DISPERSION AND REAGGLOMERATION IN NANOCOMPOSITES: THE EFFECTS OF PLASMA FUNCTIONALISATION AND MORPHOLOGY

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Abstract

Creating homogeneous dispersions in graphene/epoxy networks are essential to obtain optimum material properties, however the natural tendency of these materials to agglomerate results in this being difficult to achieve and maintain over time. This work investigates reagglomeration of Few Layer Graphene (FLG) in epoxy resins over the period of a week, after undergoing high shear mixing to varying degrees. The use of plasma functionalisation to attach oxygen functional groups to the surface of the FLG to further aid dispersion and prevent reagglomeration has been investigated. Microscopy techniques and DMA analysis have been carried out to monitor the effect of reagglomeration and assess the resultant effect of these factors on Tg. It was found that the use of functionalisation gave higher levels FLG dispersion with less mixing, as well as a reduction in reagglomeration rate compared to unfunctionalised FLG. The effect of reagglomeration was evident both visually and with reduction in measured Tg values. It was found that generally materials mixed to a higher degree of dispersion exhibit better thermomechanical properties, as well as higher homogeneity within the overall molecular network measured by the tanδ peak factor. Dispersion and properties were consistently shown to decrease over time, highlighting the need to enhance dispersion stability and to accurately estimate shelf lives of materials.

1. Introduction

After the successful extraction of graphene in 2004, the material has been of great interest due to its phenomenal material properties. The combination of high strength, good electrical and thermal conductivity and extremely low bulk density makes graphene attractive for use in nanocomposite materials [1-2]. However, it is well known that dispersion state heavily influences material properties, where having poor dispersion along with weak matrix interfaces reduces mechanical performance [3-4]. The dispersion of nanocarbons are notoriously difficult to control due to Van der Waals forces and high aspect ratios which promote agglomeration and entanglement. This has led to many researchers focusing on understanding movement of nanocarbons within various mediums and looking at surface treatments to improve stability and aid dispersion though interfacial bonding, whilst assessing the resulting effect on mechanical properties [3-7].

This paper explores the combination of graphene dispersed with epoxy resin. Epoxy resins are thermoset polymers which have great chemical resistance and high stiffness properties whilst being relatively inexpensive and easy to produce into complex parts. Epoxy resins generally have low fracture toughness properties compared to other polymer materials which has limited the use of these materials in structural applications, however the emergence of nanocarbons had led to great interest into the combination of these materials to create an optimised nanocomposite [8]. The dispersion of nanocarbons is particularly difficult within epoxy resins due to the matrix viscosity further promoting agglomeration [9]. The use of functionalisation to alter surface chemistry is popularly used to aid dispersion and stability as well as promoting interactions between graphene and epoxy, improving interfacial properties which in turn improve overall mechanical performance [6,10].

This study investigates the use of attaching oxygen functional groups onto the surface of Few Layer Graphene (FLG) to aid dispersion and promote stability over time. This study is of particular interest for commercial applications as it is important that products maintain a good shelf life with no long-term depreciation of material properties, caused by reagglomeration [4,6,9-10]. Microscopy and image analysis techniques have been utilised to assess the long-term effects of functionalisation on material properties by tracking reagglomeration behaviour and testing the corresponding thermomechanical properties over the period of a week. The materials in this study have been treated and prepared in line with methods currently being commercially used.

2. Materials and Methods

2.1. Materials

A Few Layer Graphene (FLG) morphology with a relatively small aspect ratio was utilised in this work. The FLG material was provided by Haydale Ltd in both an unfunctionalised state and plasma functionalised in an oxygen atmosphere. TEM analysis (Fig. 1) has shown that the individual flake size is less than 1μm and the number of graphene layers ranged from approximately 8-12.

The FLGs were initially incorporated into the Araldite LY 1564 resin by Dual Asymmetric Centrifugal (DAC) mixing using SpeedMixer™ DAC 600, at 10 wt.% filler loading. The combined materials were then processed further using an Exakt 80E three roll mill (3RM). Samples were taken after 5 and 10 passes through the 3RM for both the functionalised and unfunctionalised materials. The samples were then diluted down to a 1 wt.% filler loading by the addition of further resin and DAC mixing was used to ensure thorough mixing. Materials have been stored at room temperature (approx. 21°C) throughout manufacture and testing.

Samples for DMA analysis were cast in a PTFE mould with dimensions of 2 x 5 x 20mm. The LY 1564 resin was catalyzed using the Aradur 2954 hardener at a ratio of 100:35 by weight and again combined by DAC mixing prior to casting. The samples were then cured for 1hr at 80^0 C, followed by 4hr at 140^0 C, before demoulding.

2.2 Methods

Filled resin samples were prepared for microscopy by depositing resin on to a standard microscope slide and allowed to spread naturally. The samples were imaged by transmission light optical microscopy at x50 magnification using a Nikon eclipse LV100 microscope. Images were collected from 2 random locations across the slide and at each location the focal depth was adjusted to capture images from the bottom surface, top surface and mid-point of the resin film. One set of images was collected after mixing and a further set was collected after one week. The images were then post processed using ImageJ software to estimate the particle size distribution of FLG agglomerates. This was done by converting into binary images before thresholding to eliminate out of focus agglomerates. The software was then used to calculate the area of each agglomerate, which then determined an equivalent diameter for each particle, under the assumption that they were spherical. D10, D50 and D90 values were taken from particle size distributions created for each material.

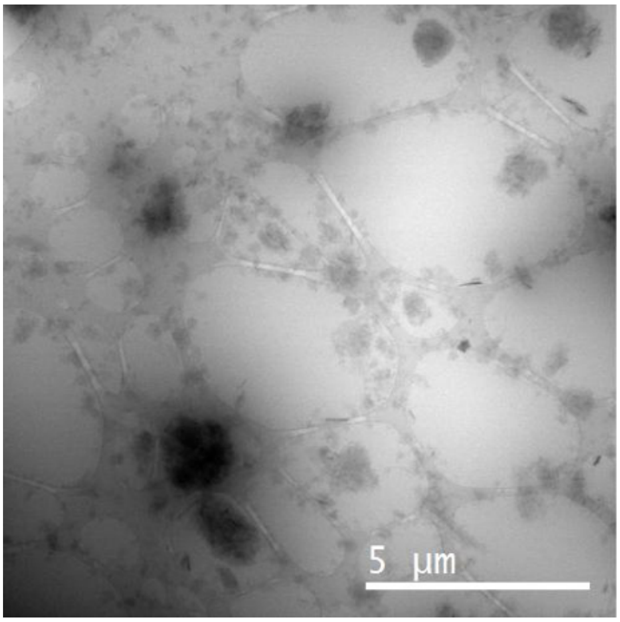


Figure 1. TEM image of FLG dispersed in resin

The D10 value is the particle diameter below which 10% of the measured particle sizes sit. Similarly, D50 and D90 are the particle diameters below which 50% and 90%, respectively, of the measured particle sizes exist. They provide a useful description for the particle size distribution. The accuracy of such optical techniques can be affected by the location of images taken, the quantity of images analysed and the threshold set for binarising of the images. To counteract this two locations are considered for each material and images at 3 different focal depths are used.

Dynamic Mechanical Analysis was carried out using a Perkin Elmer DMA8000. Samples were loaded in a single cantilever configuration with an unsupported length of 7mm. Load was applied under strain control at a frequency of 1Hz and using a displacement of 50µm. Data was collected during a temperature sweep from 25°C to 200°C at a rate of 5°C/minute. This set up is in accordance with ASTM D7028.

3. Results

3.1 Microscopy

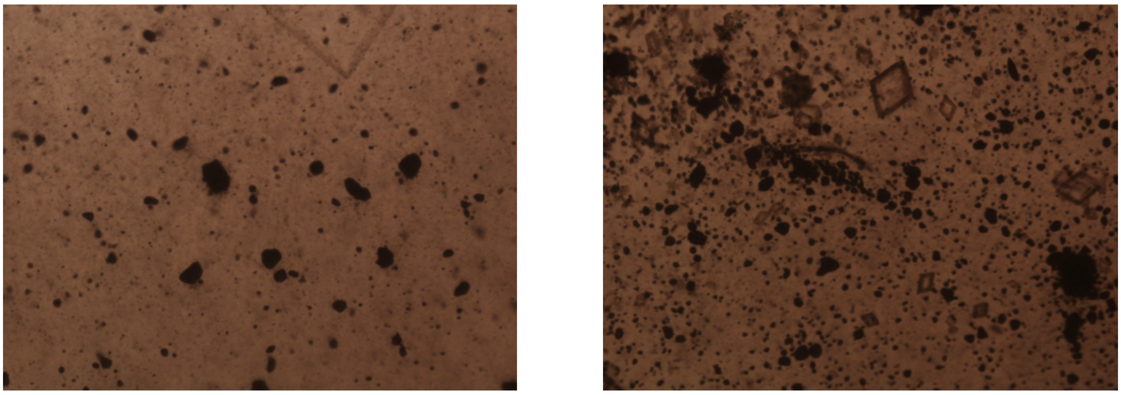
Fig. 2 presents microscopy images collected in the as mixed state and after one week of reagglomeration time for both 5 and 10 passes. The focal plane of the microscope in the presented images is aligned with the bottom surface of the resin film (i.e. at the interface with the glass slide). In the as mixed state there is qualitatively little observable difference between the unfunctionalised material after 10 passes and the functionalised materials after both 5 and 10 passes. Whereas, larger agglomerates are still observable in the unfunctionalised material after the first 5 passes. This indicates that the functionalised FLG are dispersing more easily and with less mixing compared with the unfunctionalised FLG. The dispersion state doesn’t appear to change from 5 to 10 passes for the functionalised material which suggests that a maximum dispersion state has been reached after 5 passes and additional passes are not creating any observable improvements. A similar level of dispersion can be achieved in the unfunctionalised material but a greater number (10) of 3RM passes are required. After 1 week of resting time some reaggolmeration and settling can be observed in all cases. Whilst there is a visual reagglomeration effect across all materials, it appears that this effect is delayed by both higher passes through the 3RM, as well as functionalisation, with the most noticeable reagglomeration seen for the unfunctionalised FLG after 5 passes.

In order to achieve a more quantitative analysis of the agglomeration size in each sample the d10, d50 and d90 values were derived from the particle size distributions measured from all acquired images at a range of depths through the resin film. Table 1 presents all D10, D50 and D90 parameters and Fig. 3 graphically represents the D90 parameters. The quantitative analysis of particle sizing shows a good agreement with the visually observed trends discussed above. For unfunctionalised materials there is a clear trend for decreasing agglomerate size with increasing mixing and then increasing over the duration of a week, confirming the qualitatively observed reagglomeration. Functionalised material gave similar d90 values after both 5 and 10 passes, demonstrating that the functionalisation aids rapid dispersion with low numbers of 3RM passes, but that subsequent mixing does not further enhance dispersion. Reagglomeration of the functionalised materials appears to be less than that of the unfunctionalised material. After 10 passes only a small increase in D90 value is seen, however in the case of 5 passes the D90 parameter reduces which is unlikely to be a physical effect and is expected to be an anomaly due to the limitations of this approach. It is however an indication that reagglomeration has not been significant in this case.

3.2 Dynamic Mechanical Analysis (DMA)

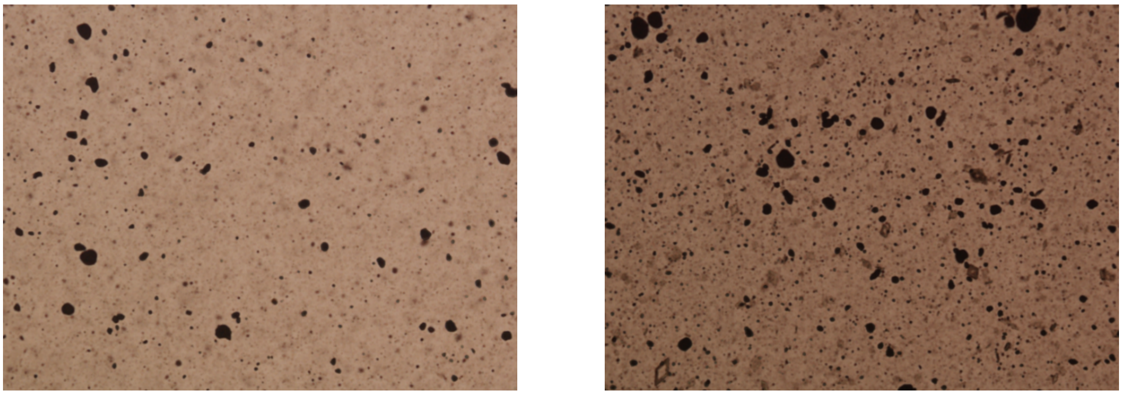
The DMA has been used to study the thermomechanical properties of the graphene-epoxy nanocomposites. Specifically it is used to determine the glass transition temperature, Tg, of the materials. Knowledge of a materials Tg is of great industrial importance as it determines the temperature range in which a material can be used with minimal degradation of properties. The glass transition occurs over a region of temperatures where the material transitions from hard and glassy to a soft, rubbery state, due to increased polymer chain mobility. As such the Tg can be defined in a number of ways. Here two standard measures of Tg are adopted: the onset of significant property loss in storage modulus and the peak of the tanδ curve. Table 2 presents the glass transition temperatures determined using both methods. This data shows that the addition of FLG leads to a small improvement in Tg for the as mixed materials and the functionalised materials offer the best improvements. It has generally been observed that well dispersed nanomaterials can constrain the motion of polymer chains hence increase the measured Tg [4].

There is a noticeable decrease in the measured Tg for materials tested after 1 week of reagglomeration time, correlating to the reagglomeration behavior observed in the particle size analysis above. The functionalised materials exhibit the smallest decrease in Tg, particularly in the case of the E’ onset value which defines the upper limit for mechanical performance. This indicates that the functionalised materials have a stabilizing effect on the dispersion and help to maintain the properties of the filled resin for a longer period of storage. The general degradation in Tg over time shows that it is very important to consider shelf life when using such materials.



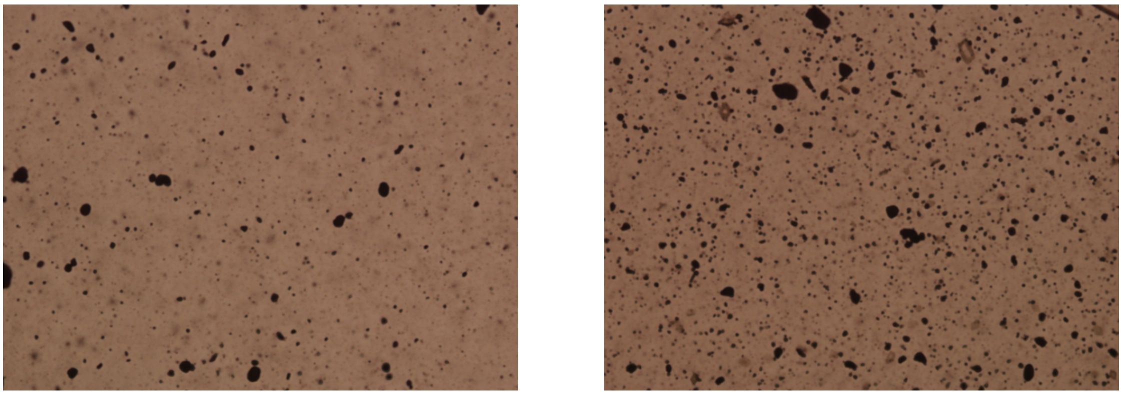
As mixed unfunctionalised 5 passes

After 1 week unfunctionalised 5 passes



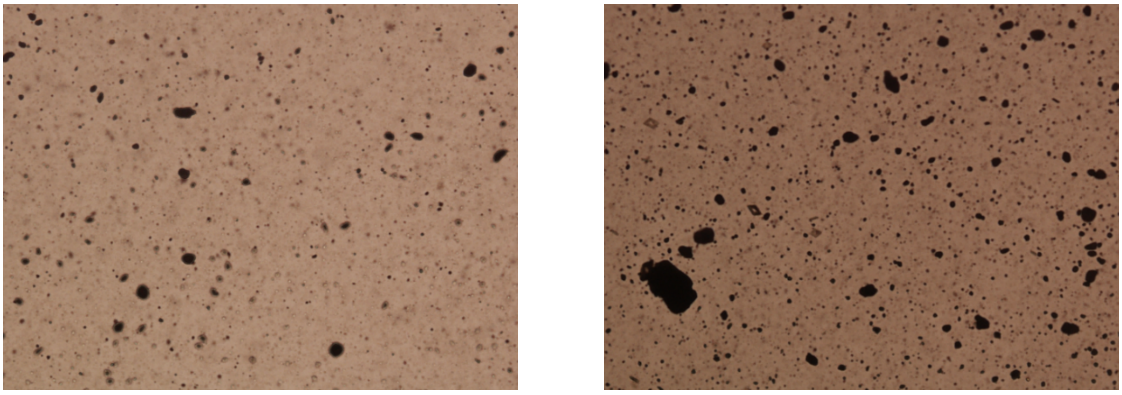
As mixed unfunctionalised 10 passes

After 1 week unfunctionalised 10 passes



As mixed functionalised 5 passes

After 1 week functionalised 5 passes



As mixed functionalised 5 passes

After 1 week functionalised 10 passes

Figure 2. Optical microscope images

Table 1. D10, D50 and D90 particle size distribution paramenters.

		Number of 3RM passes	d10	d50	d90
As mixed	Raw FLG	5	1.2	3.3	7.4
		10	0.99	2.42	4.9
	O2 - FLG	5	1.05	2.8	6.1
		10	1.26	3	6.38
After 1 week	Raw FLG	5	1.3	3.5	8
		10	1.13	2.8	6.1
	O2 - FLG	5	1	2.55	4.9
		10	1.27	3.21	6.76

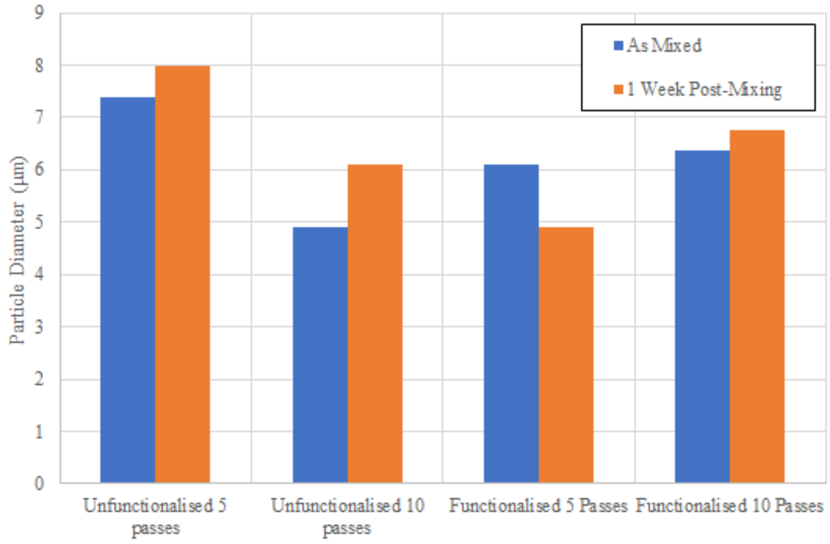


Figure 3. D90 particle distribution values for all materials

Table 2. Glass Transition temperatures determined from DMA tanδ and E' curves

Material	3RM Passes	Glass Transition Temperature, Tg (^{0} C)			
		Tan δ Peak		Storage Modulus Tangent	
		As Mixed	After 1 Week	As Mixed	After 1 Week
Araldite LY1564		161.95		144.85	
Raw FLG	5	163.59	158.94	144.09	135.82
	10	161.99	159.16	145.55	136.04
O2 -FLG	5	163.93	152.22	148.57	129.18
	10	164.46	162.16	148.32	145.63

The peak factor measured from a DMA tanδ curve has been proposed as a measure of homogeneity in an epoxy network, where a low peak factor suggests higher crosslinking density and therefore greater homogeneity. It has also been used as an indicator for the quality of dispersion in nanocomposites [11-

12]. The peak factor is calculated using Eq. 1. These values give an insight into the interactions between the graphene / epoxy interface and disruption to the epoxy crosslinked network.

$$Peak\ Factor = \frac{Width\ at\ \frac{1}{2}\ tan\delta\ peak\ height}{Maximum\ tan\delta\ peak\ height} \tag{1}$$

Fig. 4 presents the peak factors calculated for each of the materials studied. A clear increase in peak factor is seen for the filled polymers when compared with the unfilled epoxy. This increase in peak factor with the addition of graphene, indicates a disruption to the bonding/crosslinking of polymer chains. The unfunctionalised material, exhibits a decrease in peak factor with increasing 3RM passes in its as mixed state. This is likely a result of the improved dispersion inducing a more uniform disruption to the crosslinked network. The functionalised materials exhibit a similar level of peak factor to that of the unfunctionalised material after 10 3RM passes. This again indicates the ease of mixing of the functionalised materials and the limited improvement in dispersion with more than 5 passes. With the exception of the unfunctionalised material after 5 passes, all materials exhibit an increase in peak factor after one week. Again this effect is less in the functionalised materials which correlates with the microscopy and Tg studies. The increased values after one week again suggest that reagglomeration has occurred over time causing a rise in the heterogeneity of the epoxy network.

4. Conclusions

Raw and O_2 functionalised few layer graphene have been dispersed into epoxy resin using varying amounts of 3RM mixing. The effects of mixing and funcrtionalization on the dispersion state, rate of reagglomeration and the resulting thermomechanical properties has been assessed. The following conclusions were reached;

- The use of oxygen functionalisation gave higher levels of FLG dispersion with less mixing, as well as a reduction in reagglomeration rate when compared with unfunctionalised FLG
- Reagglomeration occurs over a relatively short period of time and has a measurable effect on resultant Tg, highlighting the need to investigate methods for improved dispersion stability and for the prediction of the effects of storage time.
- Better dispersion of FLG creates higher homogeneity within the polymer network, which decreases over time. Plasma functionalisation of FLG appears enhance the dispersion and delay the observed reagglomeration effect.

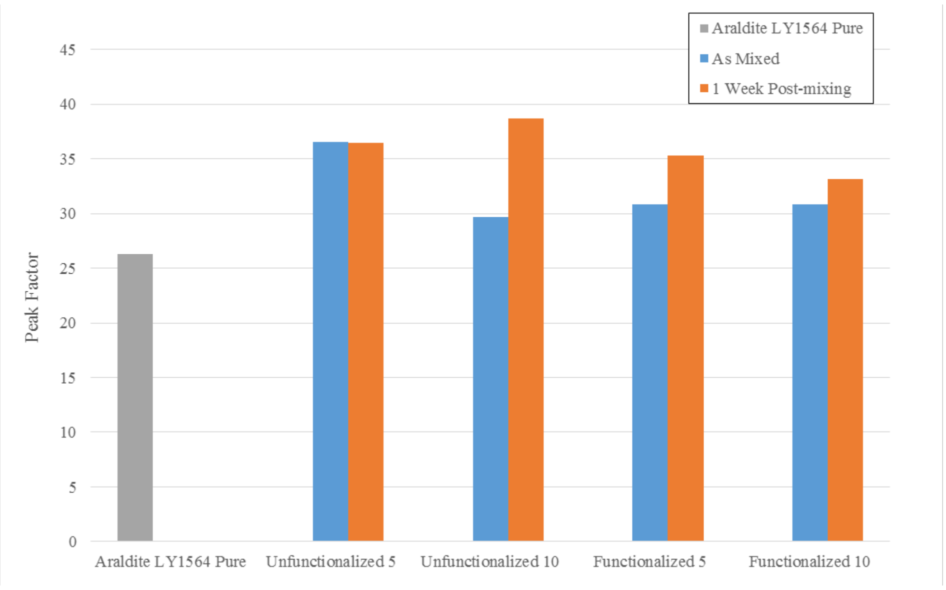


Figure 4. Peak factor values for all materials

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