Processing of expanded graphite reinforced polymer nanocomposites

Asma Yasmin, Jyi-Jiin Luo, Isaac M. Daniel *

McCormick School of Engineering and Applied Science, Northwestern University, 2137 Tech Drive, Evanston, IL 60208, USA

Abstract

Nanocomposites consisting of anhydride cured epoxy resin matrix reinforced with expanded graphite (EG) with concentrations of 1–2 wt.% were fabricated. Processing techniques such as direct, sonication, shear, and combined sonication and shear mixing techniques were employed in the fabrication of nanocomposites. It was found that both sonication and shear mixing produced in situ nanosize graphite sheets from EG. However, the occurrence of X-ray diffraction (XRD) peaks at $2\theta = 26.38°$ ($d_{002} = 3.37$ Å) irrespective of processing technique confirmed the presence of graphite nanosheets in multilayer rather than a single layer form. The mechanical behavior of the nanocomposites was investigated as a function of particle concentration and processing technique. It was found that EG reinforced nanocomposites showed higher elastic modulus than neat epoxy. However, nanocomposites prepared with the aid of shear mixing provided the best exfoliation and dispersion of graphite nanosheets and as a consequence, the best modulus enhancement over other processing techniques.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: A. Nanostructures; B. Mechanical properties; B. Microstructure; D. Scanning electron microscopy (SEM); E. Processing

1. Introduction

In recent years, polymer based nanocomposites reinforced with EG have shown substantial improvements in mechanical, electrical conductivity and barrier properties over the unmodified polymer. The plausible reason for this is the sheet-like structure of natural graphite where the atoms are strongly bonded on a hexagonal plane but weakly bonded normal to that plane. If these sheets/layers could be separated down to a nanometer thickness, they would form high aspect ratio (200–1500) and high modulus (~1 TPa) graphite nanosheets [1]. Furthermore, the graphite nanosheets could have an enormous surface area (up to 2630 m²/g) considering both sides of the sheets are accessible [2]. Therefore, the dispersion of such nanosheets in a matrix will play a key role in the improvement of both physical and mechanical properties of the resultant nanocomposite. This can be achieved by a combination of both

synthesis and processing techniques that produces complete exfoliation and good dispersion of graphite particles in the matrix. The synthesis of EG as well as graphite nanosheets is well documented in the literature [1–4]. Natural graphite is first converted to intercalated or expandable graphite through chemical oxidation in the presence of concentrated H_2SO_4 and HNO_3 acid. EG is then obtained by rapid expansion and exfoliation of expandable graphite in a furnace above 600 °C.

A number of studies have been conducted on EG reinforced conductive polymer nanocomposites [4–12]. So far, investigations have been carried out on thermoplastic materials such as polystyrene [4], PMMA [5–7], nylon-6 [8] and polypropylene [9]. These nanocomposites were prepared via in situ polymerization or solution compounding to measure the electrical properties of the resultant nanocomposites. However, there are not many studies on fabrication methods of epoxy based graphite nanocomposites and their influence on physical, mechanical and thermomechanical properties. In the present study, a significant effort has been directed to the synthesis and fabrication of EG/

---

* Corresponding author. Tel.: +1 847 491 5649; fax: +1 847 491 5227.
  E-mail address: imdaniel@northwestern.edu (I.M. Daniel).

epoxy nanocomposites using different processing techniques and their effects on the mechanical behavior.

2. Experimental

2.1. Materials

The matrix used in the present study was a three-component epoxy resin system from Vantico, consisting of epoxy resin DGEBA (GY6010), anhydride hardener (Aradur 917), and accelerator (DY070) mixed in proportions of 100:90:1, respectively. The graphite flakes were obtained from GrafTech International Ltd., in the form of intercalated compound (Grade 160-80N). The intercalation was carried out by chemical (or acid) treatment of crystalline graphite flakes, and after intercalation, the size of intercalated graphite was approximately 300 μm in diameter.

The EG was prepared by expanding the intercalated compound by thermal shock at 600 °C in a furnace. At such a high temperature, intercalates (trapped between graphite layers) decompose and force the graphite layers to separate randomly. Therefore, the expansion process causes destruc-

tion of graphite crystal structure and an enormous increase in volume (∼200 cc/g) and expansion in the thickness or c-direction of about 80–100 times [13]. After expansion, the EG emerges as a loose and porous material consisting of numerous graphite sheets of nanometers in thickness (<100 nm) and micrometers in diameter (<10 μm) as measured from SEM images. Therefore, it possesses high aspect ratio. The surface area of such EG is ∼43 m^2/g as measured by gas adsorption technique (BET) and this surface area corresponds to graphite nanosheets of 20 nm in thickness if calculated using the formula, $A = 2/\rho t$ [12], where, A is the specific surface area per unit mass, m^2/g; ρ the density, g/cc; t the platelet thickness, nm. The discrepancy between measured and calculated values regarding the thickness of graphite nanosheets (from a few nm to hundreds of nm) arises from the non-uniform expansion of graphite flakes. The loosely connected graphite nanosheets were later separated into individual nanosheets by sonication in an acetone bath. Fig. 1 shows SEM images of intercalated, expanded, and exfoliated graphite flakes. Additionally, Fig. 1(d) confirms that the individual graphite nanosheet is not a single graphite nanosheet or "graphene" but rather consists of
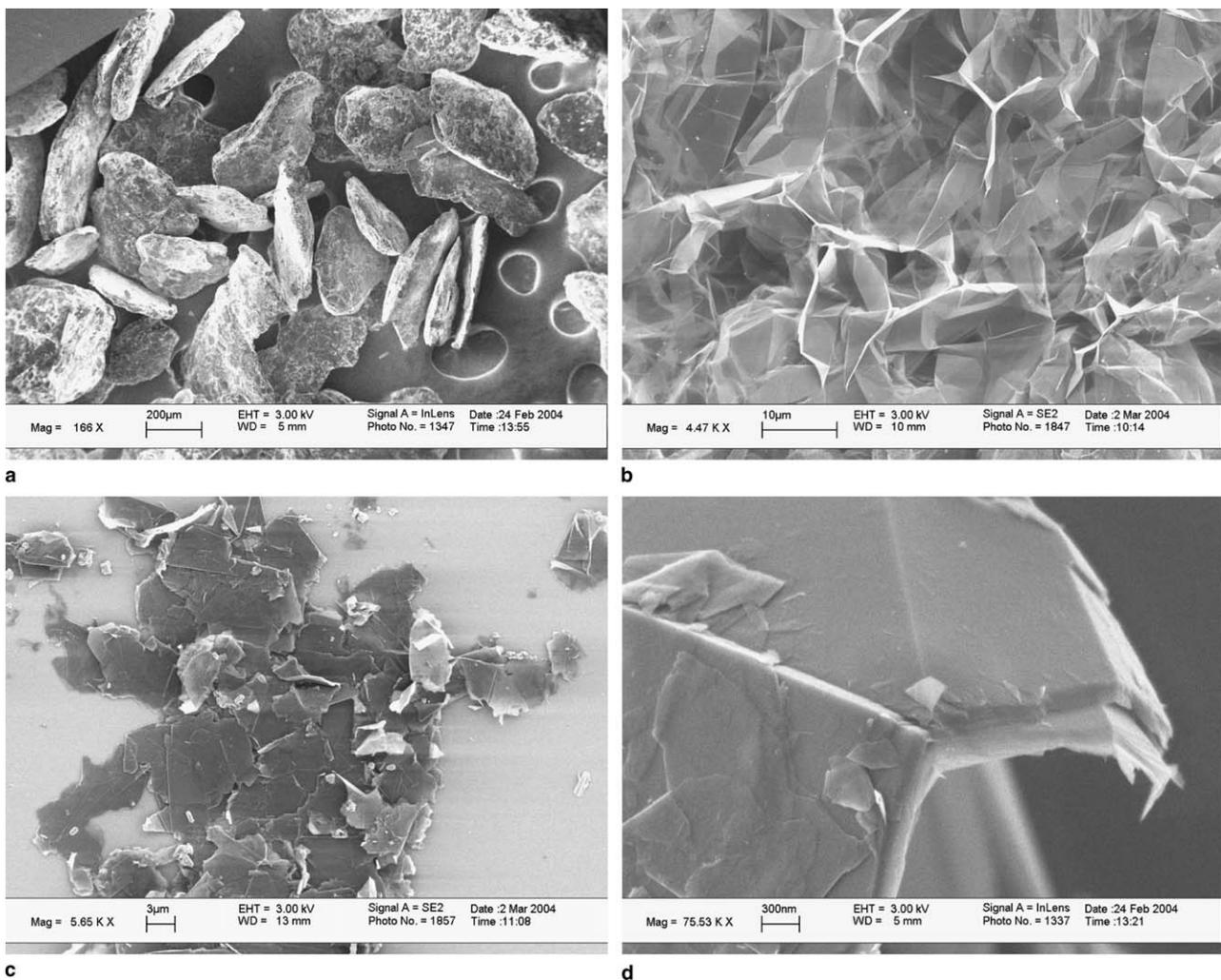

Fig. 1. SEM images of (a) intercalated, (b) expanded, (c) sonicated (exfoliated), and (d) graphite nanosheets.

several layers of graphite sheets. It is important to report that the graphite nanosheets contain functional groups such as –OH, –COOH after acid and high temperature treatments [3,7]. These functional groups are assumed to promote both physical and mechanical interaction between the polymer and graphite nanosheets.

2.2. Processing techniques

A number of techniques were used to process the EG/epoxy nanocomposites and the equipment used to process the nanocomposites is shown in Fig. 2.

2.2.1. Direct mixing
The EG was first added to the hardener due to its low viscosity and stirred continuously using a magnetic stirrer at room temperature for one day. DGEBA was then added and stirred for another 2 h on a hot plate at 60 °C. An accelerator was added to the solution at ambient temperature and stirred for 0.5 h with slow agitation followed by overnight degassing. The solution was cast in a teflon mold prepared following the ASTM standard D638-99. The tensile specimens were 165 mm long and 2.5 mm thick with a gage length of 50 mm and width of 13 mm. The mold was then placed in a hot press and the specimens cured at 148 °C for 1 h.

2.2.2. Sonication mixing
The EG was first sonicated in an acetone bath for 5 h and stirred on a hot plate using a magnetic stirrer until all the acetone was evaporated. Such a sonication technique produces graphite nanosheets as shown in Fig. 1(c). Later, graphite nanosheets were added to DGEBA and mixed with a magnetic stirrer for 3 h. Next, hardener was added and stirred for another 2 h. Finally, an accelerator was added and the solution was degassed overnight. The solution was then cast and cured as described before for the direct mixing. If otherwise not stated, the results for sonication mixing came from nanocomposites processed by this technique. In another attempt, DGEBA was added to the acetone bath of graphite nanosheets and sonicated for 0.5 and 5 h to observe the effect of sonication mixing in comparison to magnetic stirrer mixing. The solution

was then heated and stirred on a hot plate at approximately 60 °C until all acetone was gone followed by processing as discussed above.

2.2.3. Shear mixing
Processing of nanocomposites by shear mixing has been described elsewhere [14]. In the present study, EG was used instead of nanoclay particles as the reinforcement. The epoxy resin (DGEBA) was first placed between the feed and center rolls. Once the rolls started moving, the EG was spread gradually on the resin to achieve the maximum contact with the rolls. In the beginning, the solution is highly viscous and immiscible. However, with continued mixing, it becomes a homogeneous, shiny, miscible and less viscous solution. Compounding was carried out at room temperature for 2 h with a rotation speed of 500 rpm. The final product from the mill was then collected and mixed with the hardener at 60 °C for 1 h on a hot plate. After adding accelerator and mixing for a few minutes, the solution was left overnight for degassing. After degassing, the solution was cast and cured as described for the direct mixing.

2.2.4. Combined sonication and shear mixing
In this method, a solution of DGEBA and graphite nanosheets was first processed by sonication mixing followed by shear mixing as described above. This process combines the benefits of both sonication and shear processes.

Fig. 3 illustrates the flowchart for all processing techniques.

2.3. Characterization techniques

Wide angle X-ray diffraction (WAXD) was performed on cured nanocomposites to evaluate the structure, and/or the degree of expansion and exfoliation of graphite particles in the nanocomposites. WAXD was carried out on a RIGAKU diffractometer with Cu Kα radiation ($\lambda = 1.541$ Å) with a scanning speed of 0.5°/min and operating at 40 kV and 20 mA. The tensile samples were tested on an Instron 8500 servohydraulic machine at a cross-head rate of 0.13 mm/min. The micrography of intercalated,

Fig. 2. Equipment used in the present study to process EG/epoxy nanocomposites. (a) Hot plate (direct mixing), (b) sonication bath (sonication mixing), and (c) three-roll mill (shear mixing).
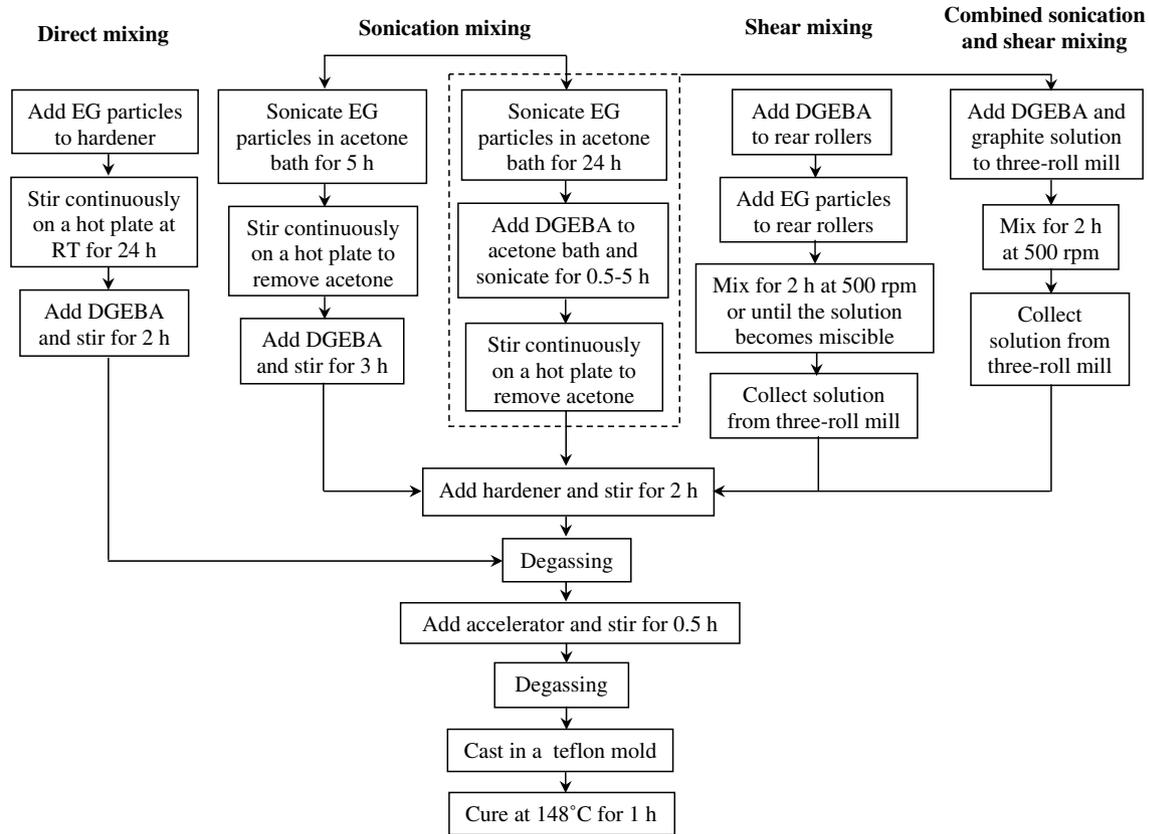
Direct mixing   **Sonication mixing**   **Shear mixing**   **Combined sonication and shear mixing**

Add EG particles to hardener	Sonicate EG particles in acetone bath for 5 h	Sonicate EG particles in acetone bath for 24 h	Add DGEBA to rear rollers	Add DGEBA and graphite solution to three-roll mill

Direct mixing:
- Add EG particles to hardener
- Stir continuously on a hot plate at RT for 24 h
- Add DGEBA and stir for 2 h

Sonication mixing (5 h branch):
- Sonicate EG particles in acetone bath for 5 h
- Stir continuously on a hot plate to remove acetone
- Add DGEBA and stir for 3 h

Sonication mixing (24 h branch):
- Sonicate EG particles in acetone bath for 24 h
- Add DGEBA to acetone bath and sonicate for 0.5-5 h
- Stir continuously on a hot plate to remove acetone

Shear mixing:
- Add DGEBA to rear rollers
- Add EG particles to rear rollers
- Mix for 2 h at 500 rpm or until the solution becomes miscible
- Collect solution from three-roll mill

Combined sonication and shear mixing:
- Add DGEBA and graphite solution to three-roll mill
- Mix for 2 h at 500 rpm
- Collect solution from three-roll mill

Common steps:
- Add hardener and stir for 2 h
- Degassing
- Add accelerator and stir for 0.5 h
- Degassing
- Cast in a teflon mold
- Cure at 148 °C for 1 h

Fig. 3. Flowchart of processing techniques used in this study.

expanded and sonicated graphite particles was investigated using a LEO 1525 FEG scanning electron microscope (SEM). The fracture surfaces of tensile specimens were examined using a Hitachi S4500 FE scanning electron microscope. The fracture surfaces were gold coated prior to SEM investigation to avoid charging and were examined at 3 kV accelerating voltage.

3. Results and discussion

3.1. Optical microscopy

Optical micrographs of the cross-section of 1 wt.% EG/epoxy nanocomposites processed by different techniques are shown in Fig. 4. From Fig. 4(a), it can be seen that the graphite particles are relatively large, and they settle under the influence of gravity before the epoxy hardens to a composite sample. Therefore, there is a variation in graphite concentration from the top to the bottom of the sample. This confirms that the direct mixing method is unable to break up EG into graphite nanosheets and to maintain a uniform distribution in the matrix. By contrast, the other methods (sonication, shear, and combined sonication and shear) show not only in situ formation of graphite nanosheets from EG but also uniform dispersion of graphite nanosheets in the matrix as shown in Figs. 4(b)–(d). However, if observed carefully it can be seen that the

shear mixing produces finer particles than the sonication, while the combined method produces even finer particles and more uniform dispersion than the shear mixing.

3.2. X-ray diffractometry

Fig. 5 shows the WAXD patterns of 1 wt.% EG/epoxy nanocomposites for different processing techniques. The WAXD pattern for pure epoxy is also shown for comparison. While pure epoxy shows a broad peak, the nanocomposites show sharp peaks at 2θ of 26.38° which corresponds to a d-spacing of 3.37 Å. This is also the characteristic peak of pure graphite [12]. Therefore, the occurrence of peaks confirms not only the presence of pure graphite but also the fact that the individual graphite nanosheets consist of multilayer graphite sheets with a d-spacing of 3.37 Å. This observation is also consistent with the SEM image of a graphite nanosheet as shown in Fig. 1(d). Therefore, it can be suggested that the synthesis and processing techniques applied here could not exfoliate or separate the graphite layers completely. However, the less intense peaks observed in the processing techniques other than the direct mixing indicate uniform dispersion of graphite nanosheets and has been confirmed by optical micrographs. Fig. 6 shows the WAXD patterns of nanocomposites containing 1 and 2 wt.% EG, processed by shear mixing. The 2 wt.% EG/epoxy shows a more pronounced peak than the
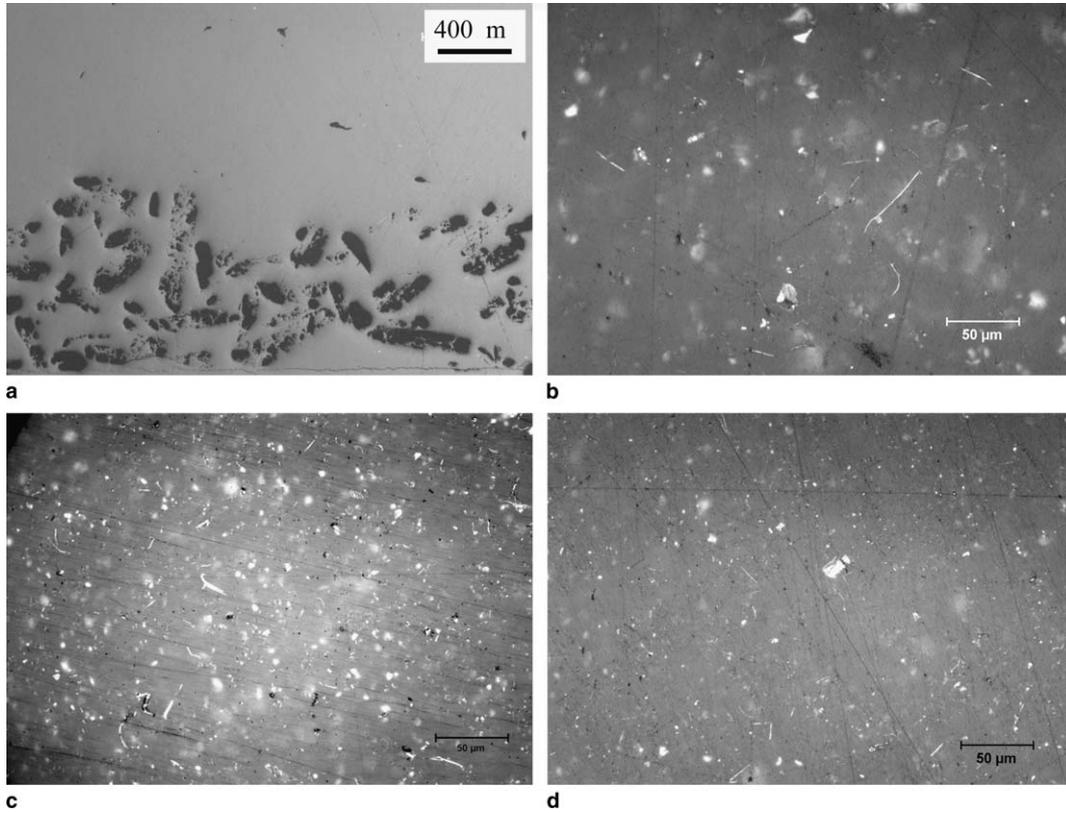
Fig. 4. Optical micrographs of the cross-section of 1 wt.% EG/epoxy nanocomposites. (a) Direct mixing, (b) sonication mixing, (c) shear mixing, and (d) combined mixing.
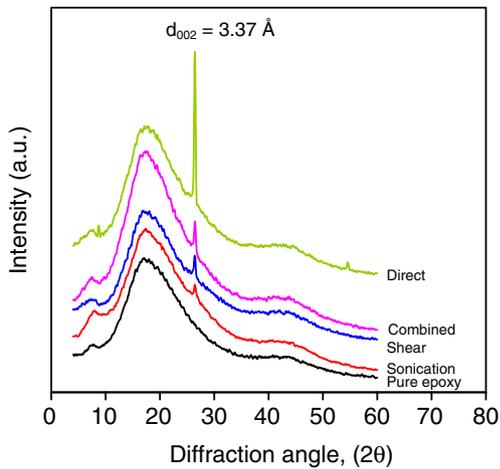

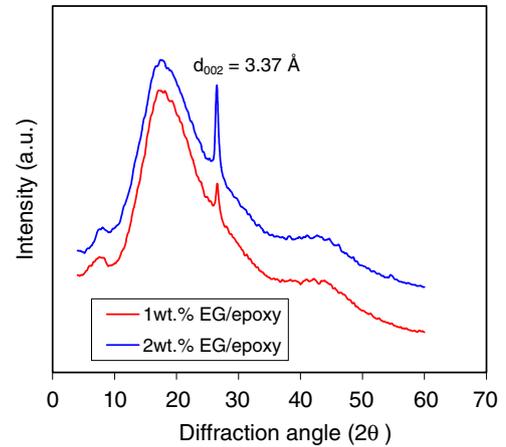Fig. 5. WAXD patterns of 1 wt.% EG/epoxy nanocomposites processed by different techniques.

Fig. 6. WAXD patterns of nanocomposites processed by shear mixing with varying graphite content.

1 wt.% EG/epoxy nanocomposite. The higher intensity for higher graphite content can be attributed to the higher number of graphite layers in the former case.

3.3. Mechanical behavior

3.3.1. Stress–strain curves

A comparison of tensile stress–strain behavior of 1 wt.% EG/epoxy nanocomposites processed by different tech-niques is shown in Fig. 7. Although all nanocomposites exhibit higher modulus than pure epoxy, they show final failure at much lower stress and strain than the pure epoxy, i.e. nanocomposites show higher elastic modulus but lower tensile strength than the pure epoxy under identical condi-tions. A similar behavior has also been observed for nano-clay reinforced epoxy nanocomposites [14–16]. In general, the improvement of elastic modulus is attributed to the good dispersion of nanosize particles and good interfacial
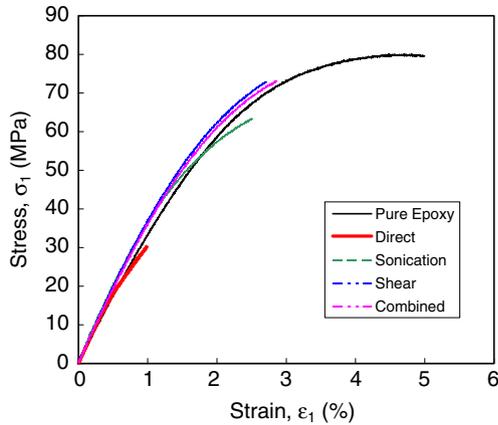
Fig. 7. Comparison of stress–strain behavior of pure epoxy and 1 wt.% EG/epoxy nanocomposites processed by different techniques.

adhesion between the particles and the epoxy matrix so that the mobility of polymer chains is restricted under loading [17]. The orientation of graphite layers and polymer chains with respect to the loading direction can also contribute to the stiffening effect [18]. The lower tensile strength of nanocomposites could be due to a number of reasons such as weak interfacial bonding at the graphite nanosheet and matrix interfaces, aggregates of graphite nanosheets, and nano to micro size process related defects. The bonding at the interface can be improved by functionalization of the graphite nanosheets and is now under investigation. The other two problems can be overcome by improving the processing technique.

Fig. 8 shows the comparison of elastic modulus of 1 wt.% EG/epoxy nanocomposites processed by different techniques. The elastic modulus of pure epoxy is 3.5 GPa. Direct mixing provides only approximately 4% increase in elastic modulus for 1 wt.% of EG, whereas the sonication, shear, and combined mixing methods show increases of 8%, 11%, and 15%, respectively, over the pure epoxy. The maximum improvement by the combined method can be correlated to the processing of nanocomposites into
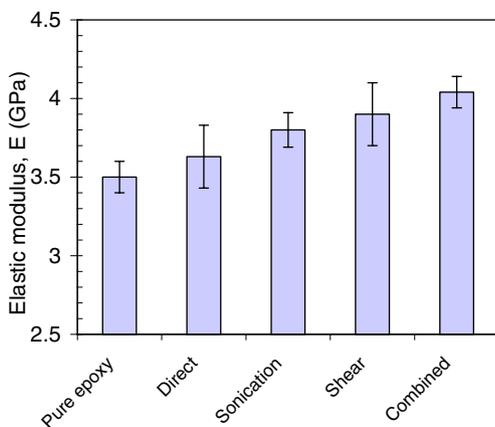
two steps. First, break up of EG into graphite nanosheets by sonication mixing. Second, exfoliation and uniform dispersion of graphite nanosheets in the epoxy resin by shear mixing. It has been confirmed by fractography that both sonication and shear mixing produce in situ graphite nanosheets as shown in Fig. 9. By contrast, direct mixing breaks the EG into smaller pieces by magnetic stirring but not into graphite nanosheets. The SEM image of Fig. 9(c) represents the graphite network of EG even on the fracture surface. The graphite particles settle at the bottom of the specimen during casting instead of being dispersed uniformly in the matrix. This is confirmed by the optical micrograph of the composite cross-section in Fig. 4(a).
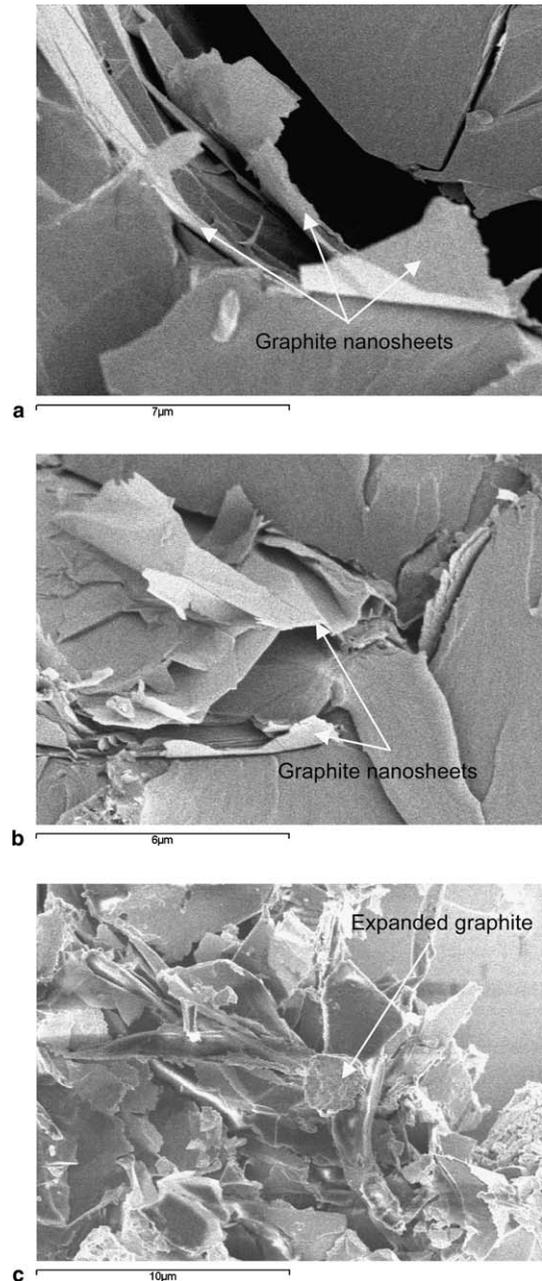

Fig. 9. SEM fractographs of 1 wt.% EG/epoxy nanocomposites. (a) Sonication mixing, (b) shear mixing, and (c) direct mixing.

Fig. 8. Variation of elastic modulus of 1 wt.% EG/epoxy nanocomposites for different processing techniques.

Fig. 10 shows the variation of elastic modulus with graphite content for nanocomposites processed by sonication and shear mixing. In both cases, the modulus of the nanocomposite is found to increase continuously with increasing graphite content. An increase of 11% and 26% is observed for 1 and 2 wt.% EG, respectively, for shear mixing. Further, nanocomposites processed by shear mixing provide higher modulus increase compared to those processed by sonication mixing. This can be attributed to the external shear forces generated in the shear mixing that separate and exfoliate the EG into graphite nanosheets followed by uniform dispersion in the resin. However, in the sonication mixing, the graphite nanosheets that collapse as aggregates after solvent evaporation (Fig. 1(c)) are added to DGEBA and dispersed by magnetic stirring. This may inhibit the complete dispersion of individual graphite nanosheets.

3.3.2. Effect of sonication time

In the present study, the sonication technique was used for two different purposes: to produce graphite nanosheets and to process nanocomposites.
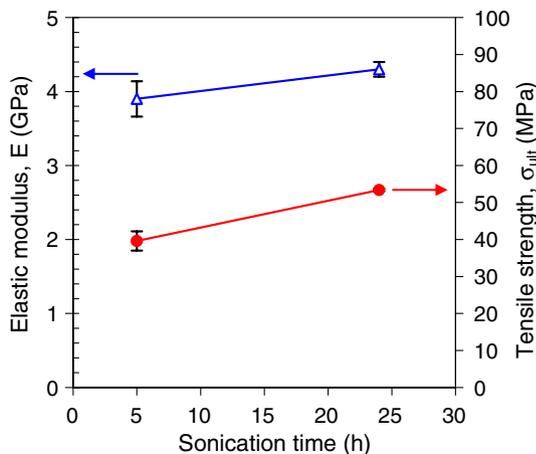
In the first case, sonication was used to break up EG into graphite nanosheets in a bath of acetone where acetone was used as a solvent. The sonication technique also allowed dispersion of nanosheets in the solvent. After evaporation of the solvent, the nanosheets were mixed with epoxy by magnetic stirring to produce the nanocomposites. Fig. 11 shows the effect of sonication time of EG on the elastic modulus and tensile strength of 2 wt.% EG/epoxy nanocomposites. Sonication for 24 h results in an average modulus of 4.3 GPa compared to 5 h sonication, which yields a modulus of 3.9 GPa, i.e. a 10% increase. The tensile strength is also observed to improve accordingly, an increase of 35% is observed for 24 h sonication. This indicates that a longer sonication time provides a better chance of producing graphite nanosheets from EG, although a critical ultrasonic irradiation time of 10 h has been reported by Chen et al. [3]. Therefore, optimization of sonication time is important.

In the second processing approach, a solution of graphite nanosheets and DGEBA was sonicated in an acetone bath. The effect of sonication time of this mixture is illustrated in Fig. 12. In fact, this sonication mixing allows better dispersion of graphite nanosheets into the DGEBA (as there is no aggregation of graphite nanosheets) compared to the one where graphite nanosheets are dispersed by magnetic stirring. Consequently, the 1 wt.% nanocomposite processed by sonication mixing for 0.5 h shows an elastic modulus of 4.1 GPa which corresponds to 8% and 5% higher modulus compared to 1 wt% (3.8 GPa) and 2 wt.% (3.9 GPa) EG/epoxy nanocomposites, respectively, processed by magnetic stirring. The tensile strength is also found to be higher in the former case. However, it is to be noted that if the sonication mixing continues for a prolonged period, it may degrade the mechanical properties of the resultant nanocomposite. For example, sonication mixing for 5 h was found to degrade both the elastic modulus and tensile strength of the nanocomposite. The elastic modulus of 1 wt.% EG/epoxy subjected to sonication for 5 h (3.6 GPa) becomes close to that of pure epoxy
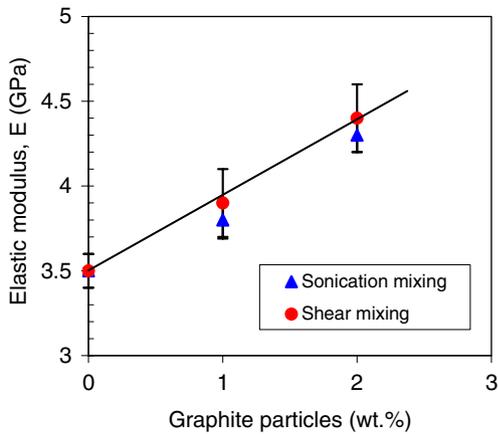
Fig. 10. Variation of elastic modulus with graphite content.

Fig. 11. Effect of sonication time on elastic modulus and tensile strength of 2 wt.% nanocomposite.
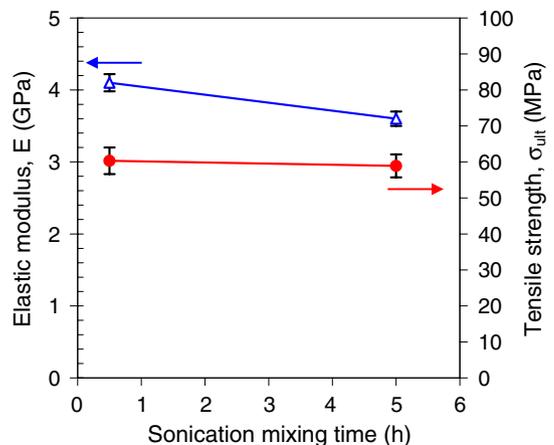
Fig. 12. Effect of sonication mixing time on elastic modulus and tensile strength of 1 wt.% nanocomposite.
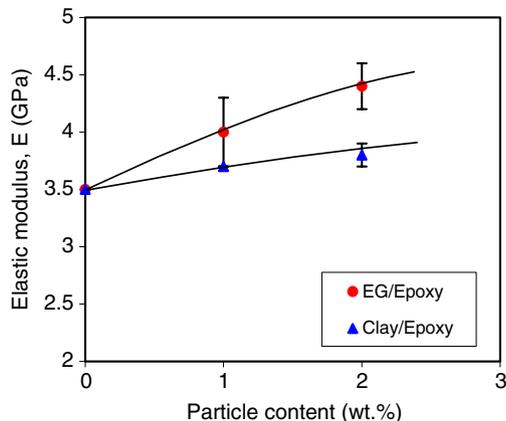
Fig. 13. Variation of elastic modulus as a function of particle content.

(3.5 GPa), therefore, no apparent change is observed by the addition of graphite nanosheets. This may be due to increase in temperature during sonication, which in turn, may cause early polymerization of the polymer chains if mixing continues for a prolonged period.

Fig. 13 shows the variation of elastic modulus as a function of particle content for both EG/epoxy and clay/epoxy nanocomposites, processed by shear mixing. At room temperature, both nanocomposites show higher elastic modulus as the particle content increases. However, the EG/epoxy shows much higher elastic modulus compared to the clay/epoxy for the same particle content. The EG/epoxy shows an increase in modulus of 8% and 16% higher over that of clay/epoxy for 1 and 2 wt.% particle content, respectively. Therefore, graphite offers better reinforcement than clay particles, which may be primarily due to the higher stiffness of graphite (1 TPa compared to 170 GPa for the clay). Furthermore, graphite is well known for its lightweight and superb thermal and electrical conductivity which are absent in clay materials. Finally, it can be assumed that the development of such multifunctional nanocomposites has potential for tailorability of desired properties in a wide range of applications.

4. Conclusions

Nanocomposites reinforced with 1–2 wt.% of EG were fabricated by direct, sonication, shear, and a combination of sonication and shear mixing methods. Of these, the combination of sonication and shear mixing provided the best results in terms of elastic modulus and tensile strength, whereas the direct mixing produced the lowest results among all processing techniques. A 15% improvement of elastic modulus in 1 wt.% EG/epoxy nanocomposite over pure epoxy can be attributed to the in situ formation of graphite nanosheets as well as uniform dispersion and exfoliation of graphite nanosheets in the former case. However, both XRD and SEM images confirmed that the graphite nanosheets were in multilayer rather than single graphite layer form. A strong influence of sonication time on the

mechanical properties of the resultant nanocomposites was also observed in this study. While a longer sonication time provides a better chance of producing graphite nanosheets from EG, prolonged sonication of graphite nanosheets and DGEBA degrades the mechanical properties of the nanocomposite by early polymerization of the polymer chains.

References

[1] Drzal LT, Fukushima H. Graphite nanoplatelets as reinforcements for polymers. Polym Prep 2001;42(2):42–3.
[2] Viculis LM, Mack JJ, Kaner RB. Science 2003;299:1361.
[3] Chen G, Weng W, Wu D, Wu C, Lu J, Wang P, et al. Preparation and characterization of graphite nanosheets from ultrasonic powdering technique. Carbon 2004;42:753–9.
[4] Chen G, Wu C, Weng W, Wu D, Yan W. Preparation of polystyrene/graphite nanosheet composite. Polymer 2003;44:1781–4.
[5] Chen G, Weng W, Wu D, Wu C. PMMA/graphite nanosheets composite and its conducting properties. Euro Polym J 2003;39:2329–35.
[6] Sheng W, Wong S-C. Electrical conductivity and dielectric properties of PMMA/expanded graphite composites. Compos Sci Technol 2003;63:225–35.
[7] Zheng W, Wong S-C, Sue H-J. Transport behavior of PMMA/expanded graphite nanocomposites. Polymer 2002;73:6767–73.
[8] Pan Y-X, Yu Z-Z, Ou Y-C, Hu G-H. A new process of fabricating electrically conducting nylon-6/graphite nanocomposites via intercalation polymerization. J Polym Sci: Part B: Polym Phy 2000;38:1626–33.
[9] Shen J-W, Chen X-M, Huang W-Y. Structure and electrical properties of grafted polypropylene/graphite nanocomposites prepared by solution intercalation. J App Polym Sci 2003;88:1864–9.
[10] Chen G-H, Wu D-J, Weng W-G, Yan W-L. Preparation of polymer/graphite conducting nanocomposites by intercalation polymerization. J App Polym Sci 2001;82:2506–13.
[11] Wang W-P, Pan C-Y. Synthesis and characterization of poly (ethylene oxide) methyl ether grafted on the expanded graphite with isocyanate groups. Euro Polym J 2004;40:543–8.
[12] Yasmin A, Daniel IM. Mechanical and thermal properties of graphite platelet/epoxy composites. Polymer 2004;44:8211–9.
[13] GrafTech International Ltd., Personal Communications..
[14] Yasmin A, Abot JL, Daniel IM. Processing of clay/epoxy nanocomposites by shear mixing. Scripta Mat 2003;49:81–6.
[15] Yasmin A, Abot JL, Daniel IM. Characterization of structure and mechanical behavior of clay/epoxy nanocomposites. In: Proceedings of the 14th international conference on composite materials. San Diego, CA; 2003..
[16] Yasmin A, Abot JL, Daniel IM. Processing of clay/epoxy nanocomposites with a three-roll mill. Mat Res Soc Symp Pro 2002;740:75–80.
[17] Wei CL, Zhang MQ, Rang MZ, Friedrich K. Tensile performance improvement of low nanoparticles filled-polypropylene composites. Compos Sci Technol 2002;62:1327–40.
[18] Liu X, Wu Q. PP/clay nanocomposites prepared by grafting-melt intercalation. Polymer 2001;42:10013–9.