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

Raja Nor Othman*, Ku Zarina Ku Ahmad, Mohamad Faizal, and Adam Bachtiar Ibrahim

Department of Mechanical Engineering,Faculty of Engineering,Universiti Pertahanan Nasional Malaysia,Kem Sungai Besi, 57000 Kuala Lumpur, Malaysia

*Corresponding Author : kavinkabil2023@gmail.com

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

Epoxy composites has been widely used as materials in various industries such as aerospace, automotive, constructions, electrical components, which is due to their superior mechanical and thermal properties. However, properties such as fracture toughness and high temperature properties still needs to be improved to enable its usage in other applications. As such, various fillers including silica [1,2], graphene [3,4], and Carbon Nanotube (CNT) [5,6] are often added to epoxy matrices, which often resulted in a significant improvement in the mechanical properties of the epoxy. The effects of utilizing carbonaceous fillers in enhancing mechanical properties generally and fracture toughness specifically have been reported previously. For example, Chandrasekaran et al. [3] prepared epoxy composites with fillers thermally reduced graphene oxide (TRGO), graphite nano- platelets (GNP), and MWNT, added separately at various loadings. They reported an increase in the toughening effects for all fillers, where 0.5 wt.% TRGO recorded an increment of 40% in KIC. Maheswari et al. [7] experimented with various carbonaceous fillers and reported impressive improvement in various mechanical properties such as Rockwell hardness, compressive strength, glass transition temperature and modulus properties. The authors reasoned the improvement due to the oxygen bearing functionalities over graphene on the tested fillers. Synergistics effects refer to the improvement recorded in the properties of composites by employingmore than one fillers. This is typically achieved for the case of fillers having various structure Recent study by Ankita et al. [8] demonstrated the enhancement in the properties by adding nanodiamonds (ND) to epoxy composites containing graphene and CNT. In their study, ND assisted in the formation of 3D network by acting as barrier and preventing restacking and by providing pathways between the ends ofCNTs. As a result, tensile strength was reported to improve from 46% for 0.5 wt.% loading (Gr+CNT) to 51% for 0.8 wt. % loading (Gr+CBT+ND). On top of that, the value of fracture toughness was also reported to increase from 140% (without ND) to 165% with 0.8 wt% (with ND). The synergistic effects demonstrated with dual fillers are also reported by Nisha et. al [9] where the authors measured an improvement of employing graphene and carbon nanotube on mechanical, electrical, and EMI properties of polycarbonate/ethylene methyl acrylate nanocomposites. The composites containing dual fillers demonstrated an 17 and 27% increase in tensile strength, compared to composites with single filler. An improvement in the values of tensile strength for composites containing dual fillers are also reported. The authors reasoned this due to the improvement in the fillers' dispersion, where CNTs functioned as bridge in between graphene layers, consequently resulting in the improvement of interfacial adhesion between matrix-filler, that helps in the transfer of load to GCNT.

The studies presented in the previous paragraph demonstrated synergistic effects obtained by employing dual fillers in improving particularly mechanical properties of the composites. As such, thisresearch intends to study the effects of employing dual fillers, as well as three fillers in epoxy composites. Among mechanical properties that will be included are glass transition temperature, storage modulus, Young's modulus, and fracture toughness.

2 Experimental

CB + CNT, CB + Graphene, and CNT + Graphene are 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.

added with 1:1 wt.% ratio into the epoxysystems. 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 aswell 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 (KIC) 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.% ternaryloading, with the values of Tg is recorded to be 74.28 °C.

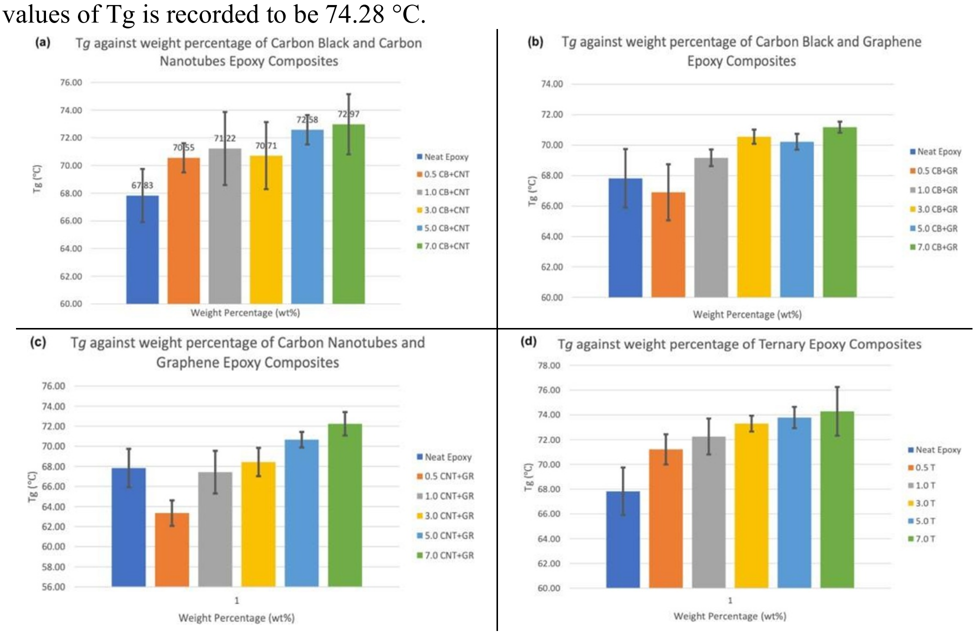

Fig. 1. Graph of Glass Transition Temperature (*T*g) for CB + CNT fillers (a); CB + Graphene fillers (b), CNT + Graphene fillers (c), and CB + CNT + Graphene fillers (d).

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 rubberyregion 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.

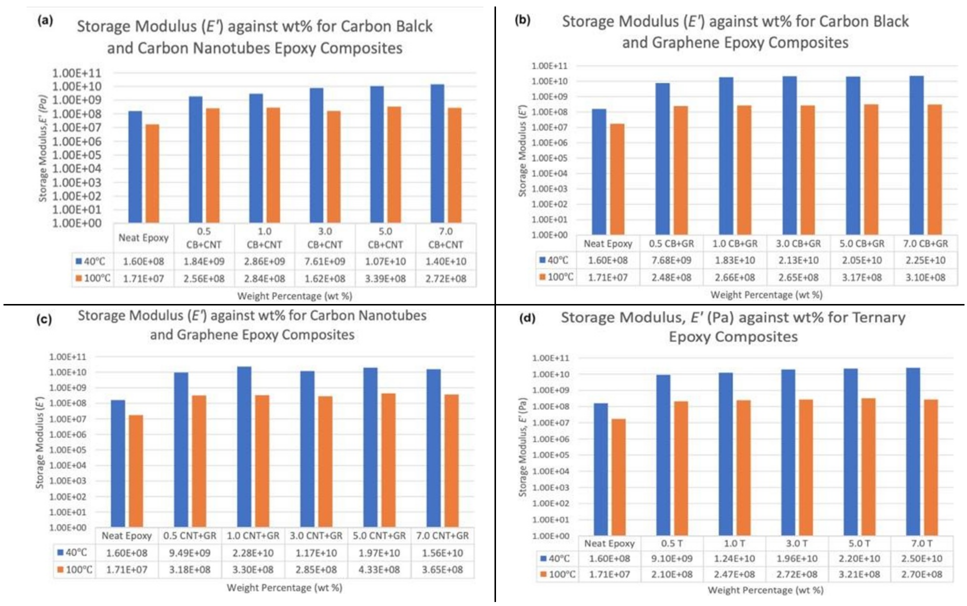

Fig. 2. Storage Modulus (E') for CB + CNT fillers (a); CB + Graphene fillers (b) CNT + Graphene fillers (c), and CB + CNT + Graphene fillers (d).

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 recordedYoung'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 are21066.24 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 usinghybrid 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.

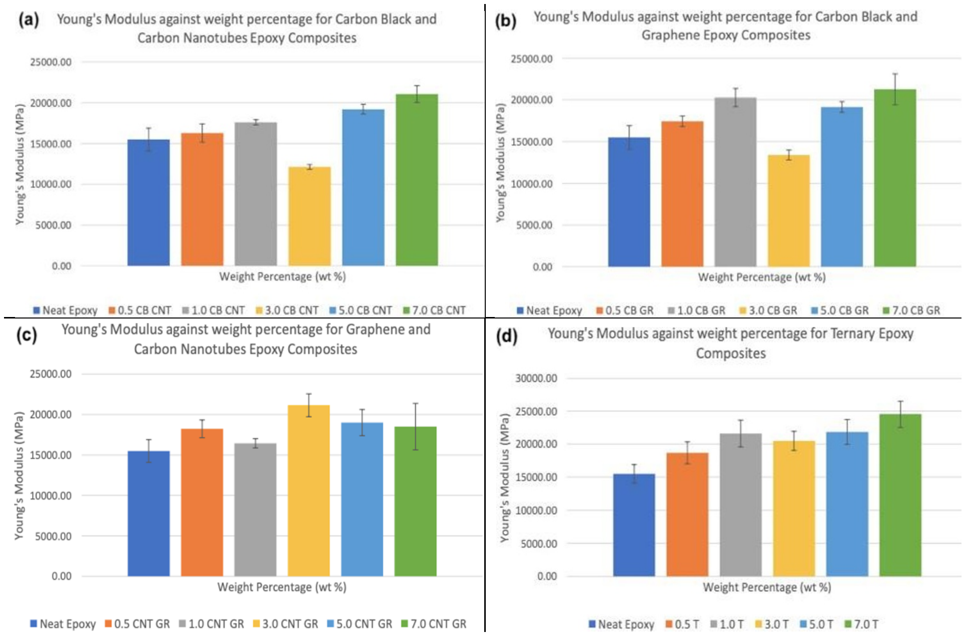

Fig. 3. Young's Modulus for CB + CNT fillers (a); CB + Graphene fillers b), CNT + Graphene fillers (c), and CB + CNT + Graphene fillers (d).

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%.

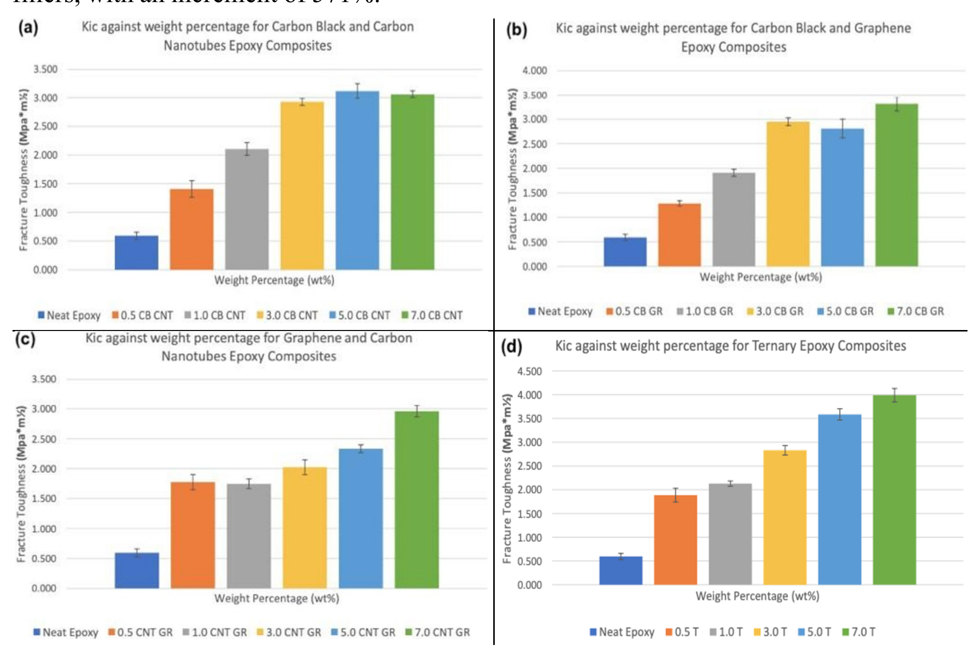

Fig. 4. K_{IC} values for CB + CNT fillers (a); CB + Graphenefillers(b),CNT+Graphene fillers(c), and CB + CNT + Graphene fillers (d)

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4 Conclusion

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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