Enhancement of mechanical properties of epoxy/graphene nanocomposite

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Abstract. Graphene is a novel class of nanofillers possessing outstanding characteristics including most compatible with most polymers, high absolute strength, high aspect ratio and cost effectiveness. In this study, graphene was used to reinforce epoxy as a matrix, to enhance its mechanical properties. Two types of epoxy composite were developed which are epoxy/graphene nanocomposite and epoxy/modified graphene nanocomposite. The fabrication of graphene was going through thermal expansion and sonication process. Chemical modification was only done for modified graphene where 4,4’-Methylene diphenyl disiocyanate (MDI) is used. The mechanical properties of both nanocomposite, such as Young’s modulus and maximum stress were investigated. Three weight percentage were used for this study which are 0.5 wt%, 1.0 wt% and 1.5 wt%. At 0.5 wt%, modified and unmodified shows the highest value compared to neat epoxy, where the value were 8 GPa, 6 GPa and 0.675 GPa, respectively. For maximum stress, neat epoxy showed the best result compared to both nanocomposite due to the changes of material properties when adding the filler into the matrix. Therefore, both nanocomposite increase the mechanical properties of the epoxy, however modification surface of graphene gives better improvement.

1. Introduction
Epoxy polymer have outstanding properties including good thermal and mechanical properties, compatible with most fibre, chemical and wear resistance and low cost [1]. Due to this properties, it makes them more attractive to be used in wide application such as adhesives, coatings, structural material or as the matrix of the composite [2,3]. As a thermoset material, epoxy has a high degree of crosslinking which make them very useful in term of high rigidity and strength. However, because of
the crosslinking structure, it also make epoxy brittle and vulnerable to cracks, and has limitation on its application. Due to this limitation of epoxy, many researchers are interested to improve the epoxy toughness. The effective method to enhance this problems is by adding fillers into the polymer.

Graphene is a single layer of graphite in the form of a hexagonal lattice of carbon atoms bonded in the sp$^2$ configuration [4]. It is also known as the thinnest material in the universe which allows many new and exciting applications potential. Historically, graphene becomes well-known materials when Nobel prized winners, Prof. A.K. Geim and Prof. K. S. Novoselov fabricates the graphene materials by using a sticky tape to peel off the graphite layer by layer [5]. Graphene has excellent properties such as; higher electrical and thermal conductivities than copper materials and superior mechanical properties which are 1 TPa in Young’s modulus [6], intrinsic strength values is 139 GPa [7] and 130 MPa in ultimate strength [8]. Graphene are preferred as a nanofiller compared to other other materials because of its layered structural fillers which has high surface area which is up to 2630 m$^2$/g [9]. According to Park and his colleagues, graphene shows a property enhancement at a small loading of graphene contents due to its high aspect ratio. In some case the graphene content less than 0.5 wt% already give the best enhancement of the composite [10].

Polymer/graphene based nanocomposite have attracted most academia and industry in the recent years due to its remarkable enhancement in the polymer properties at low filler fractions [11]. Nanocomposite is leading to a reduction in the filler size of composite from microscale to nanoscale. The effects of reduction increased the interphase and reduced surface interparticle distance. In this past few decades, polymer contains layered-structure molecule, for example, layer graphene which demonstrated a capability of mechanical toughness improvement due to its good properties [12,13].

In this study, various amounts of expanded graphite are used which is 0.5 wt%, 1.0 wt% and 1.5 wt%. The modification interface of graphene was developed by using chemical modification which is to study the effects and differences of unmodified and modified interface of graphene towards the mechanical properties of nanocomposite.

2. Experiments

2.1 Materials
Graphite carbons was purchased by Asbury Carbons, Asbury NJ. Epoxy resin, DER 331 which is a reaction product of epichlorohydrin and bisphenol A, and the hardener, Jointmine 925-3 were supplied by Epochemie International Pte Ltd, Singapore. The 4,4’-Methylene diphenyl diisocyanate (MDI) was purchased by Sigma-Aldrich.

2.2 Synthesis of graphene materials

2.2.1 Thermal expansion. Silica crucible was preheated in the laboratory furnace at 1000°C. 0.5 gram of raw graphite was poured into the silica crucible by using spatula. After 60 seconds, the silica crucible was taken out and place on a ceramic plate for 2 minutes. Then, after the expanded graphite was cooled down, it was transferred into a container. Figure 1 shows the raw graphite material and expanded graphite. The operator must be extra careful when conducting this process and should wear personal protective equipment such as goggle, heat resistant glove and closed shoes.
2.2.2 Sonication process. Expanded graphite was put in acetone solution inside a metal container for 30 minutes. The metal container was covered and this process was done in the ultrasonic bath at the frequency, 50-60 Hz. The ratio of expanded graphite to acetone is 1:150. The acetone is used as a solvent to make sure the expanded graphite were able to split into graphene platelets. This sonication process was done in order to make sure that the expanded graphite dispersed well. Figure 2 shows the sonication bath used in this experiment.

Figure 2. Sonication bath.

2.2.3 Fabrication of epoxy - graphene nanocomposite
The desired amount of epoxy was added into the mixture and mix manually for 5 minutes followed by sonication process for 1 hour. Then, the mixture was transferred into a beaker and stirred by using mechanical stirrer at 300 rpm for 2 and a half hours where the temperature of the hot plate was 120°C. Then the mixture was degassed inside the vacuum oven for 15 minutes to eliminate air bubbles. The presence of air bubbles will affect the mechanical properties of the composite. Hardener was added into the mixture and mixed manually for 5 minutes. Then, the mixture was poured into the mold. Make sure that the mold already been waxed. The mold was cured inside the drying oven at the preheated temperature of 80°C for 3 hours and followed by 120°C for 12 hours. The curing time as shown in Figure 3.

Figure 3. Curing time for the samples.
2.3 Synthesis of epoxy - modification graphene nanocomposite

The expanded graphite which already undergoing the sonication process was transferred into a round bottom flask equipped with a condenser as shown in figure 4. The weight ratio of MDI towards expanded graphite was 0.5:1. The MDI was poured into the mixture, and followed by mixing at ~80°C for 6 hours by using a magnetic stirrer. For the next process, the mixture was transferred into a metal container and epoxy was added, followed by sonication process for 1 hour. Then, the mixture was poured into a beaker and was stirred at 300 rpm for 2 hours and 30 minutes at the temperature of 120°C. Later, the mixture was degassed for 15 minutes and hardener was added. The mixture was poured into the mold and followed by curing process inside the drying oven, similar to step in Section 2.3.

2.4 Characterisation

2.4.1 Modification of filler. Infrared spectra were measured with a Fourier transform infrared spectroscopy (FTIR), within the region of 4000 cm\(^{-1}\) – 600 cm\(^{-1}\) at 4 cm\(^{-1}\), using a minimum of 32 scans collected at 2 cm\(^{-1}\) resolutions.

2.4.2 Mechanical property. Tensile test was performed on dumbbell samples at a strain rate of 0.5 mm/min according to ASTM D-638. This testing was conducted by using Gotech Testing Machine which the maximum load is 100 kN at room temperature. An extensometer was used to get the accurate displacement data for the Young’s modulus measurement which was calculated from the range 0.01 mm to 0.17 mm. The gauge length of the extensometer is 25 mm.

3 Result and discussion

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 5 illustrate FTIR spectra of raw graphite, expanded graphite and modified graphene. Raw graphite spectra show a weak absorption at 2116 cm\(^{-1}\), relating to the presence of C= C. For the expanded graphite, it shows the highest absorbance which is 3723 cm\(^{-1}\), corresponding to the presence of O-H group. It also shows the presence of weak C=C at 2116 cm\(^{-1}\) and strong wave number at 870 cm\(^{-1}\) caused by the bending vibration of C-H. After expanded graphite was modified by 4,4’-Methylene diphenyl diisocyanate (MDI), the spectra show the lowered absorbance at a strong band 3305 cm\(^{-1}\) lies under O-H group. Modified graphene also showed a medium absorbance at 2889 cm\(^{-1}\)
caused by stretching vibration of C-H. Then the absorbance increase at strong band at 2323 cm$^{-1}$ of stretching vibration represent the O=C=O. The last spectra band for modified graphene is 1553 cm$^{-1}$, strong stretching vibration of Nitro compound, N=O.

Figure 5. FTIR spectra of raw graphite, expanded graphite and modified graphene.

3.2 Mechanical Properties
Table 1 shows the result of Young’s modulus and tensile strength for tensile test of the neat epoxy and nanocomposite with and without modification for three proportions of graphene contents while Figure 6 shows its comparison in graph form. The Young’s modulus of 0.5 wt% of modified graphene indicates the best enhancement compared to the neat epoxy and other weight percentage of modified and unmodified epoxy/graphene nanocomposite. The value of 0.5 wt% of modified graphene increased the Young’s modulus of neat epoxy from 0.675 to 8 GPa, with the increment of 91.56%. For 0.5 wt% of modified towards unmodified graphene, the differences was 25%; with the values are 8 GPa and 6 GPa, respectively. Nevertheless, the elasticity begins to degrade when adding more graphene contents. Thus, 0.5 wt% was the optimum value for both modified and unmodified nanocomposite. The result shows that, at 0.5 wt% of modified graphene provide a significant toughening effect caused by its high interface strength.

Both nanocomposite shows reduction of tensile strength compared to the neat epoxy. By adding ductile material of fillers, will change the composite from brittle to more ductile properties [13-15]. The result gained also proves the theory, while there are increment in the young’s modulus. In comparison of all weight percentage used, 0.5 wt% of modified graphene obtained the best value. However, the value is lesser than neat epoxy, where the neat epoxy gives the tensile strength of 39.82 MPa while for 0.5 wt% of modification is 23.01 MPa. This is due to the changes of mechanical properties when adding filler to the neat epoxy. From both results, it shows that the interface modification of graphene gives better enhancement in term of its tensile properties of the nanocomposite.
| Graphene Content (wt%) | Young’s Modulus (GPa) | Tensile Strength (MPa) |
|------------------------|-----------------------|------------------------|
|                        | Unmodified | Modified | Unmodified | Modified |
| 0                      | 0.675      | 39.82    |            |          |
| 0.5                    | 6.0        | 8.0      | 16.96      | 23.01    |
| 1.0                    | 3.2        | 5.5      | 12.28      | 18.26    |
| 1.5                    | 3.0        | 5.4      | 8.75       | 13.39    |

**Figure 6.** Value of (a) Young’s modulus and (b) tensile strength of epoxy/graphene and epoxy/modified graphene

### 4 Conclusion

In this study, two types of epoxy nanocomposite was developed by using graphene materials in order to study the effects of modification of graphene interface towards its mechanical properties. Graphene was prepared from raw graphite and facing through three main process which are thermal expansion, sonication process and chemical modification. The chemical modification is done through grafting the 4,4’-Methylene diphenyl disocyanate (MDI) into expanded graphite to produce modified graphene. At 0.5 wt% of modified graphene created 91.6% increment of Young’s modulus at tensile properties compared to the neat epoxy. The differences value of maximum stress of modified nanocomposite and neat epoxy were 42.21%. It shows a decrement in the value when added filler because of the changes of neat epoxy mechanical properties which become more ductile. However, 0.5 wt% of modification
graphene gives better result compared to unmodify with the increment of 25% and 26.29% for Young’s modulus and maximum stress, respectively. Based on the experimental results, adding graphene will increase the elasticity of the neat epoxy where the modified one gives better result. Therefore, modification interface of graphene creates a strong interface between neat epoxy and graphene, where can restrain micro crack occurred in the epoxy/modified graphene nanocomposite.

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