the mechanical properties of the products (Potts et al. 2011).

Incorporating fillers such as carbon nanofibers (CNF), carbon nanotubes (CNT) and graphene has been proven to be able to improve the properties of epoxy nanocomposites with low filler content (Kaynak et al. 2005; Martin-Gallego et al. 2011; Zhou et al. 2007). Graphene is gaining momentum among researchers for its potential utilization in nanoscale composite reinforcement (Kuila et al. 2012). Graphene exhibits unique structure which has a two dimensional single layered made of carbon. Thermal treatment or chemical reducing agent is an efficient method to reduce graphene oxide (GO) to graphene (Dubin et al. 2010). Despite being applied as graphene precursor, GO along with other carbon nanostructures have been labeled as integral part in the nanotechnology development. GO is a derivation of graphite which undergo a chemical surface modification using strong oxidizing agents such as $KMnO_4$ and H_2SO_4 (Potts et al. 2011). Yang et al. (2010) reported the purpose of nanocarbon's surface treatment is to introduce new functionalized group for better covalent bonding with the polymer matrix. Covalent bonding helps to improve interfacial interaction between filler and matrix polymer thus determine composite final mechanical performance (Medhekar et al. 2010). Better wettability and homogenous dispersion was observed from surface modification.

Chen et al. (2008) fabricated functionalized 1.5 wt% multi-wall carbon nanotubes (MWCNT) nanocomposites and reported the significant improvement of impact strength from 5.5 kJ/m² (neat epoxy) to 10.6 kJ/m². Previous study by Ma et al. (2010) showed that, amino-functionalization led to improve hydrophilicity, wettability and also enhanced interfacial interactions between CNT with epoxy. The result obtained by Montarezi et al. (2010) showed that dispersion of acid treated MWCNT in epoxy matrix was more uniform compare with untreated MWCNT. The addition of 0.9 wt% graphene into polystyrene resulting in 57.2 and 69.5% increase in Young's modulus and tensile strength, respectively, as reported by Fang et al. (2009). Yang et al. (2010) studied the uniform dispersion of 1 wt% GO in chitosan matrix successfully increased tensile strength and Young's modulus by 122 and 64%, respectively. Ganguli et al. (2008) observed reinforcing effect of 4% graphite in epoxy resin, increasing T_g value from 155 to 175°C (Ganguli et al. 2008).

In this study, the effects on the addition of GO on the mechanical (flexural and impact properties) and thermal properties of epoxy nanocomposites were characterized. Thermogravimetric analysis (TGA) and dynamic mechanical thermal analysis (DMTA) were performed to examine the thermal properties of the epoxy samples. The fractured surface of impact test was examined by a Field emission scanning electron microscope (FESEM).

EXPERIMENTAL DETAILS

Graphite flakes (code no 3061), were purchased from Graphite Mills, Inc. Sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), potassium permanganate ($KMnO_4$) and hydrogen peroxide (H_2O_2) were supplied by Darmstadt, Germany while hydrogen chloride (HCl) was obtained from Sigma Aldrich. The resin type Epikote 828 of Bisphenol-A-(DGEBA) was used along with the curing agent, epoxy epicure Jeffamine D230 were supplied by Asa Chem Sdn. Bhd. Ethanol are ACS reagent-grade chemicals supplied by Systerms and were used as received.

GO were synthesized using simplified Hummer's method (Huang et al. 2011). For surface modification, GO was prepared by oxidation of graphite, H_2SO_4:H_3PO_4 (in the ratio of 320:80 mL) and 18 g $KMnO_4$ at room temperature. The materials were mixed using magnetic stirrer for 3 days. Next, H_2O_2 was added to stop the oxidation process and the resulting solution was washed with 1 M of HCl for three times. Again, the solution obtained was washed using deionized water via centrifugation until a pH of 4 was achieved.

The neat epoxy resin sample was fabricated by mixing the epoxy resin and curing agent, epicure D230 (32 wt% of epoxy) using magnetic stirrer under moderate speed at room temperature for 20 min. The mixture was degassed at 80°C for 10 min and curing at 110°C via hot press method (pre heat for 10 min, followed with full press for 20 min). GO was first dispersed and sonicated in ethanol to break the agglomeration. For the preparation of GO/epoxy nanocomposites, the desired amount of GO (0.1, 0.3 and 0.5 wt%) was added into the epoxy resin. The mixture was then subjected to ultrasonication at room temperature for 2 h. The composite mixture was conditioned in an oven at 80°C for 24 h to evaporate the excess ethanol. Next, epicure D230 was added into the mixture solution. The mixture was then hot-pressed into sheets and cut into different dimension according to the standard requirement for characterizations.

Flexural test was performed using a 10 kN Testometric machine model M350-10CT according to ASTM D790-96 in a three point bending mode at a cross head speed of 1.35 mm/min. At least five specimens of dimensions 70 × 12.7 × 3 mm³ sample were analyzed with a fixed span length of 50 mm. Testing were carried out at room temperature.

In order to determine the mechanical performance of impact strength, Izod tests were carried out using Digital impact testing RR/MT according to standard test method of ASTM D256. Five replicate notched specimens with dimensions of 60.3 × 12.7 × 3.2 mm³ were prepared for this testing to ensure the reliability of the test results.

Field emission scanning electron microscope (FESEM) was performed on the fractured surface from each composite sample after impact tests. Samples were first sputter-coated with gold prior to being scanned in a high resolution scanning electron microscope.

Data for glass transition temperature (T_g) analysis was obtained using a dynamic mechanical analyzer (DMA-2980 TA INSTRUMENT) in a three point bending mode. Rectangular bar specimens of 53 × 12.7 × 3 mm³ were tested in temperature range of 30 to 220°C at a scanning rate of 10°C/min and oscillation frequency of 1 Hz.

Thermogravimetric (TGA) was carried out on a Mettler Toledo SDTA 851e thermal analyzer at heating rate of 10°C/min under nitrogen gas purging. About 6-10 mg samples was placed on an alumina crucible and heated from 30 to 600°C.

RESULTS AND DISCUSSION

Figure 1 presents the average value for flexural modulus and flexural strength as the functions of GO content. For comparison purpose, value for each elastic modulus and flexural strength are shown in Table 1. Figure 1 shows that increasing GO content up to 0.3 wt% resulting in a positive mechanical improvement for both values. The results showed increasing around 55 and 35% in flexural strength and flexural modulus for the addition of 0.3 wt% GO. A previous study has recommended that GO has superior strength (Medhekar et al. 2010). This may be good indicators for better cross linking, uniform dispersion and good interfacial interaction via covalent bonding between GO and the matrix. Good interfacial bonding facilitates the effectiveness of load transfer (Glaskova et al. 2012). However, further addition of GO to 0.5 wt% has decreased the flexural strength and flexural modulus. At higher GO content, the filler structures are in a cluster form because of a weak distribution. This may be attributed to poor

dispersion of GO due to agglomeration of GO in the epoxy matrix. Agglomeration is a typical stress concentration led to failure in most matrix system (Theodore et al. 2011).

The Izod impact strength for the epoxy nanocomposites as function of GO content (%) is shown in Figure 2. As can be seen from the chart, the impact strength increased around 3% when 0.1 wt% GO were added into the epoxy resin. Insignificant or neglected improvement of impact strength can be explained due to rigid reinforcement and brittle matrix at ambient temperature (Sengupta et al. 2011). The impact strength was maintained at small loading of 0.1 wt% GO. Decreasing trend of impact strength was expected as functions of increasing 0.3 wt% GO in GO/epoxy nanocomposites. The maintenance of Izod impact strength is a challenge in 0.3 wt% GO/epoxy nanocomposites that resulting in excellent effect on flexural properties without sacrificing the impact strength. Non-homogeneity distributions of 0.5 wt% GO caused by
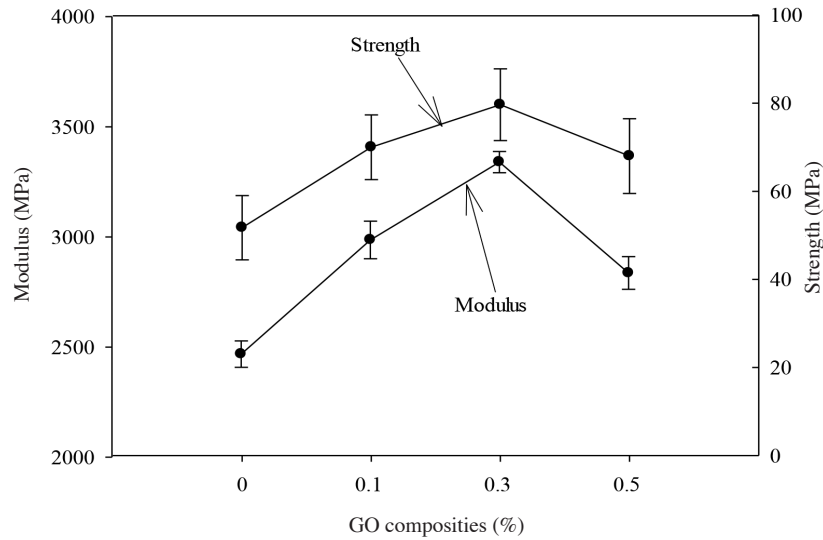

FIGURE 1. Flexural properties of GO/epoxy nanocomposites

TABLE 1. Flexural strength and flexural modulus of epoxy and GO/epoxy nanocomposites

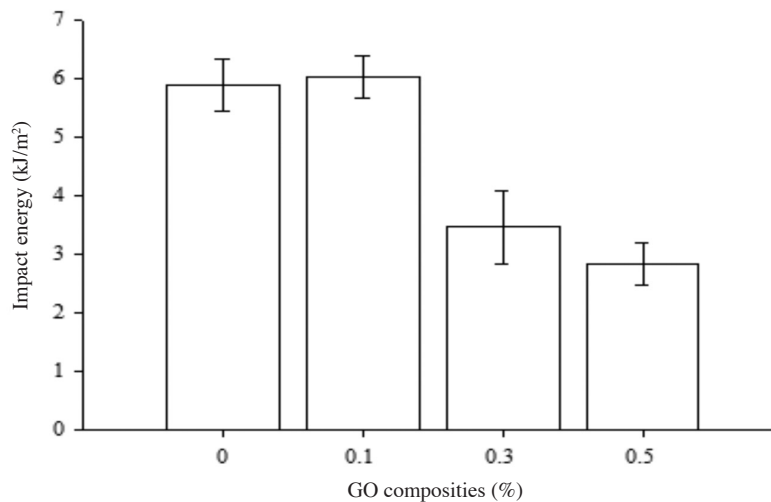| Sample	Flexural strength (MPa)	Flexural modulus (MPa)
Epoxy €	51.74	2468.40
E-0.1 wt% GO	70.11	2986.33
E-0.3 wt% GO	79.66	3340.04
E-0.5 wt% GO	68.03	2836.50

FIGURE 2. Impact strength vs. filler content of neat and GO/epoxy nanocomposites

high viscosity mixture solution from sample preparation led to failure in stress transfer in matrix system and this was proven by SEM morphology analysis. Theodore et al. (2011) also found the transparency of the Epoxy/MWCNT increased with the addition of the nanofillers.

FESEM morphology studies were conducted in order to examine the impact fractured surface of the neat epoxy and GO/epoxy nanocomposites. The neat epoxy sample exhibited a typical brittle fracture behavior as evidenced by smooth line and clear surface in SEM image (Figure 3(a)). This finding indicates the low fracture toughness and impact resistance of epoxy (Pervin et al. 2005). Increasing in the fracture surface roughness was observed (Figure 3(b) & 3(c)) with the increment of GO content from 0.1 to 0.3 wt% in the GO/epoxy sample. This can be attributed to the substantial increase in mechanical performance due to better covalent bonding. Zhou et al. (2007) proposed that filler resistance towards crack propagation is responsible for the increasing in surface roughness. Agglomeration of GO indicated by dark region was observed in 0.5 wt% GO fracture surface image (Figure 3(d)). The stress concentration between epoxy and GO due to agglomeration caused mechanical failure for 0.5 wt% GO/epoxy sample. Poor distribution which led to poor interfacial bonding is expected at higher GO contents (Ma et al. 2010).

DMA analysis was used to derive information tan δ and storage modulus of these nanocomposites. The maximum glass transition temperature (T_g) was determined from the peak position of tan δ. Figure 4 shows the curves of tan δ vs. temperature and the peak temperature is defined as the glass transition temperature (T_g). Broad glass transition peaks were observed from the curves. It is noted, that the T_g shoulders shifted to the right which indicate increment of T_g temperature. About 0.3 wt% GO exhibited higher value of T_g (102°C) than neat epoxy (96°C). This can be attributed to the limitation of epoxy molecular chain motion as a result of higher degree cross linking and better dispersion (Geng et al. 2008; Martin-Gallego et al. 2011; Sui et al. 2009). However, T_g value drops at 0.5 wt% GO content may be contributed by GO agglomeration thus cause disturbance on polymer heat flow.

The storage modulus shown in Figure 5 displays the same trend with flexural modulus data. Storage modulus is an indication of interaction among the fillers and matrix phase (Ganguli et al. 2008). Neat epoxy has the lowest storage modulus compare to GO/epoxy nanocomposites. Enhancement of storage modulus was observed at 0.3 wt% GO directly indicates good interfacial interactions between GO and epoxy resin. Good dispersion of GO improved the efficiency of load transfer from matrix to filler (Ma 2010). Once the GO content exceed a certain limit (0.5 wt%), storage modulus started to decrease as the epoxy and curing agent ratio exceeded the value required by the reaction stoichiometry, which caused the decreased in the degree of cross-linking in the nanocomposites (Ma et al. 2007).

Figure 6 shows the TG thermogram for the thermal degradation behavior of neat epoxy and GO/epoxy
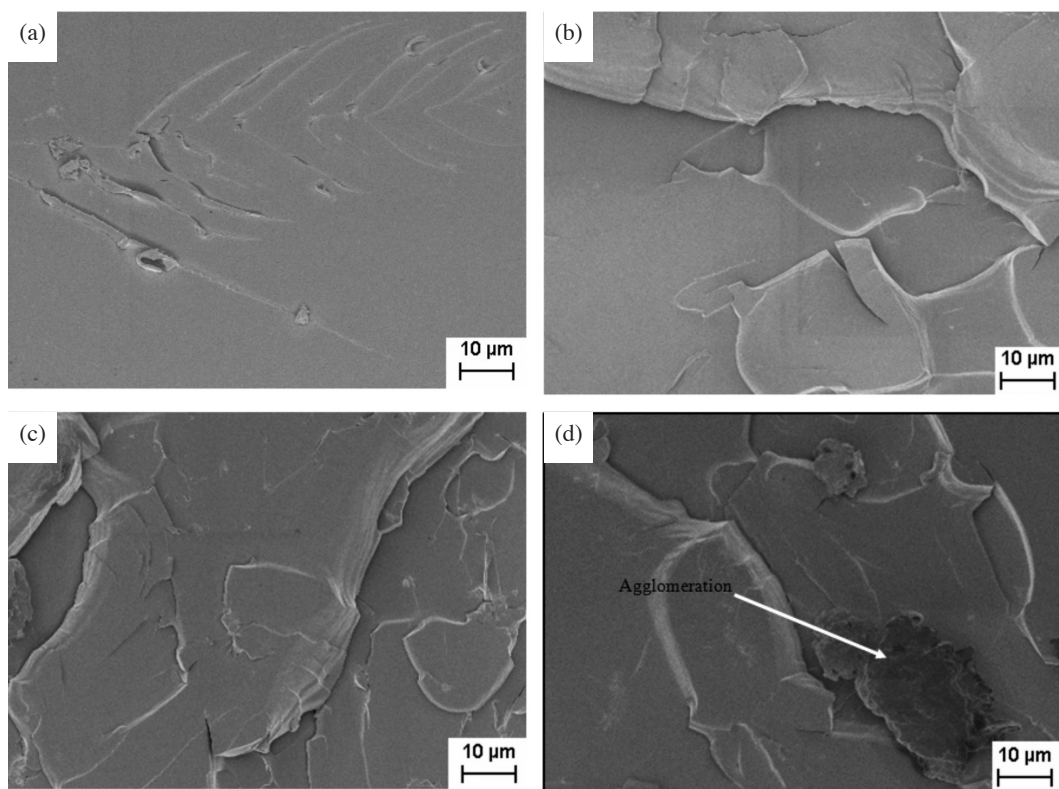

FIGURE 3. Fracture surface of (a) neat epoxy (b) 0.1 wt% GO/epoxy, (c) 0.3 wt% GO/epoxy and (d) 0.5 wt% GO/epoxy
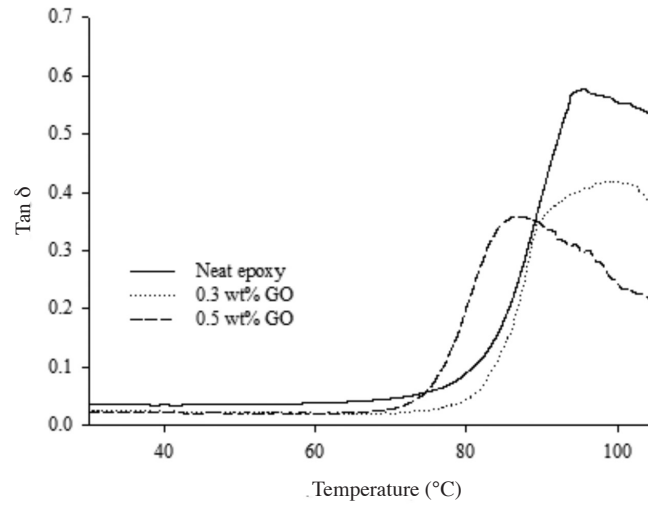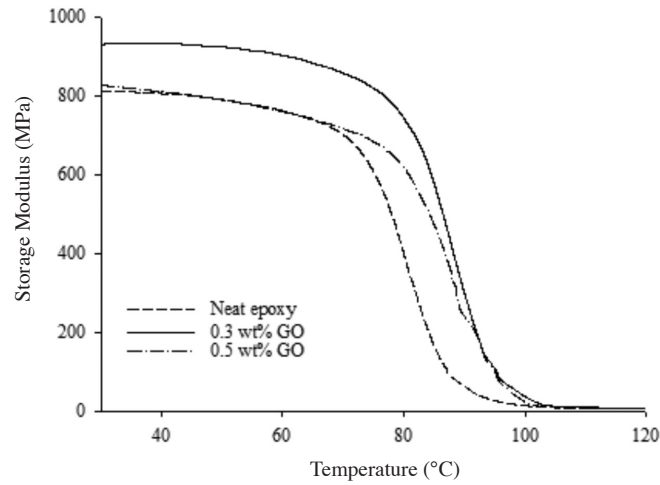
FIGURE 4. DMTA curves of tan δ vs. temperature

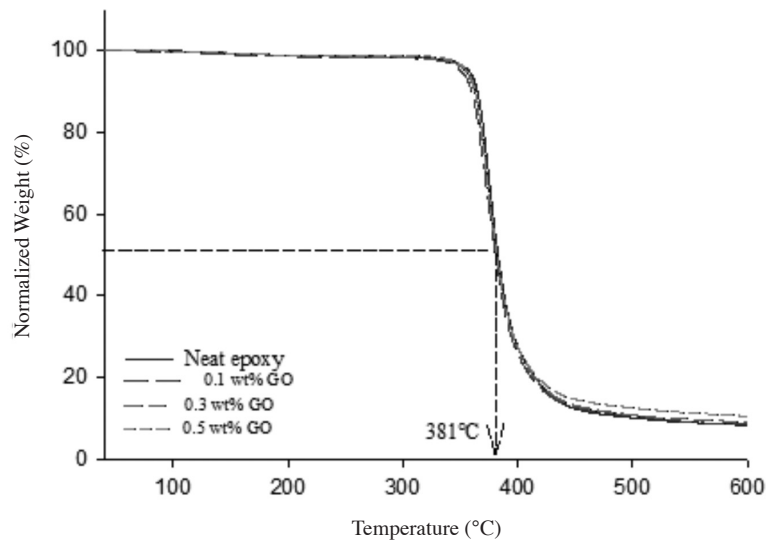FIGURE 5. DMTA curves of storage modulus vs. temperature

FIGURE 6. TGA curves of neat and GO/Epoxy nanocomposite

nanocomposites. T_g curves ~ 360-440°C with maximum decomposition peak at 381°C represents structural decomposition of the epoxy (Zhou et al. 2006). Weight loss of GO/Epoxy samples up to 600°C showed increasing residue pattern of thermal stability with the increment of GO content. The changes in thermal stability are related to strong interfacial bonding effect of GO which involves covalent bonding and higher cross-linking system. More energy (heat) required to overcome the good interfacial interaction in the nanocomposites sample. Several studies showed the outstanding of GO properties can enhance the thermal stability of polymer composite compared to neat polymer, despite being thermally unstable itself (Potts et al. 2011). However, thermal decomposition of all samples is almost the same since the plotted graph are overlap to each other.

CONCLUSION

In this study, GO/epoxy nanocomposites were successfully fabricated by mixing GO with epoxy resin, followed by a curing process. Ultrasonic has proven to be a good method to dispersed GO into epoxy resin. The additions of 0.3 wt% GO has resulted in the improvement of flexural properties as compared to the neat epoxy sample. The fractured surface of GO/epoxy nanocomposites appeared to be rougher than neat sample. The DMA results showed increase glass transition temperature and storage modulus for nanocomposites compared to neat epoxy.

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