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Dichlorobenzene: an effective solvent for epoxy/graphene nanocomposites preparation

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It is generally recognized that dimethylformamide (DMF) and ethanol are good media to uniformly disperse graphene, and therefore have been used widely in the preparation of epoxy/graphene nanocomposites. However, as a solvent to disperse graphene, dichlorobenzene (DCB) has not been fully realized by the polymer community. Owing to high values of the dispersion component (δ_d) of the Hildebrand solubility parameter, DCB is considered as a suitable solvent for homogeneous graphene dispersion. Therefore, epoxy/graphene nanocomposites have been prepared for the first time with DCB as a dispersant; DMF and ethanol have been chosen as the reference. The colloidal stability, mechanical properties, thermogravimetric analysis, dynamic mechanical analysis and scanning electron microscopic images of nanocomposites have been obtained. The results show that with the use of DCB, the tensile strength of graphene has been improved from 64.46 to 69.32 MPa, and its flexural strength has been increased from 97.17 to 104.77 MPa. DCB is found to be more effective than DMF and ethanol for making stable and homogeneous graphene dispersion and composites.

1. Introduction

Epoxy resins can be seen to be widely used in aerospace, automotive, marine, structures and construction, owing to their superlative mechanical properties and favourable thermal stability, which are important for various applications [1,2]. Epoxy resins are of particular interest to engineering because these resins provide a unique balance of chemical and mechanical properties combined with ease of processing [3].

For epoxy/graphene nanocomposites, graphene can significantly improve the physical and chemical properties of

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matrix at extremely low loadings, and this improvement could only be achieved when the filler is homogeneously dispersed in the matrix [4,5]. The uniformly dispersed graphene could share external stress and blocks advancing cracks, which improve the mechanical properties [6–8]. However, for practical applications, graphene is not suitable to disperse in epoxy just by simple mixing, as graphene tends to reaggregate in the matrix due to the strong van der Waals force between separately dispersed graphene sheets [9,10].

Therefore, solvents are widely used as dispersants to overcome the van der Waals force between graphene nanosheets, and hence lead to uniform graphene dispersion. For example, ethanol [11–14] has been widely adopted as a dispersant for graphene materials, and showed good dispersability and stability. Dimethylformamide (DMF) [15–20] is also well recognized in polymer communities as a good dispersant for graphene. By using DMF, a lot of works reported enhancements in the final properties of epoxy/graphene nanocomposites. Other solvents like tetrahydrofuran [21–24], acetone [25–28], dichloromethane [29–32], isopropyl alcohol [33,34], water [35–39], etc. have also been reported in the processing of epoxy/graphene nanocomposites.

Besides those commonly used solvents, dichlorobenzene (DCB) has also been widely reported as a good dispersant for preparing graphene dispersions because of the following reasons. Firstly, DCB is a commonly used reaction solvent for fullerenes and is known to form stable single-walled nanotube dispersions [40]. Secondly, DCB is a convenient dispersant and is compatible with a variety of chemicals. Thirdly, DCB, being aromatic, is able to interact with graphene via π–π stacking [41]. Fourthly, it has been reported that solvents with high values of the dispersion component (δ_d) of the Hildebrand solubility parameter are the best for making homogeneous and aggregate-free dispersions of graphene [42,43]. DCB shows a high δ_d of 19.2 $MPa^{1/2}$. In the light of this, DCB tends to be suitable to produce stable graphene dispersion. Song *et al*. [44] dispersed graphene in DCB, and tested the stability of the dispersion by measuring its light absorbance. Naebe *et al*. [45] surface-treated graphene with DCB to prepare functionalized graphene. Some other works [46–53] also involved the use of DCB and reported positive effects.

However, though DCB has been used a lot in the dispersion of graphene, the use of DCB to prepare epoxy/graphene nanocomposites is not yet fully realized by the polymer community. To the best of our knowledge, there is no work reported using DCB as a dispersant for epoxy/graphene nanocomposites. In this work, *o*-DCB has been chosen and used for the first time to prepare epoxy/graphene nanocomposites. Another two commonly used solvents, DMF ($\delta_d = 17.4\ MPa^{1/2}$) and ethanol ($\delta_d = 15.8\ MPa^{1/2}$), have been used for comparison in this work.

2. Material and methods

2.1. Materials

The epoxy system used in this study was purchased from Polyfibre UK Ltd. This system offers good all-round properties and consists of a EPOPHEN EL5 bisphenol A-based liquid epoxy and EPOPHENEHA 57 diamine hardener. Graphene nanoplatelets were offered by Graphene Laboratories Inc., USA with an average lateral size of 4.5 µm and a specific surface area of 80 $m^2\ g^{-1}$. *o*-DCB, DMF and ethanol were purchased from Sigma-Aldrich Company with a purity of 99.9%.

2.2. Sample preparation

According to our previous research [7], 0.3 wt% graphene loading shows the maximum property enhancement to epoxy; therefore, in this work, 0.3 wt% nanocomposites were prepared with different solvents to compare their dispersing efficiencies.

One set of samples was prepared without any solvent, marked as G-0.3. DCB, DMF and ethanol were used to prepare another three sets of samples; 0.45 g of graphene was first dispersed in 100 ml of solvent (DCB, DMF and ethanol, respectively) and bath-sonicated for 0.5 h; then 99.7 g of epoxy monomer was added to the dispersion and sonicated for another 0.5 h. To remove the solvent, the mixtures were heated with stirring; all the mixtures were then weighed to ensure evaporation of the solvents fully. Then the mixtures were cooled down to room temperature and 49.85 g of hardener was added with hand stirring for 5 min followed by 5 min of bath sonication; then the entrapped air bubbles were removed by vacuum degassing. Finally, the liquid mixtures were mould cast and cured for 6 h at room temperature and then for 6 h at 80°C.

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2.3. Characterization

Tensile properties, flexural properties and fracture toughness were measured by a universal mechanical testing machine (Instron 3382); for all tests the crosshead speed used was 2 mm min^{-1}. Tensile tests were conducted according to ASTMD638 (Type V) with a specimen thickness of 4 mm. Flexural properties were measured according to ASTM D790 with a specimen dimension of 48 × 12.7 × 3 mm. A single-edge-notch three-point bend specimen was used to measure the fracture toughness (K_{1C}) according to ASTM D5045; the specimen dimension was 36 × 6 × 3 mm with a crack of length of 3 mm. The K_{1C} was calculated using

$$K_{1C} = \frac{P_{\max} f(a/w)}{BW^{1/2}}, \tag{2.1}$$

where W is the sample width (millimetres), a is the crack length and kept between 0.45 and 0.55 W, B is the sample thickness (millimetres), $f(a/w)$ was calculated using equation (2.2), which is constant and related to the sample geometry and $P_{\max}$ is the maximum load of the load–displacement curve. The critical strain energy release rate (G_{1C}) was calculated using equation (2.3), where v is Poisson's ratio of the polymer and taken as 0.35 and E is Young's modulus obtained from the tensile tests (MPa).

$$f\left(\frac{a}{w}\right) = \frac{(2 + a/w)\{0.0866 + 4.64(a/w) - 13.32(a/w)^2 + 14.72(a/w)^3 - 5.6(a/w)^4\}}{(1 - a/w)^{3/2}} \tag{2.2}$$

and

$$G_{1C} = \frac{K_{1C}^2(1 - v^2)}{E}. \tag{2.3}$$

Vickers microhardness was measured by Buehler Micromet II. A dwell time of 10 s with a load of 200 g was used for all the samples. Six samples were measured for each set of conditions and mean values were then reported.

A Perkin Elmer-8000 dynamic mechanical analysis (DMA) instrument was used to conduct the analysis to determine the storage modulus (E') and loss factor (tan δ). Sample dimensions of 30 × 8 × 2.5 mm were tested by the single cantilever method. All tests were carried out under the temperature sweeping mode (temperature ramp from 30°C to 150°C at 5°C min^{-1}) at a constant frequency of 1 Hz. The glass transition temperature (T_g) was taken as the temperature value at the peak of tan δ curves. Thermogravimetric analysis (TGA) of the nanocomposites was carried out with a TA Instruments Q500 thermal analyser. The temperature range was from room temperature to 600°C at a ramp rate of 5°C min^{-1} under N_2 atmosphere. To evaluate the fracture modes of the nanocomposites, a FEI Quanta 200 electron microscope was used to obtain scanning electron microscopy (SEM) images. A layer of gold with 10 nm thickness was applied to the samples' fractured surfaces using an Emscope sputter coater model SC500A.

3. Results and discussion

3.1. Visual stability

Successful fabrication of nanocomposites crucially depends on maintaining a stable dispersion of graphene before polymer curing. Figure 1 shows the colloidal suspensions of graphene in DCB, DMF and ethanol at different time intervals after sonication. The pictures show that graphene settled down in ethanol within two hours after sonication; the graphene–DMF suspension also reaggregated significantly and settled down within 12 h of sonication. However, stable dispersion was achieved only by DCB, which suggests that DCB is the best for preparing uniformly dispersed epoxy/graphene nanocomposites. Figure 2 shows the SEM image of as-received stacked multilayer graphene.

3.2. Mechanical properties

The uniformly dispersed graphene in the matrix will in return affect the macroscopic properties of the nanocomposites, while most of the work on epoxy/graphene nanocomposites aims at exploiting the mechanical enhancement of the nanocomposites. Therefore, the mechanical properties of nanocmposites have been tested and are summarized in figure 3.

As can be seen from the figure, G-0.3 shows the lowest values in the properties, such as a tensile strength of 64.46 MPa, flexural strength of 97.17 MPa and hardness of 0.235 GPa. DCB samples show the highest properties, with a tensile strength of 69.32 MPa, flexural strength of 104.77 MPa and Vickers

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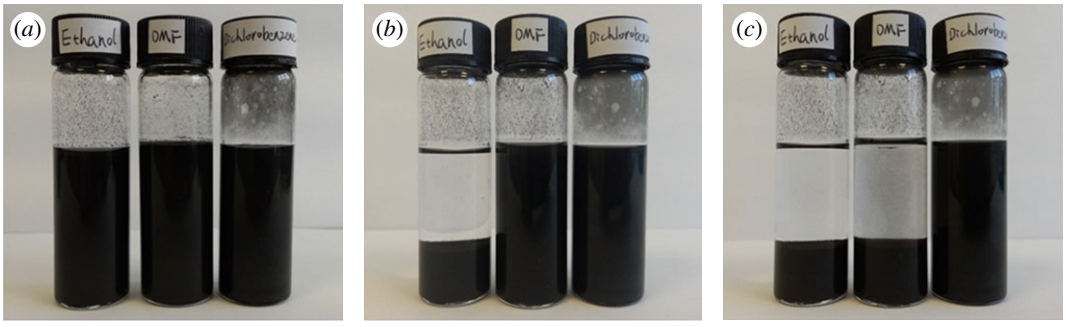

Figure 1. Visual stability of 3 g l^{-1} graphene suspensions (*a*) 5 min after sonication, (*b*) 2 h after sonication and (*c*) 12 h after sonication. Samples from left to right: ethanol, DMF, DCB.

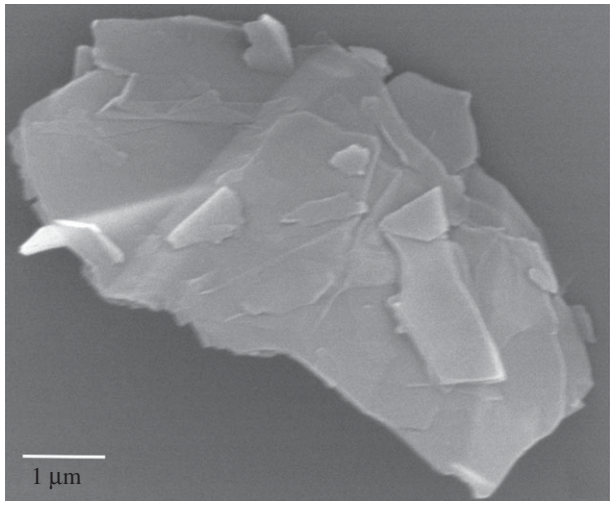

Figure 2. SEM image of as-received multilayer graphene.

hardness of 0.247 GPa. Meanwhile, DMF- and ethanol-prepared samples show only medium increase in the properties, indicating that DCB produces better graphene dispersion than DMF and ethanol. To sum up, the improvements in the macroscopic properties of epoxy/graphene nanocomposites are due to the enhanced dispersion of graphene. The uniformly dispersed graphene forms a continuous network in the matrix, which could release the stress concentration, and thus enhance the mechanical strength and improve the energy-absorbing capacity. Moreover, the uniformly dispersed graphene has changed the microstructure of the polymeric network, which will be discussed in below.

3.3. Thermogravimetric analysis test

Thermal decomposition is one of the fundamental thermal properties and is critical for practical applications. Figure 4 shows the TGA curves of the nanocomposites in a nitrogen atmosphere. It can be seen that all samples have a similar two-stage weight loss, indicating that all the samples have a similar thermal degradation mechanism. The first weight loss from 100°C to 230°C was attributed to the decomposition of small molecules on the side chain. The second weight loss that occurred from 250°C to 500°C shows the decomposition of the main polymer chain [54,55]. As can be seen from the figure, DCB samples show the lowest decomposition rate, which means the highest thermal stability compared with that of the DMF and ethanol samples.

The reason of this phenomenon can be explained by the fact that graphene has affected the cross-linking structure of the matrix. Generally, the cross-linking density means the concentration of cross-linked bonds per volume. For typical polymeric materials, the higher the cross-linking density, the stronger the polymer chains bond with each other, thus resulting in a stronger capacity to withstand heat. Compared to the structures of DMF- and ethanol-prepared samples, DCB-prepared samples tend to produce more uniform graphene dispersion, and thus an increase in the cross-linking density [56,57].

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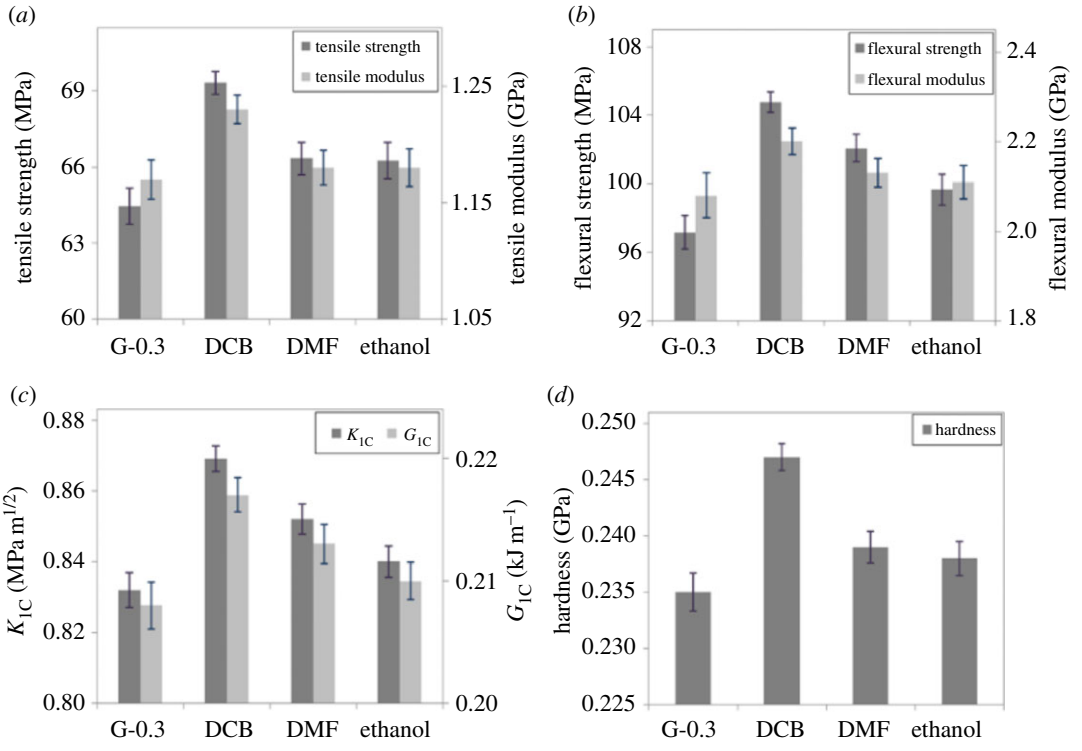

Figure 3. Mechanical properties of epoxy/graphene nanocomposites: (*a*) tensile properties, (*b*) flexural properties, (*c*) fracture properties and (*d*) hardness.

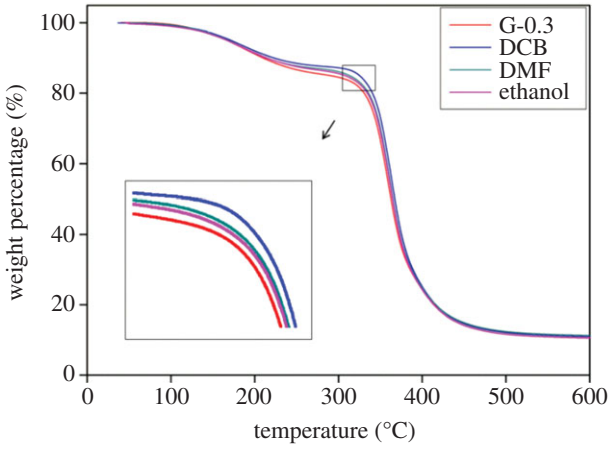

Figure 4. TGA curves of the nanocomposites.

On the other hand, the homogeneously dispersed graphene could form a continuous network in the matrix, and thus could reduce the volatilization rate of the decomposition products.

In general, the increased thermal stability of DCB samples resulted in a higher heat capacity of nanocomposites and a better barrier effect of the graphene network, which was caused by the uniform dispersion of graphene by using DCB.

3.4. Dynamic mechanical analysis test

Figure 5*a* shows the storage moduli (E') of the nanocomposites. As can be seen from the figure, the storage moduli of samples prepared with solvents increased obviously over the G-0.3 samples throughout the temperature range. Especially, DCB-prepared samples show a 2.61 GPa storage modulus, which is higher than the 2.45 GPa of DMF samples and 2.38 GPa of ethanol samples.

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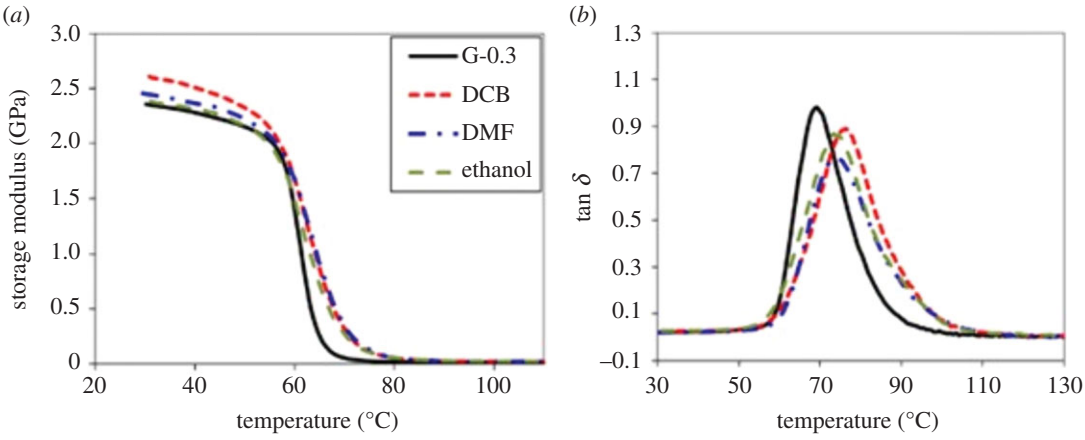

Figure 5. DMA curves of nanocomposites: (*a*) storage modulus and (*b*) tan δ.

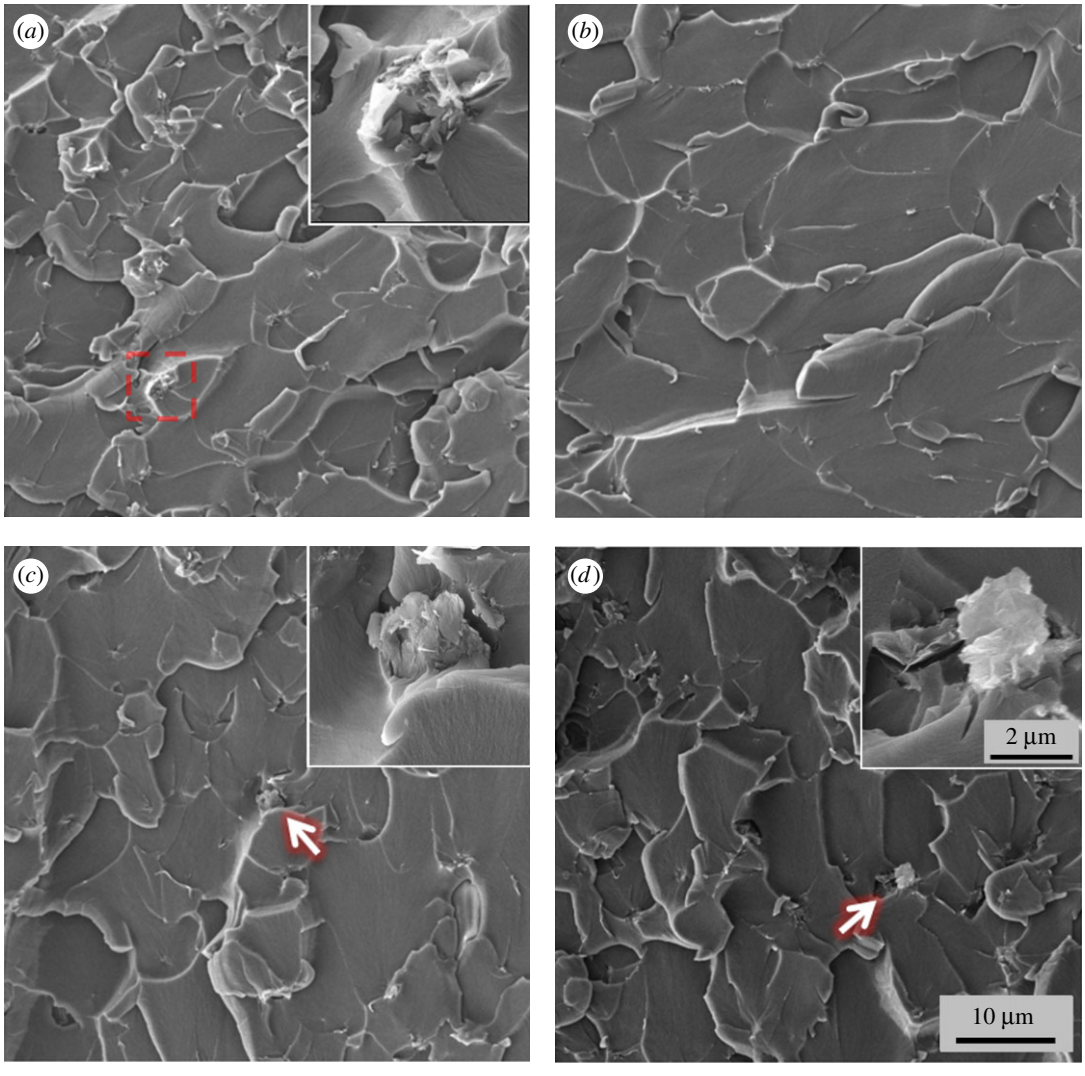

Figure 6. SEM images of fracture surfaces of (*a*) G-0.3, (*b*) DCB samples, (*c*) DMF samples and (*d*) ethanol samples.

The segmental motion of polymers is characterized by glass transition temperature (T_g), which was taken as the temperature value at the peak of tan δ curves and are shown in figure 5*b*. In this figure, it can be seen that the tan δ peak is observed at 69.28°C for G-0.3 samples. For nanocomposites processed by DCB, DMF and ethanol, the T_g were observed at higher temperatures. This can be ascribed to the phenomenon that the uniformly dispersed graphene has restricted the chain mobility of the epoxy

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matrix, and thus increased the T_g values [58]. Among all the samples, DCB-prepared samples show the highest T_g of 76.57°C, which is a more than 7°C increment compared with the G-0.3 samples, while only slight increases (approx. 4°C) in T_g are obtained for samples prepared with DMF and ethanol. As mentioned above, the uniformly dispersed graphene increased the cross-linking density of the nanocomposites, and then plays a positive role in improving the thermal stability.

3.5. Scanning electron microscopy test

The fracture surfaces of nanocomposites were examined by SEM and are shown in figure 6. For G-0.3 samples, as shown in figure 6*a*, graphene aggregates are sparsely located on the surface; the inset of figure 6*a* shows the typical morphology of a graphene aggregate. This poorly dispersed surface indicates a poor interfacial interaction between the epoxy matrix and graphene, and features the brittle nature of the material and its poor resistance to crack initiation and propagation. Compared to the G-0.3 samples, the fracture surfaces of DCB samples are smoother, as shown in figure 6*b*. The clear fracture patterns show the fracture mechanism of sheet/sheet delamination of this nanocomposite, and reveals that the usage of DCB leads to uniform graphene dispersion. The homogeneously dispersed graphene is able to bridge growing cracks, impede crack propagation and thus improve the properties of nanomaterials. However, for DMF- and ethanol-prepared samples, as shown by the insets in figure 6*c*,*d*, some poorly dispersed graphene can still be seen on the surface. The non-uniformly dispersed graphene forms defects in the nanocomposites, which act to concentrate the stresses locally, effectively causing a localized weakness, thus decreasing the properties of the nanocomposites.

4. Conclusion

A prerequisite for property enhancement of epoxy/graphene nanocomposites is the uniform dispersion of graphene in the matrix; however, the ultra-high specific surface area of graphene results in high van der Waals forces and thus induces a strong tendency to reaggregate. Solvents are able to provide a low-viscous medium, which is an ideal environment for graphene to disperse. While dispersing, lower viscosities are responsible for promoting the de-bundling of graphene sheets. This results in the triggering of the van der Waals force on graphene surfaces in lower proximity with each other, thus leading to dispersion. Therefore, the selection of dispersion media is very important for the final properties of nanocomposites.

In this work, DCB was selected to test its effectiveness for epoxy/graphene nanocomposites preparation. The colloidal stability and mechanical properties were determined, and TGA, DMA and SEM imaging of nanocomposites were conducted. The results show that DCB is able to produce stable graphene dispersion; however, DMF and ethanol are not sufficient to disperse graphene homogeneously in the nanocomposites. Nanocomposites prepared with DCB also show higher mechanical properties and better thermal stability compared to the samples prepared with DMF and ethanol.

In general, it is concluded that DCB is more efficient than DMF and ethanol for making uniform and stable graphene dispersions. The usage of DCB can endow the nanocomposites with outstanding mechanical properties and improved thermal stability. This finding can be significant in practical applications and gives an impetus for DCB usage not only in epoxy/graphene nanocomposites preparation, but also in other polymer nanocomposites where the usage of solvents is required in the processing.

Data accessibility. All the data are provided in the main text.

Authors' contributions. J.W. conducted most of the laboratory work and wrote the manuscript. M.S.S. assisted in part of the experiments and testing. T.V. and F.I. supervised the project and gave research guidelines. All the authors contributed to the revision and proofreading of the manuscript.

Competing interests. The authors declare that they have no competing interests.

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