Measurement of dispersion and homogeneity of functionalized graphene/CNT hybrid epoxy composite

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Abstract

Fabrication of amine-functionalized multi-graphene layers and multi-walled carbon nanotube nanofillers (0.25, 0.50, 1 and 2 wt%) reinforced with epoxy resin has been successfully performed to obtain hybrid epoxy composite. Effect of filler ratio on dispersion and homogeneity of hybrid composite mixture is investigated. Particle size distribution (PSD) pattern and tensile properties of hybrid composite are correlated with the degree of dispersion. The PSD is performed by dynamic light scattering technique and image analysis method. Analyses of scanning electron microscopy images are performed using ImageJ software. The pattern of PSD for composites is found to be similar by both the methods. Hybrid composite reinforced with filler content 0.5 wt% shows best homogeneous mixture. The value of PDI is observed to be lowest by both PSD analysis methods which make agreement of results. Determination of tensile properties shows that maximum tensile stress of 49.91 MPa and elastic modulus of 2302 MPa are obtained for 0.5 wt% composite. Analysis of PSD of composite mixture provides a direction for selecting appropriate filler content and fabrication process.

Keywords Particle size distribution (PSD) · Hybrid composite · Image analysis (IA) · Tensile strength · Elastic modulus

1 Introduction

Nanofillers such as graphene and carbon nanotube (CNT) are widely used as reinforcement agent with epoxy polymer matrix due to its favorable mechanical and thermal properties [1]. Synergetic effect of both graphene and CNT forms 3-D interconnected network thus improving microstructure and mechanical properties of hybrid composite [2]. Efficient load transfer between graphene and CNT fillers depends upon the extent of homogeneity of mixture [3]. Surface treatment of fillers by functionalization can increase its dispersion in the pool of epoxy matrix [4]. The significance of homogeneity is further verified from the fact that clustering of particle affects the various mechanical properties of composite [5]. Degree of dispersion or homogeneity of mixture can be investigated by distribution of particles in the matrix which can be further verified by microstructural (SEM image) analysis [6]. Qualitative

analysis of homogeneity is performed, but the quantitative calculation is still to be explored in detail [7].

Various aspects of particle size such as morphological (SEM) [8], size (DLS) [9] can be analyzed through advanced testing methods. Particle analysis, PSA and PSD analysis help in finding out measurement of average of mean size of particle in the specimen [10]. Particle sizes determine and affect the properties [11] and dispersion [12] of hybrid composite material. Increment in tensile properties is observed on addition of AMLG and AMWCNT in epoxy resin [13]. A novel method is proposed for computing the dispersion index and extent of agglomeration by image analysis [6]. The extent to which hybrid composite mixture is homogeneous in liquid form and degree of dispersion are analyzed by DLS. Nanoparticle dispersions are often polydisperse; there may be particles with a distribution of sizes and shapes rather than particles of a single size and shape. Dispersion is measure of heterogeneity of

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sizes of particles in a mixture [8]. PDI is calculated from a cumulants analysis of the DLS measured intensity. A low value of PDI indicates good thermostability of composite [14]. The anisometric variation in mechanical properties is observed, which depends on small particle size, polymer–filler and filler–filler interactions [15].

In the current research work, the combined effect of AMLG and AMWCNT on PSD and tensile properties of aforementioned hybrid composites has been investigated. Another objective of this study has been made in the form of comparisons of SEM images of tested samples through DLS method using imageJ software. Thus, determination of PSD and its correlation with dispersion of filler matrix configuration with respect to nanofillers weight percentage is investigated and analyzed in the present research work. Hence, current research will help in finding out suitability of fabrication process after computation of dispersion and homogeneity of mixture.

2 Experimental

2.1 Materials and sample preparation

Amine-functionalized multi-graphene layer (AMLG) and amine-functionalized multi-walled carbon nanotube (AMWCNT) is reinforced in epoxy resin (diglycidyl ether bisphenol A (DGEBA)). Equal weight percentage (1:1 ratio) of AMLG and AMWCNT filler material is used, and the amount of filler reinforced in epoxy resin is 0.25, 0.50, 1.0 and 2% weight percentage as per Table 1. The weighted amount of epoxy resin is mixed with ethanol and sonicated in water/ice bath at room temperature for reducing viscosity followed by mechanically stirring of mixture for 10 to 15 min. After this pre-weighted quantity of filler is added with the mixture. During this process, reactive volatile vapor bubbles are created which are removed by high vacuum degassing for 30 min. Finally, the mixture is poured in molds and cured in oven for 24 h. The samples are further post-cured at 100 °C for 4 h.

Table 1 Sample code corresponding to different composition of AMLG/AMWCNT epoxy hybrid composites

Sample code	Filler (wt%) (AMLG + AMWCNT)
A	0
B	0.25
C	0.50
D	1
E	2

2.2 Characterization

The PSD in fabricated sample is identified by using DLS Zeta potential analyzer. Microstructure of fractured surface of tensile tested sample is analyzed through HR-SEM (high-resolution scanning electron microscopy) images (Zeiss-ULTRA plus SEM instrument) using *ImageJ* software. Tensile test has been performed in an automated, Instron-H25KS machine of 25 kN load capacity as per ASTM D 638 standard to calculate the elastic properties of hybrid composites. Dimensions of samples are being kept as 57 × 14 × 5 mm in length, width and thickness, respectively. During tensile test, displacement rate of 5 mm/min with an operating room temperature of 30 °C is maintained.

2.3 Image analysis

The SEM micrographs depicting the microstructure of composite were used for qualitative and quantitative analysis of homogeneity and dispersion of mixture. For this investigation, PSD is performed by using *ImageJ* software, which operates on Java platform and is developed by National Institutes of Health (NIH) under Department of Health & Human Services, USA [16]. In order to collect best results from PSD, three numbers of specimens of each sample code are analyzed. The image processing steps carried out in *ImageJ* software are briefly described in this section.

Estimation of PDI by Image analysis [17]:

$$PDI = \frac{\chi(16, i)}{\chi(84, i)} \quad (1)$$

$\chi(n, i)$: where n is percentage at which particles are considered in total sample and i is particular parameter of particle considered. Value of i can be 0, 1, 2 and 3 corresponding to number, length, area and volume, respectively, of particle. $\chi(n, i)$ is number of particles for definite n and i selected, for example, $\chi(50, i)$ is median particle size.

3 Results and discussion

3.1 Measurement of homogeneity by DLS

The affinities of AMLG/AMWCNT filler particles with epoxy resin depend on its distribution and dispersion in the mixture which are investigated through characterization by DLS test method. PSD pattern of different hybrid composite samples are shown in Fig. 1. Cumulated volume distribution of particle is shown in the DLS plot. The results

Fig. 1 Analysis of PSD of hybrid epoxy composite based on their volume

Table 2 Cumulated results obtained using DLS

Sample	χ (16, 3) nm	χ (50, 3) nm	χ (84, 3) nm	PDI
A	0.18	0.23	23.85	0.523
B	1.17	24.12	38.16	0.878
C	0.14	6.81	13.83	0.714
D	1.18	28.83	44.96	0.918
E	0.21	29.99	49.45	0.955

χ (16, 3), χ (50, 3) and χ (84, 3) nm represent the size of particles comprising 16, 50 and 84% of the total volume of the composite sample respectively

Sample Sample code of composite; PDI Poly Dispersity Index

are further quantified in Table 2. Mainly DLS considered three types of volume contribution of particles such as 16, 50 and 84% denoted by χ (16, 3), χ (50, 3) and χ (84, 3) nm, respectively, χ (x, 3) nm, i.e., how many percent of the complete sample volume is filled with particles smaller than x nm which may be further defined as two extreme volumes on either side, partitioned by mean value, i.e., 50%. Presence of small particles shows the least cluster formation in sample C which indicates that it has performed optimally and henceforth maximum expectations of producing best results when they undergo series of tensile tests. Microstructure of sample C had been best dispersion of filler particles within epoxy resin pool. However, with presence of large PSD in sample E, it signifies a maximum agglomeration of the particles in epoxy pool and consequently degrades the overall properties of hybrid composites with least homogeneity in the mixture.

It has been clearly observed from Table 2 that minimum and maximum cumulate diameter of particles comes out for 0.50 and 1 wt% samples, respectively. This may be

attributed to the best exfoliation of graphene and tubular formation of MWCNT which improves filler dispersion in the composite. Furthermore, degree of homogeneity of all constituents in epoxy pool can be evaluated by PDI investigated during the analysis of different hybrid composite samples. From Table 2, this has been depicted that sample C has lowest value 0.714 of PI which indicates the best dispersion of nanofillers in an epoxy environment as expected from its PSD. This may be due to the least cluster formation particularly for this hybrid composite sample code. However, exact proportion of both nanofillers is still a challenge for the researchers of this community.

3.2 Measurement of homogeneity by image analysis

An image analysis was presented for the quantification of the degree of distribution or homogeneity in composite materials and to verify the results obtained from DLS test. The analysis is restricted to particles constituting 90% of total volume of composite which covers major constituents of sample; beyond this noise in the data is experienced. The size and distribution of particles for each variant of hybrid sample are observed by image analysis of SEM micrographs. Typical SEM image depicting the microstructure of fractured surfaces of hybrid composite samples code with filler contents of 0.25, 0.5 and 1 wt% is shown in Fig. 2 (a-1, b-1, c-1, d-1 and e-1). The best exfoliation of graphene and optimal length-to-diameter ratio of MWCNT have been observed in sample C. This may be attributed to the best dispersion and homogeneity of these two functionalized nanofillers in the vicinity of epoxy matrix. In order to justify the aforementioned conditions of both nanofillers, SEM images are analyzed in detail through image analysis (IA) software.

SEM images are further processed for obtaining PSD within the composite, and the obtained results are grouped in Figs. 3 and 4. For performing image analysis of SEM micrographs, the image is imported in the *ImageJ* software and processed with appropriate settings. Sample code B and C shows comparatively uniform microstructure. In contrast, microstructure of sample D shows evidence of disruption of network structure with partial distribution of particles. However, as filler wt% is increased, these filler particles are found to cluster at the grain boundaries, thereby decreasing the homogeneity of their distribution in the mixture of composite as shown by sample E.

Fractography of hybrid composite as shown in Fig. 2 exhibits rough surfaces which signify that crack initiation is resisted to propagate; this may be due to the deep rooted nanofillers in epoxy matrix and also the enhanced resistance offered by epoxy to the nanofillers when being pulled out from the surface. This may also be justified through the

Fig. 2 Image analysis of AMLG/AMWCNT hybrid epoxy composite nanofiller wt% **a** 0 **b** 0.25 **c** 0.50 **d** 1 **e** 2

Fig. 3 Image analysis showing PSD of AMLG/AMWCNT hybrid epoxy composite on volume basis

minimal point and edge dislocation for sample D, when it experiences a series of tensile tests. However, beyond 1 wt% of both the filler contents, cluster formation in the form of irregular patterns has been observed which deficit the efficacy of hybrid composite; this may also be justified through the cavity formation as seen in Fig. 2 (e-1) because of inadequate dispersion, resulting in poor load transfer capability of nanofillers to the epoxy matrix.

Results obtained in the form of processed figures after image analysis is shown in Figs. 3 and 4. For increasing accuracy of image in terms of particle size and pattern detection, color threshold is induced, which erases all unnecessary colors. Binary method can also be used for increasing the processability of images. However, for present set of images, binary and threshold method exhibits nearly same results for PSD analysis due to good contrast of SEM images, though improvement of image through threshold method is used for image analysis.

Fig. 4 PSD of AMLG/AMWCNT hybrid epoxy composite on volume and frequency basis

Afterward, an automatic detection of the particles is run which yields results in terms of layout indicated in Fig. 2 (a-2, b-2, c-2, d-2 and e-2). Output from Image J delivers image indicating particle size showing the cumulated particle size distribution which is calculated and shown in Table 3. It is observed that primary particles and aggregates, which are in contact with other particles, constitute agglomerates. Continuous black dark portion present in Fig. 2 (a-2, b-2, c-2, d-2 and e-2) shows agglomeration occurred among the epoxy and

Table 3 Cumulative result of image analysis

Sample	χ (16, 3) nm	χ (50, 3) nm	χ (84, 3) nm	PDI
A	0.090	0.42	1.000	0.0900
B	0.120	0.50	1.100	0.0954
C	0.062	0.29	0.650	0.1091
D	0.140	0.39	1.220	0.1148
E	0.150	0.42	1.300	0.1154

nanofillers. Traces of AMLG and AMWCNT are seen in the SEM images as expected.

Graphical representation of results obtained after image analysis is shown in Figs. 3 and 4. Cumulated volume of particles indicating particle diameter in the complete volume of hybrid composite is shown Fig. 4. It is observed that there is little variation in PSD among hybrid epoxy composites of different configurations in comparison with DLS analysis. However, the diameter of particles is smallest for sample C. The pattern of PSD observed from DLS test resembles the result of image analysis. Histogram of PSD of each sample of hybrid composite is shown in Fig. 4.

The image analysis results are further presented in Table 3 indicating the characteristic values such as maximum/minimum diameter and PDI. The values of these parameters depend upon different factors such as portion of image selected, quality of image and processing method followed. Minimum value of PDI is observed for sample B (0.0954) followed by sample C (0.1091). Similarly, maximum PDI is present in sample E which is 0.1154. The volume-based distribution shown in Fig. 4 delivers particle distribution over complete volume of composite. Pattern of PSD obtained from image analysis resembles with DLS outcomes which confirm suitability of both methods.

The qualitative observation regarding the change in homogeneity from visual observation of SEM micrographs is found to be consistent with results obtained from image analysis results as shown in Fig. 2. It is seen from these plots that homogeneity of composite mixture decreases with increasing filler wt% and best homogeneous mixture is obtained for sample code D. However, for sample code E, the movement of cluster formation of filler particles is due to an increase in viscous drag in the liquid sample indicating decrease in dispersion of particle in the pool of epoxy resin matrix. Therefore, better degree homogeneity and dispersion are obtained for low filler content up to 1 wt%; beyond this limit mixture uniformity is worsened as shown by 2 wt% filler in the composite sample. Probably further increase in dispersion requires better sonication process. This indicates that further investigation is required on improving the extent of mixing and amount of homogenization of particle distribution in the mixture.

3.3 Tensile properties of hybrid composites

The tensile properties observed from the investigated hybrid samples have been plotted against the filler wt. shown in Table 4 in order to examine the correlation of mechanical properties with the homogeneity of mixture and particle distribution. As expected the results indicate a relationship of particle distributions with mechanical properties of hybrid epoxy composite. The maximum resistance to failure can be depicted through the curve for samples C

Table 4 Tensile test and PSA result of hybrid composite

Sample	Elastic modulus, MPa	Tensile strength, MPa	PDI	
			DLS	IA
A	2036	32	0.523	0.0900
B	2428	40.91	0.878	0.0954
C	2302.2	49.91	0.714	0.1091
D	2039	46.08	0.918	0.1148
E	1597	28.07	0.955	0.1154

and D; however, the overall strength of hybrid composites gets impaired when the nanofillers wt% increases up to 2.0. This may be attributed to difficulties faced in obtaining homogeneous dispersion at 2 wt% nanofiller contents, which has also been observed in SEM images as previously shown in Fig. 2. As shown in Table 4, a little differed trend is observed in tensile modulus properties of functionalized nanofiller-based hybrid composites, when compared with tensile strengths. An increment of 19.25 and 13.10% in tensile modulus is noticed for samples B and C, respectively, when compared with neat epoxy sample A.

Table 4 also reveals the effect of filler ratio on tensile properties and PDI of hybrid composite. Tensile strength is maximum (i.e., 49.91 MPa) when filler content is 0.5 wt%, and PDI is minimum; the pattern of filler size is validated by DLS and IA methods. However, numerical value of PDI at 0.5 wt% filler content by DLS is 0.714 and by IA method is 0.1091. Moreover, it is observed that as the filler content is increased beyond 0.5 wt%, particle size becomes coarser and dispersion is also degraded. Thus, maximum tensile properties can be obtained when dispersion and homogeneity of graphene/MWCNT are uniform. The variation in value is due to method of analyzing PSD. PDI of nanofillers reinforced in the hybrid composites is varied from 0.523 to 0.955 as observed from DLS test, while image analysis of SEM produced in the range of 0.0900 to 0.1154, though the pattern of PSD for different filler ratio is observed to be same by DLS and image analysis (IA) method. Reason attributed for this behavior is that the number of particles evaluated according to SEM image is several decades lower in comparison with those considered with help of the measuring techniques DLS [17]. Though, analyses performed with the help of imaging processes indicate only mirror of certain sections. A variation in statistical result is observed. Also the results also vary if the sphericity of the aggregates differs. Therefore, it is observed that though the pattern of PSD by both the methods is validated, variation in numerical value is observed. The range of maximum and minimum diameter is justified w.r.t. DLS method. But the pattern or trend of PSD is observed to be the same from DLS and IA. Reason for this lies in the basic principle of methodology and operation of both the methods. In

DLS, PSA is performed in 3-D environment, whereas in IA specific 2-D image at particular section of surface is analyzed. The present approach will be helpful in further optimizing the selection of filler particle size for obtaining best mechanical properties of hybrid composite.

4 Conclusions

The synergetic effect of variation of wt% on the homogeneity of distribution of AMLG and AMWCNT particles in the AMLG/AMWCNT epoxy hybrid composite has been examined and correlated with the mechanism of tensile fracture. DLS and image analysis has been performed for quantitative evaluation of the homogeneity of AMLG/AMWCNT particle distribution. Using the qualitative and quantitative assessment of homogeneity of dispersion, the distribution of particle is found to be more significant when AMLG/AMWCNT is 0.5 wt%. However, beyond 0.5 wt% homogeneity and dispersion of AMLG/AMWCNT particle decrease as these particles tend to recluster along the grain boundaries. Similarly, the approach may be applied for other systems with the objective of quantifying the homogeneity of distribution of the reinforcement phase. In general, the proposed method can be efficiently applied to different types of binary composite microstructures for characterizing the degree of distribution. The presentation of this index will help in the correlation of microstructures and properties and, thus, assist in presenting a direction for controlling processing parameters for improved homogeneity and the associated physical properties of the composites. The tensile properties are found to increase with increase in dispersion of AMLG/AMWCNT particle and the formation of uniform homogeneous mixture of hybrid composite sample. This information can be applied in selection of wt% of nanofillers for initial fabrication process of hybrid composites. Continued studies are needed for improving its accuracy and practical use, and also transferring it for faster quantitative image analysis on more complex composite microstructures.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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