Dynamic mechanical analysis of graphene nanoplatelets/glass reinforced epoxy composite

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Abstract. This paper presents a study on dynamic mechanical analysis (DMA) of graphene nanoplatelets (GNPs)/glass reinforced epoxy composite. The composite was fabricated by a hand lay-up technique followed by vacuum bagging technique. GNPs weight fraction was 0.5 and 1.5 wt.% for a fixed glass fibre fraction. The test was carried out in terms of storage modulus (E'), loss modulus (E''), and tan δ. The result indicates that 1.5 wt.% GNPs/glass reinforced epoxy composite obtain the maximum value of the dynamic mechanical properties due to the incorporation of GNPs nanofiller. The improved dynamic mechanical properties were related to better interfacial interaction of the nanofiller with the epoxy matrix. The glass transition temperature (T_g) value for 0.5 and 1.5 wt.% GNPs/glass were 62.84 and 66.01 °C, respectively.

1. Introduction
Graphene nanoplatelet (GNPs) is one of the nanofiller with great potential in manufacturing a composite due to their excellent physical characteristic, electrical properties, and high mechanical properties [1]. Therefore, a recent investigation has been conducted on developing a high performance of polymer nanocomposite in the use of graphene nanotechnology that can be applied to various fields. Graphene improves the properties at very low loading, and it has a very high surface conductivity that can lead to the formation of the polymer conductive composites. For example, the graphene composite has been widely used in chemical sensor, bipolar plates, and anti-static material.

Graphene composite can be easily fabricated into intricately shaped components with the preservation of structure and properties using the conventional processing method. However, graphene tends to agglomerate when dispersed into epoxy resin that limits its application in the improvement of polymer nanocomposite properties. Thus, to achieve homogeneous dispersion of graphene into epoxy matrix need to be well enough dispersed initially. From previous research, there are many dispersion methods for the graphene nanofiller such as mechanical stirring, surface chemical modification, ultrasonic sonication, and high shear mixer [1]–[3].

The failure behavior of the fibre-matrix interface characteristic of material can be determined from the dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and solid gas chromatography [4]–[6]. DMA receive a lot of attention due to the non-
destructive detection of the interfacial region and also high sensitivity when conducting the test [7]. This testing separates the dynamic modulus of the material into two different parts such as the storage part ($E'$) and the viscous part ($E''$). While, the ratio of $E''/E'$ gives the tangent of the phase angle (tan $\delta$), that measure the dissipation of energy in the material. The glass transition temperature ($T_g$) can be obtained from the curve of loss modulus or tan $\delta$ to evaluate the material characteristic.

This paper focused on the effect on GNPs nanofiller loading of dynamic mechanical properties of GNPs/glass reinforced epoxy composite. This work is to determine the significance of adding more GNPs nanofiller concentration into the glass reinforced epoxy composite.

2. Material and methods

2.1. Material

GNPs and woven glass fibre were used as the reinforcement material supplied by Innovative Pultrusion Sdn. Bhd. Malaysia. The epoxy resin used was EpoxAmite 100 series resin with 103 slow hardeners was purchase from a local supplier in Malaysia. The material specification of GNPs obtained from supplier was analytical grade and used without further purification as shown in Table 2.1. Furthermore, this work used a commercial plain-woven E-type glass with a density of 2.54 g/cm$^3$ as the reinforcing woven glass fibre.

| Properties                        | Value  |
|-----------------------------------|--------|
| Thickness (nm)                    | 6-8    |
| Average particle diameter (m$^2$/g)| 120-150|
| Surface area (%)                  | 99.5+  |
| Thermal expansion (K$^{-1}$)      | 4-6 $\times 10^{-6}$ |
| Thermal conductivity (W/ (m.K))   | 3000   |

2.2. Fabrication process

GNPs in nanoscale size was reinforced into epoxy resin to produce the composite. Fig. 2.1 shows the processing steps used to fabricate the GNPs/glass reinforced epoxy composite. Epoxy resin was mixed with 0.5 and 1.5 wt. % GNPs. The mixture was stirred thoroughly using a mechanical stirrer and Thinky mixer (ARE 310) to ensure consistent mixing. A curing agent was added to the mixture of GNPs with epoxy resin according to the weight ratio as suggested by the manufacturer. Then, the mixture was laminated onto five layers of woven glass fabric and cover with a vacuum bag. The composite was left to cure at room temperature (RTP) for 12 hour. Next, the specimen was cut in proper dimension using Dremel cutter 4000 tools.

![Fig. 2.1: Schematic fabrication of GNPs/glass reinforced epoxy composite](image)
2.3. Dynamic mechanical analysis

The dynamic mechanical properties of GNP/s/glass were studied using a Pyris diamond DMA (Perkin Elmer) with three-point bending mode as a function of temperature. The composite was cut into a specimen having a dimension of 50×10×2.3 mm as per ASTM D5418-07 [8]. The test was carried out at 1 Hz frequency within the temperature range of 30-150 °C at the rate of 3 °C /min [6].

3. Results and discussion

The mechanical behaviour of GNPs/glass reinforced epoxy composite was investigated in the linear range using DMA to determine the properties of nanofiller loading on the fibre matrix and adhesion. Fig. 3.1 shows the variation of storage modulus \((E')\), loss modulus \((E'')\), and \(\tan \delta\) for the composite specimen containing 0.5 and 1.5 wt.% GNP/s nanofiller as a function of temperature in the range of 40-140 °C. The storage modulus decreased as the temperature increases as represented in Fig. 3.1 (a). When the temperature increased beyond \(T_g\) the material transition from glassy to rubbery state start to occur. The components of the composite in a glassy state were tightly packed and have strong intermolecular which contribute to higher storage modulus. As the temperature increases, the molecular movement start to increase that result in the loss of stiffness hence reduce the storage modulus of the composite. From Fig. 3.1 (a) it can be observed that there was a sudden fall in storage modulus between 50-70 °C due to the enhanced mobility of polymer chain induced when approaching \(T_g\) [9]. The 1.5 wt. % GNP/s/glass has better behaviour and higher modulus compared to 0.5 wt. % GNP/s/glass. Besides, the superior reinforcement and effective stress transfer from matrix to glass fibre also enhanced the storage modulus. As depicted in Fig. 3.1 (a), the storage modulus was enhanced with the increasing of nanofiller weight fraction due to the stiffening effect offer by GNP/s nanofiller to the epoxy matrix in the composite. The incorporation of nanofiller into the epoxy matrix also increases the glass transition phases. This high storage modulus may be due to the restriction caused by GNP/s nanofiller in the mobility of epoxy chain with the beginning of glass transition temperature \((T_g)\) [6], [10]–[11].

Fig. 3.1 (b and c) show the effect of incorporation of GNP reinforcement to the epoxy matrix on the loss modulus and \(\tan \delta\) plot as a function of temperature in the range of 40-160 °C. It can be observed from both plots show that the curves start to increase, reach maximum, and then decreases in the \(T_g\) range. From Fig. 3.1 (b) it can be seen that loss modulus for 1.5 wt. % GNP/s/glass was higher in comparison with 0.5 wt. % GNP/s/glass. This indicates the enhanced energy dissipation and higher mechanical properties of the composite. Fig. 3.1 (b) does not show much influence of GNP/s in the stiffness of composite and their temperature position. However, the incorporation of GNP/s nanofiller was sensibly increasing the relaxation temperature of the epoxy matrix composite. The shifting temperature toward higher temperature shows that 1.5 wt. % GNP/s/glass has better thermal stability than 0.5 wt. % GNP/s/glass composite. This can be explained by the increase in GNP/s nanofiller weight fraction that restricted the chain mobility of the molecular motion of the epoxy matrix thus delayed the thermal degradation and have better thermal stability [12]. Rasana et al. (2019) also found that the synergistic effect of MWCNT nanofiller and glass fibre in the nanocomposite justified with the higher loss modulus values and peak shifted to a higher temperature in comparison with others.

As for \(\tan \delta\) curves, it explains the elastic and viscous nature of the polymer composite. Fig. 3.1 (c) shows that the 1.5 wt. % GNP/s/glass exhibit a slightly higher \(\tan \delta\) compared to 0.5 wt. % GNP/s/glass composite. This suggests that GNP/s nanofiller in the epoxy matrix had a marginal effect on the immobilization of polymer molecules. Some factors influence the \(\tan \delta\) such as the nanofiller content, interfacial adhesion of filler and matrix in composite, and relaxation of nanofiller and matrix in the composite [13]. Thus, it could be assigned that addition of GNP/s construct a good interfacial adhesion between the nanofiller and epoxy matrix and increased the thermal stability. A previous study by researcher states that loss modulus was more appropriate for determining \(T_g\) compared to \(\tan \delta\) [6], [14].

Table 3.1 represent the \(T_g\) value determine for the GNP/s/glass reinforced epoxy composite. 0.5 wt. % of GNP/s/glass had a \(T_g\) value of 62.84 °C while the 1.5 wt. % GNP/s/glass have a higher \(T_g\) value of 66.01 °C. The shift in \(T_g\) to a higher temperature related to the lower mobility of matrix molecules could result in changes in crosslinking density of the network. The increasing of GNP/s nanofiller weight
Fraction improve the interfacial interaction between nanofiller and epoxy resin which enhanced the thermal properties of the composite. The frictional resistance to the molecular movement could result in the dissipation of heat. The increase in the rate of heat dissipation increases the internal forces within the composite. Thus, the incorporation of GNP nanofiller resulted in the increases of energy dissipated.

![Fig. 3.1: Dynamic mechanical properties of GNP/glass reinforced epoxy composite](image)

| Composite      | $T_g$ from loss modulus (°C) | $T_g$ from tan δ (°C) |
|----------------|-----------------------------|-----------------------|
| 0.5 wt.% GNP/glass | 62.84                       | 70.08                |
| 1.5 wt.% GNP/glass | 66.01                       | 71.23                |

### 4. Conclusion

GNP/glass reinforced epoxy composite was successfully developed by hand lay-up and vacuum bagging technique. The dynamic mechanical properties were studied and can be concluded as followed:

a) The incorporation of GNP nanofiller into glass reinforced epoxy composite has influenced the dynamic mechanical properties.

b) The 1.5 wt.% GNP/glass reinforced epoxy composite has higher values of storage modulus, loss modulus, and tan δ.

c) The DMA results also indicate an increase in the $T_g$ value by 5 % for 1.5 wt. % GNP/glass reinforced epoxy composite.

d) The reinforcement of GNP nanofiller has improved the performance of glass reinforced epoxy composite that makes them suitable to be used in industrial application.
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6. References
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