Research on Failure Mechanism of Graphene Based Epoxy Composites

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Abstract

The present study investigates the effect of addition of three different types on carbon nano-fillers on fracture toughness (KIC) and failure mechanism of epoxy based polymer nano-composites. The carbon nano-fillers were dispersed in the epoxy matrix using a three-roll mill and the three nano-fillers used for this experiment were (i) thermally reduced graphene oxide (TRGO); (ii) graphite nano-platelets (GNP); and (iii) multi-wall carbon nano-tubes (MWCNT). The fracture toughness was measured as a function of weight percentage of the filler using single edge notch three-point-bending tests. The toughening effect of TRGO was most significant resulting in 40% increase in KIC for 0.5 wt% of filler. On the other hand, the enhancements in toughness were 25% for GNP/epoxy and 8% for MWCNT/epoxy. Investigations on fracture surface revealed that crack pinning or bi-furcation by TRGO and crack face separation initiated from TRGO contributed to enhance the fracture toughness. Based on the observations, a schematic explaining the crack propagation in graphene/epoxy composite and the interaction of crack front with graphene particles was proposed.

Keywords

A. Nano-composites; B. Fracture; B. Fracture toughness; D. Fractography; D. Scanning electron microscopy.

1. Introduction

Epoxy polymers that fall under the class of thermoset polymers are used as matrices for fiber reinforced composites and also as adhesives. In view of their cross-linked network structure, these polymers are used in structural engineering applications owing to their low moisture absorption, high modulus and high temperature performance. However, they also come with an undesirable property of brittleness with low fracture resistance because of their structure. Thus, the enhancement in fracture toughness has been a critical issue when it comes to their application and hence engineers have been working on the toughening of epoxies for several decades [1][2].

A comparative graph on the normalized fracture toughness of nano-composites based on nano-clay, multi walled carbon nano-tubes and graphene as a function of filler content is shown in Fig. 1.

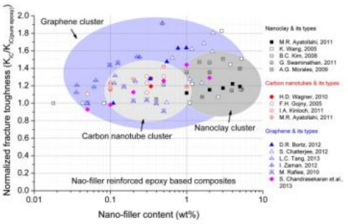

Fig. 1. Normalized fracture toughness as a function of filler content for different nano-filler reinforced epoxies. References used for the plot

2. Materials and methods

The matrix chosen for this work is an epoxy resin. It has a modulus of 2.7–3.0 GPa and glass transition temperature (Tg) ~140 °C and can be used later in preparing structural components. The SEM images of as-received MWCNT, GNP and TRGO are shown in Fig. 2.

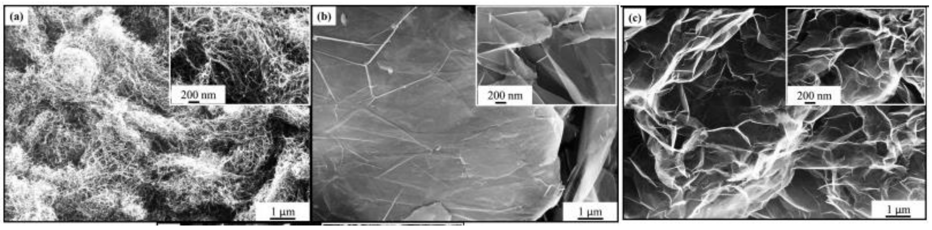

Fig. 2. Scanning electron micrographs of as-received fillers (a) MWCNT (NC7000); (b) GNP and (c) TRGO respectively. Insets show higher magnification images.

The state of dispersion of the fillers in epoxy matrix has been characterized by scanning electron microscope at a low magnification on thin slices cut from the cured nano-composite as shown in Fig. 3.

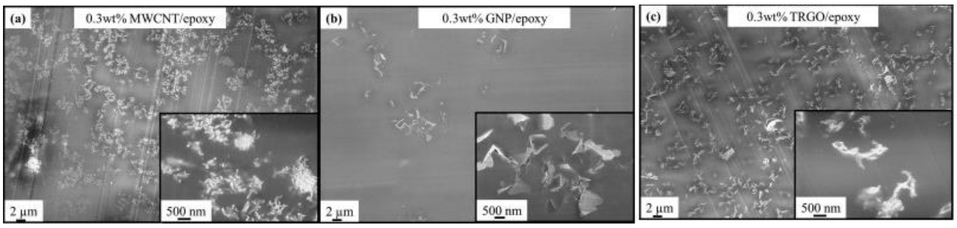

Fig. 3. Scanning electron micrograph of thin slices (500 nm thick on Si wafer) of cured composite in “in-lens” mode (a) 0.3 wt% MWCNT/epoxy; (b) 0.3 wt% GNP/epoxy and (c) 0.3 wt% TRGO/epoxy, showing the distribution of fillers in the matrix.

A scheme explaining the specimen geometry along with the notch preparation process is shown in Fig. 4. A minimum of 5 specimens were evaluated for each composite.

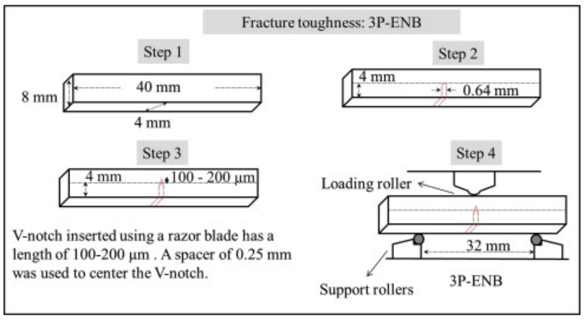

Fig. 4. Specimen geometry and notch preparation for fracture toughness test.

3. Results and discussion

The fracture toughness of the nano-composites measured by 3P-ENB test is plotted as a function of weight percent of filler for each filler type in Fig. 5. It is evident that as the filler content increases, K_{IC} also increases for low filler content (0–0.5 wt%). For higher weight fraction of GNP (more than 1.0 wt%), a decreasing trend is observed. It is reported in literature that the fracture toughness of the nano-composite starts to decrease beyond certain weight fraction. The current result also supports this fact. Note that, for all of the composites, the crack propagated unstably, and there is no non-linear tendency in load–displacement (L–D) curves and hence the L–D curves are not presented here.

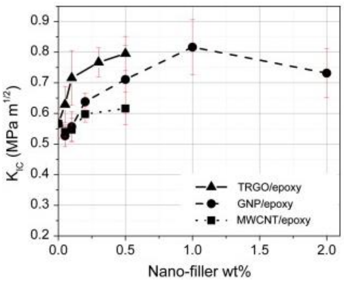

Fig. 5. Fracture toughness as a function of weight percent of filler (3P-ENB test).

Fig. 6 shows the SEM micrographs of the fracture surface of pure epoxy, and the epoxy resin toughened with 0.1 wt% nano-filler. The dotted lines indicate the crack propagation direction from top to bottom. The fracture surface of pure epoxy (Fig. 6a) was very smooth. The observed flow pattern at higher magnification is well known as the typical fracture surface of epoxy resin, and the local crack propagation direction can be estimated by following the pattern [3][4]. The fracture surface of 0.1 wt% MWCNT/epoxy (Fig. 6b) was also smooth. However, the fracture surface is slightly rougher than that of pure epoxy owing the existence of MWCNTs as shown in high magnification inset. The failure mechanism for MWCNT/epoxy is a well discussed topic in literature and it has been shown that it is governed by crack bridging, de-bonding and pull-out of nano-tubes which in turn contributes for higher toughness for the present composite [5][6]. On the other hand, the fracture surfaces of GNP/epoxy and TRGO/epoxy (compare Fig. 6c and d respectively) were much rougher than those of neat epoxy and 0.1 wt% MWCNT/epoxy. Furthermore, the fracture surface of GNP/epoxy and TRGO/epoxy consists of several small and different height fracture surfaces. Narrow bands were observed at the boundary of these fracture surfaces, and these bands run parallel to the crack growth direction.

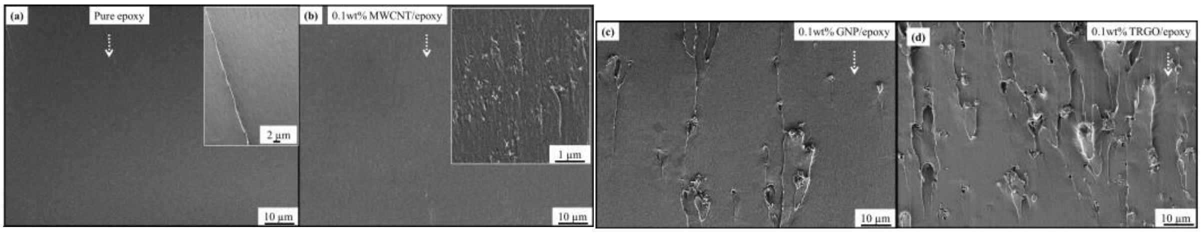

Fig. 6. Representative fracture surfaces of 0.1 wt% nano-filler/epoxy after 3P-ENB test, (a) pure epoxy, (b) MWCNT/epoxy, (c) GNP/epoxy and (d) TRGO/epoxy. Insets in (a) and (b) show higher magnification micrographs.

In order to reveal the failure behaviors of GNP/epoxy and TRGO/epoxy in detail, the fracture surfaces were studied using SEM through both SE2 detector and in-lens detector on both sides of the fracture surfaces after 3P-ENB tests as shown in Fig. 7. As a result, most fracture behaviors were categorised into three failure modes, (a) crack pinning by filler, (b) separation between the graphitic layers, and (c) shear failure due to difference in height on fracture surfaces. In the following paragraph each failure mode is explained with showing representative SEM images.

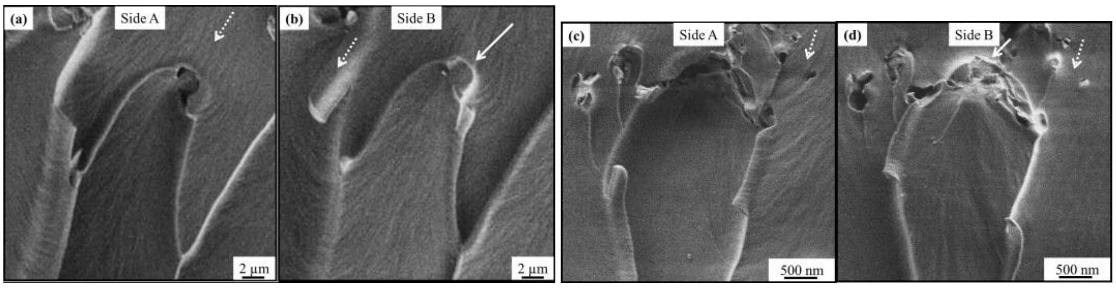

Fig. 7. Examples of crack pinning failure (a), (b) GNP/epoxy and (c), (d) TRGO/epoxy on both the fracture sides. Dotted lines indicate crack propagation direction.

The second failure mode is separation between the GNP/TRGO sheets which is representatively shown in Fig. 8. Both the opposite pairs of the fracture surface are shown in Fig. 8a and b for

GNP/epoxy and Fig. 8c and d for TRGO/epoxy. In the image, the arrow indicates the separation between TRGO/GNP sheets. In the flat surface, no flow patterns that are typical for the fracture surface of epoxy resin are observed. This fact indicates that this face is not the fracture surface of epoxy resin but the surface of TRGO/GNP. This is one of the toughening mechanisms of TRGO/epoxy and GNP/epoxy and is clearly visible in those sheets that are oriented in a direction perpendicular to the crack propagation direction.

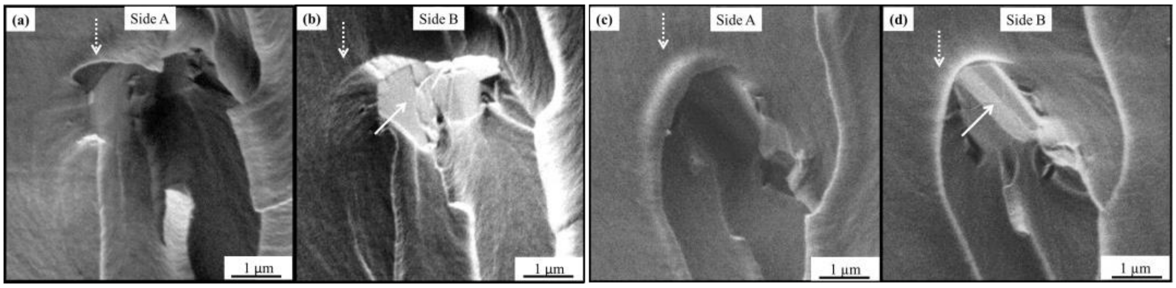

Fig. 8. Examples of failure by separation in between the GNPs on both fracture sides (a), (b) and TRGO (c), (d) where the white arrow indicates the delaminated surface of nano-filler.

In Fig. 9, are shown examples of GNP/epoxy and TRGO/epoxy using both SE2 and in-lens mode. In-lens mode enables to visualize the nano-fillers which appear in white in Fig. 9c and d. However, electron transparency of these nano-fillers depends on the number of layers present. In both the nano-composites, TRGO/epoxy and GNP/epoxy the white arrows indicate the exfoliation in-between the graphitic layers. It can be seen that the nano-fillers are oriented perpendicular to the crack propagation direction which shows the separation in-between the graphite sheets. Based on the two failure modes observed from the fracture surfaces, a schematic representation of the crack propagation mechanisms is shown in Fig. 10.

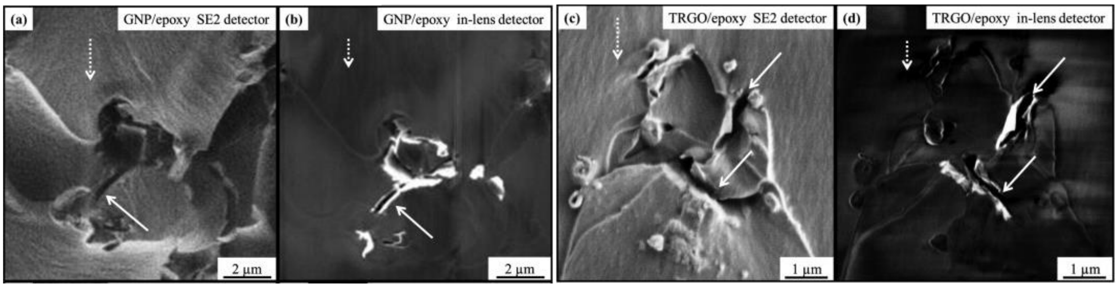

Fig. 9. Examples of GNP/TRGO separation in between the graphitic layers: (a) GNP/epoxy and (c) TRGO/epoxy through SE2 detector; (b) GNP/epoxy and (d) TRGO/epoxy through in-lens detector (arrows indicate the nano-filler layers oriented perpendicular to crack front).

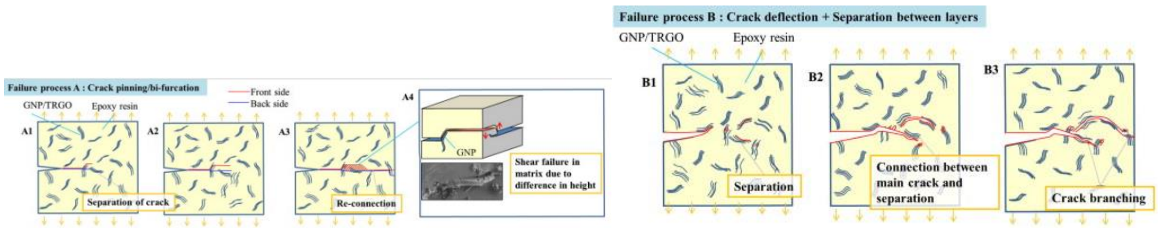

Fig. 10. Schematic of the observed crack propagation mechanism in TRGO/GNP epoxy composite.

Further, it is observed from the failure mode (B) i.e., the crack deflection and/or separation between the sheets, see Fig. 11. In other words, the crack runs along the surface (B1) that means along the TRGO or GNP/epoxy interface.

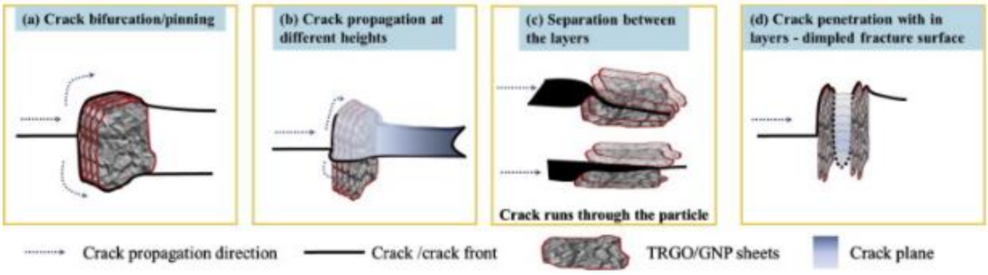

Fig. 11. Schematic on the interaction of crack front with GNP/TRGO particles.

The dependence of fracture toughness of GNP/epoxy, on the weight percentage of filler, as seen in Fig. 5, shows that after 1.0 wt% of filler, the *K*IC values start to drop. The fracture surfaces GNP/epoxy at different weight percentage were viewed in the SEM to explain the drop in *K*IC as summarized in Fig. 12.

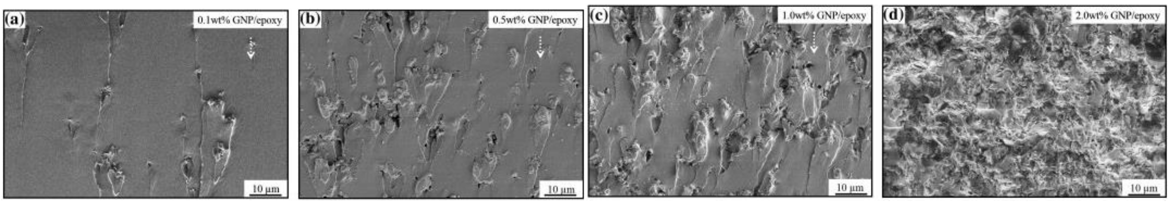

Fig. 12. SEM micrograph of fracture surface of GNP/epoxy (a) 0.1 wt%; (b) 0.5 wt%; (c) 1.0 wt% and (d) 2.0 wt% respectively (dotted arrow indicate crack propagation direction).

4. Conclution

Based on the findings, it can be concluded that pure epoxy show a more or less flat fracture surface, the deformation zone formed in a graphene nano-composite is higher and which may be due to the shearing in-between the graphitic sheets (particles) which in turn increases the fracture toughness of graphene toughened epoxies. Based on the above observation a schematic on the failure mechanism on graphene based epoxy nano-composites is proposed.

Acknowledgements

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