Enhanced mechanical properties of multi-scaled carbon reinforcements in ternary epoxy composites materials

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Abstract. Carbon nanotubes (CNT) and graphene have widely used as reinforcements in epoxy for various aims and applications since their 'discovery'. For example, in the area of aviation and aerospace materials, carbon reinforcements are desirable as they offer solutions for light weight yet mechanically enhanced materials. The objective of this work is to investigate the effects of adding combination of carbon fillers of different aspect ratios on the thermal mechanical, Young's Modulus and Fracture Toughness properties of the resultant epoxy composites. The carbon fillers include carbon nanotubes (CNT), graphene, and carbon black (CB) and their combined loading will be varied from 0.5 wt. % until 7 wt. % to form sets of binary epoxy composites and a ternary epoxy composites. All of the fillers are kept at the 1:1 weight ratio for CB + CNT, CB + Graphene, CNT + Graphene, and CB + CNT + Graphene. Among these combinations, the system with ternary fillers at 7 wt.% demonstrated the highest value of glass transition temperature (T_g) and K_{IC}, and Young's Modulus. The percent improvement for glass transition temperature (T_g) and K_{IC}, and Young's Modulus compared to neat epoxy are 9.5 %, 571%, and 58.3%, respectively. This work clearly demonstrated the effectiveness of employing various carbon fillers with different aspect ratio and morphology in enhancing the values of mechanical properties of epoxy system.

1. Introduction

Due to its exceptional mechanical properties, epoxy composite has been widely used in various areas including aerospace, structural, automotive or electrical components. Epoxy with a higher cross-link density contributes to low absolute strength and poor fracture toughness, limiting its applications in most industrial applications [1]. In an effort to improve various mechanical properties of the epoxy, different types of fillers were added. Types of fillers added include silica [2, 3], CNT [4, 5], graphene [6, 7], carbon black [8, 9] and clay [10]; among others. These studies reported an enhancement in the mechanical properties of epoxy.

Graphene is, basically, a single atomic layer of graphite; an abundant mineral which is an allotrope of carbon that is made up of very tightly bonded carbon atoms organized into a hexagonal lattice. What makes graphene so special is its sp^2 hybridization and very thin atomic thickness. These properties are what differentiate graphene to be highly distinguished than other compound [11]. In recent researches, an increased attention has been seen in graphene nanoplates and graphene nanoparticles as possible nanofillers for nanocomposite materials [12]. It is reported in literature that the fracture toughness of the nano-composite starts to decrease beyond certain weight fraction [13]. As the filler content increases, K_{IC} also increases for low filler content (0–0.5 wt%) and for higher weight fraction of GNP (more than

1.0 wt%), a decreasing trend is observed as reported in [13]. As the graphene content has a loading of 0.1 wt% into neat epoxy resin, the fracture toughness values increases up to 128% [14]. For higher weight fraction of graphene nanoplatelets, GNP which is a composition of stacked 2-D graphene sheets, (more than 1.0 wt%), a decreasing trend is observed. It was discovered that the fracture toughness value starts decreasing for GNP/epoxy at 1.0 wt% [13]. The incorporated nano-sized fillers are usually selected according to the desired properties of the final composite. A research done by [15] on the comparison of fracture performance of epoxy composites with 0.1%wt of pure graphene, single walled and multi walled carbon nanotubes finds that the composite which present with graphene has the highest fracture toughness among the composites. At low nanofiller content, graphene nanocomposite depicts significant improvement in mechanical properties when compared to CNT. A report shown on the fracture toughness of epoxy polymer reinforced with various weight percentage of graphene. Remarkably, only at loading 0.125% of graphene shows an increment of fracture toughness of pristine epoxy by 65%. Fractography analysis indicated that impressive effectiveness of graphene ability to resist fracture is interrelated to the deflection process which associated with the planar (two dimensional) structure of one-dimensional CNTs or low-aspect-ratio nanoparticles. Drastic improvement can be noticed from the addition of 0.125 wt% of graphene into the epoxy matrix at 1.75 MPa*$m^{1/2}$ which corresponds to a 65% increase in fracture toughness. The higher loading weight percentage profound to be a diminishing factor for enhancement in fracture toughness which begins to approach the neat epoxy value at loading 0.5 wt%. This might be a result of degradation in the dispersion of the FGS additives above a weight fraction of 0.125%. The Young's Modulus of the nanocomposite also project a 50% increase from baseline epoxy with the UTS being increased by 45% both at loading of 0.125 wt% [16].

The results of the tensile tests showed that adding graphene oxide, GO increased the tensile strength, load, Young's modulus and elongation. The fracture strain was seen to decrease [17]. The loading of 0.1wt% graphene shows a significant value for tensile strength (78 MPa) which is 40% larger than pristine epoxy (55 MPa) thus far out-perform Single Walled Carbon Nanotube (SWNT) and Multi Walled Carbon Nanotube (MWNT) at 11% and 14% increase. Regarding to the fact that it was achieved at nanofiller weight fraction of 0.1 wt. % is remarkable. The incorporation of 0.1 wt% loading of graphene increases the Young's Modulus from neat epoxy at 31% increment from 2.85 GPa to 3.74 GPa while the increment of SWNT and MWNT both yield a lower increment at (<3%). Fracture toughness also shows a significant increment for 0.1wt% graphene filled epoxy at 53% improvement from neat epoxy. The fracture toughness of GPL is also impressive in relation to nanoparticle composites [12]. In summary, graphene are tremendously effective at reinforcing the fracture energy, stiffness, strength, fracture toughness, and fatigue resistance of epoxy polymers at significantly lower nanofiller loading fractions [16].

Previous studies have shown promising results in improvement of mechanical properties of epoxy composites as a result of incorporating CB and graphene. It is interesting to find out the synergistic effects demonstrated by incorporating these two fillers. There are also several studies that reported improvement of mechanical properties of composites from utilizing dual fillers. For example, it was reported that the incorporation of CB as a second filler accordingly enhanced the plasticity and fracture strength properties of the epoxy-CNT-CB hybrid nanocomposite while having the same high strength and flexural modulus [18]. The enhancement of strength properties of hybrid composite mainly regard to the fact that homogeneous distribution of the filler particles in the epoxy matrix and the formation of a bond between the matrix and the fiber surface at the interface [19]. The introduction of small amount of CNTs or GNPs to CB/polymer composites can significantly enhanced their properties. An excellent synergistic effect was also observed for flexural modulus measurements where the composites with CNT:GnP ratio of 9:1 showed the highest increase of 17% compared to an increase of 9% and 5% with pure CNT and GnP respectively. The flexural modulus for the CNT:GnP ratio of 5:1 was also observed to be higher than that of composites with pure CNT and GnP [20]. The carbon-graphene epoxy nanocomposite with 0.1 wt. % fracture toughness indicate 11.4% enhancement at (33.55 MPa*$m^{1/2}$) in comparison with traditional carbon-epoxy composites. Although, neat epoxy exceeds the improvement of fracture toughness from this finding, it is evident that the gains observed represent a partial enhancement over carbon-epoxy composites [14].

The objective of this report is to study the synergistic effects obtained by incorporating CB and graphene in epoxy composites. All processing parameters are kept constant, and the values of KIC, Young's Modulus and yield strength will be compared among neat epoxies, single fillers, and dual fillers.

2. Experimental

Diglycidyl ether of bisphenol-A (epoxy) CP 812P and hardener CP 812P were used in this work, at 2:1 weight ratio, as supplied by local manufacturer. The conductive Carbon Black (CB) used was with 99% and purchased from Shandong JI QI International Trade Co Ltd in Shandong, China with 99.9% purity. Multiwalled Carbon Nanotube (CNT) used has purity of more than 95%, with diameter less than 8 nm. The Graphene used was manufactured by Chengdu Organic Chemical Co Ltd in China.

CB + CNT, CB + Graphene, and CNT + Graphene are added with 1:1 wt.% ratio into the epoxy systems. The combined loadings are kept at 0.5 wt. %, 1.0 wt. %, 3.0 wt. %, 5.0 wt. % and 7.0 wt. %. Epoxy composite that contains ternary fillers, which consists of CB + CNT + Graphene are prepared as well at the same combined loadings. Fillers are first into resin and stirred for 20 minute with the stirring rate of 500 rpm. Then, hardener will be add to the mixture and further stirred for 20 minutes, also at 500 rpm. Mixture is then poured into mould and the sample is left in room temperatures for 24 hours for curing.

High temperature mechanical properties are measured by using Dynamic Mechanical Thermal Anlyser (DMTA), under single cantilever mode. The measurement is performed by using Perkin Elmer DMA 800, with heating range and heating rate are 35 °C – 150 °C and 5 °C/min; respectively. Tensile test was conducted by using INSTRON 5569A Universal Testing Machine, in accordance to ASTM D638. The test was operated at a constant rate of 2 mm/min with a 20kN load cell. Fracture toughness (K_{IC}) was evaluated by using the three point end notch bending (SENB) test mode, which has the load cell capacity of 10kN based on ASTM5045. The fracture test was also conducted by using INSTRON 5569A Universal Testing Machine.

3. Results and Discussion

Figure 1 below shows the values of T_g obtained after adding fillers at loadings in the range of 0.5 wt. %, 1.0 wt. %, 3.0 wt. %, 5.0 wt. % and 7.0 wt.%, with the standard deviation markers. The values shown here are for CB + CNT fillers (Fig 1a), CB + Graphene fillers (Fig 1b), CNT + Graphene fillers (Fig 1c), and CB + CNT + Graphene fillers (Fig 1d), kept at 1:1 wt.% ratio. In the case of CB + CNT fillers, the values of T_g can be seen to increase steadily, with the highest value recorded to be 73 °C at 7 wt.% CB + CNT. This shows an improvement of 7.6%, compared to the T_g of neat epoxy (67.83 °C). Similarly, Tg shows an increasing trend for the fillers of CB + Graphene, as shown in Figure 1b. Although the T_g drops sightly at the loading of 0.5 wt.%, the value continues to rise, with the maximum value recorded at 71.18 °C, at 7.0 wt.% CB + Graphene. The T_g for CNT + Graphene shows similar trend where the T_g increases starting from the loading of 3 wt.% (68.43 °C) until 7 wt.% (72.24 °C), as shown in Figure 1c. Incorporation of three fillers also showing an interesting result, where the increase of Tg of 4.98% can be seen as low as 0.5 wt. % loading (Figure 1d). The highest improvement is recorded at 7 wt.% ternary loading, with the values of Tg is recorded to be 74.28 °C.

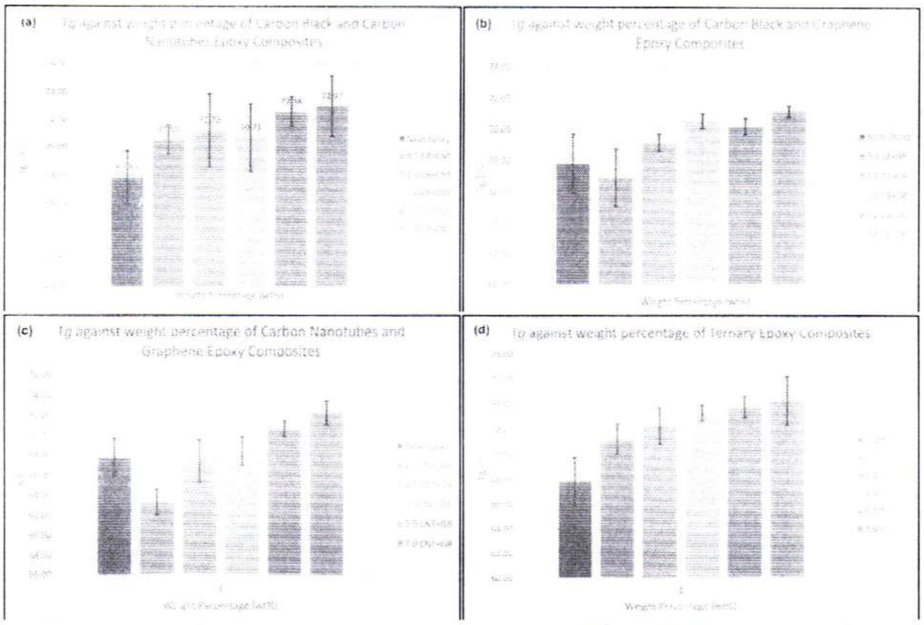

Figure 1: Graph of Glass Transition Temperature (T_g) for CB + CNT fillers (a); CB + Graphene fillers (b), CNT + Graphene fillers (c), and CB + CNT + Graphene fillers (d).

Figure 2 below show the values of storage modulus (E'), recorded at both glassy region (40°C) and rubbery region (100°C) for all combination of fillers. The values of E' for both glassy and rubbery region are seen to increase as fillers of various combinations are added. For glassy region, the highest E' is recorded at 7 wt. % for CB + CNT (14 GPa), 7 wt.% for CB + Graphene (22.5 GPa), 5 wt.% for CNT + Graphene (19.7 GPa), and 7 wt.% for CB + CNT + Graphene (25 GPa). This shows tremendous improvement for E' of neat epoxy (0.16 GPa), measured at glass region. In the case of rubbery region, the highest E' is recorded at 5 wt. % CB + CNT (0.34 GPa), 5 wt.% CB + Graphene (0.32 GPa), CNT + Graphene (0.43 GPa), and 5 wt.%. CB + CNT + Graphene (0.32 GPa). E' at rubbery region for neat epoxy is recorded to be 0.017 GPa. The data demonstrated the effectiveness of adding binary and ternary fillers to enhance high temperature mechanical properties of epoxy.

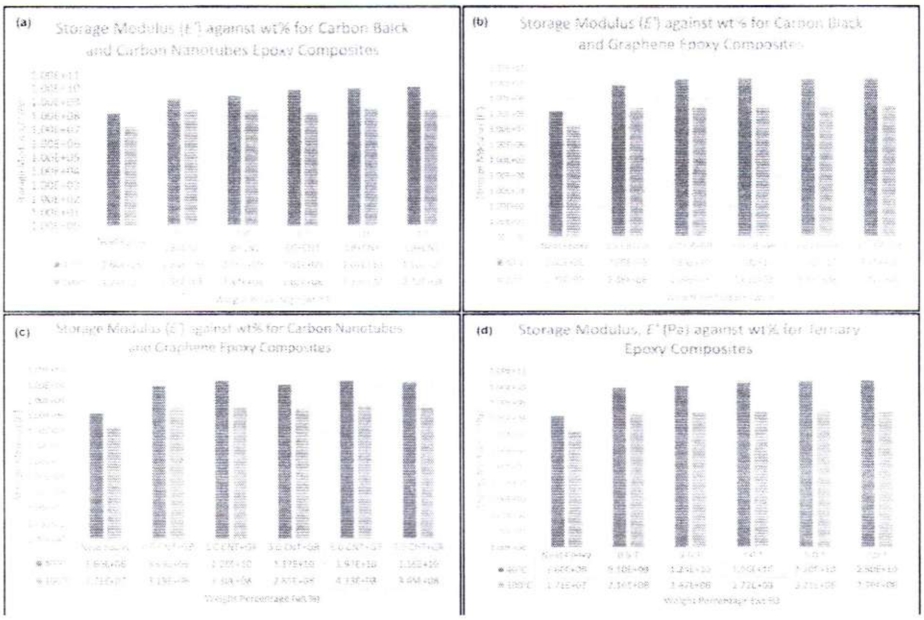

Figure 2: Storage Modulus (E') for CB + CNT fillers (a); CB + Graphene fillers (b), CNT + Graphene fillers (c), and CB + CNT + Graphene fillers (d).

The results of Young's Modulus for all fillers combination are as shown in Figure 3 below. Although most samples are showing an increasing trend in the values as the loading increased, there are a few exceptions. For example, samples at 3.0 wt. % CB + CNT and 3.0 wt.% CB + Graphene recorded Young's Modulus of 12129 MPa and 13403 MPa, which are slightly less than Young's Modulus of neat epoxy (15496 MPa). For each fillers combination, the highest values of Young's Modulus recorded are 21066.24 MPa, 21276 MPa, 21149 MPa, and 24541 MPa for CB + CNT, CB + Graphene, CNT + Graphene, and CB + CNT + Graphene fillers, respectively. This demonstrated the effectiveness of using hybrid fillers in enhancing the Young's Modulus values of epoxy, where an increase as high as 58% is recorded for 7 wt.% CB + CNT + Graphene fillers.

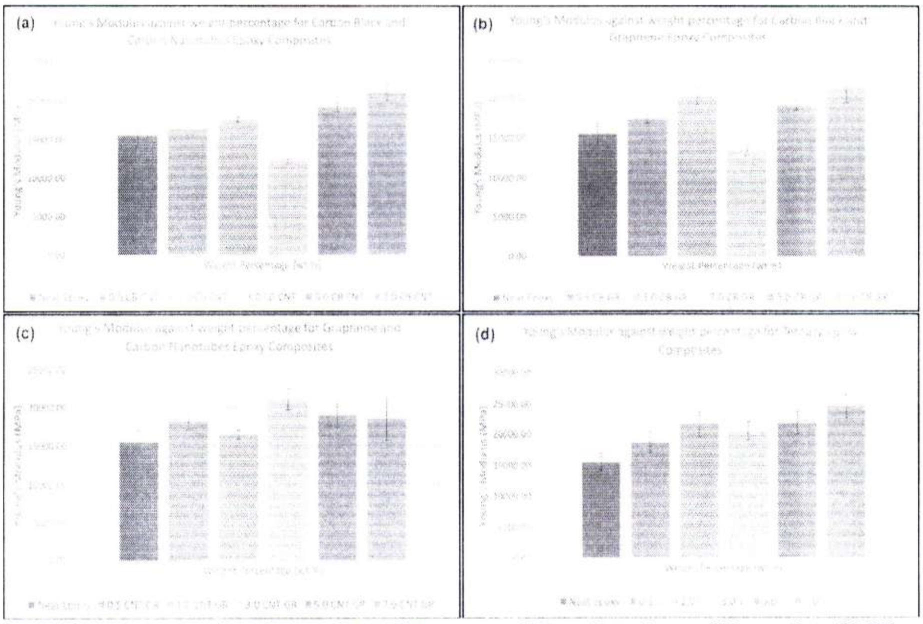

Figure 3: Young's Modulus for CB + CNT fillers (a); CB + Graphene fillers (b), CNT + Graphene fillers (c), and CB + CNT + Graphene fillers (d).

Besides Young's Modulus, plane strain fracture toughness, K_{IC} is also measured. Our data showed tremendous improvement in the values of K_{IC}. The K_{IC} increased from 0.595 MPa.m$^{1/2}$ for neat epoxy to 3.064 MPa.m$^{1/2}$, 3.310 MPa.m$^{1/2}$, 2.959 MPa.m$^{1/2}$, and 3.990 MPa.m$^{1/2}$ for 7 wt.% CB + CNT, 7 wt.% CB + Graphene, 7 wt.% CNT + Graphene, and 7 wt.% CB + CNT + Graphene fillers, respectively. The highest improvement is recorded for 7 wt.% CB + CNT + Graphene fillers, with an increment of 571%.

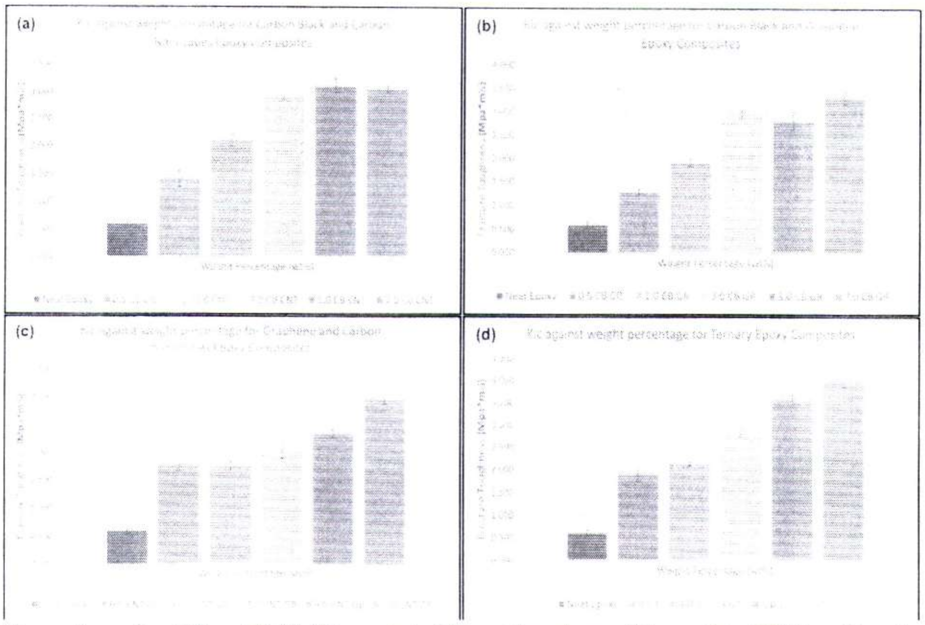

Figure 4: K_{IC} values for CB + CNT fillers (a); CB + Graphene fillers (b), CNT + Graphene fillers (c), and CB + CNT + Graphene fillers (d)

4. Conclusions

The glass transition (Tg), storage modulus (E') and loss modulus (E") value of epoxy composite can be found from thermomechanical properties by incorporation CB, CNT, and Graphene into epoxy matrix. The addition of ternary fillers with different weight percentage into epoxy resins can improve the thermomechanical properties of the epoxy composites. The values of the T_g of ternary epoxy composites are the highest of all loading of the samples prepared. The addition of ternary fillers at various loading can improve the storage modulus (E') at both glassy and rubbery region. The mechanical properties of the ternary epoxy composites are enhanced as the ternary epoxy composites have the highest value of K_{IC}, which is 3.990 MPa.m$^{1/2}$, recorded for 7.0 wt.%.

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