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Enhanced Dispersion and Tensile Properties of Graphene/CNT Epoxy Composites by Varying the Filler Ratio

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Abstract: ***In this study a three phase hybrid composite is fabricated comprising of graphene and carbon nanotube (CNT) nano-fillers reinforced in epoxy resin. The filler contents were maintained 0 and 1 wt. % and the ratio of graphene and CNT fillers were 1:1, 1:3 and 3:1. Effect of filler ratio on dispersion and tensile properties of hybrid composite mixture are investigated. Observations of the samples by Dynamic Light Scattering (DLS), Scanning Electron Microscopy (SEM), and Image Analysis (IA) confirmed formation 3-D hybrid nanostructure. The best dispersion is observed for graphene: CNT content 1:3 indicating good bonding between both the fillers and epoxy matrix. The maximum tensile strength of 50.28 MPa and elastic modulus of 2848 MPa is observed for filler ratio 1:3 (graphene: CNT) which is 57 and 40 % increase as compared with pristine epoxy composite. For this configuration homogeneous mixture with Poly Dispersity Index (PDI) of 0.513 is investigated for the sample. The value of PDI is observed to be lowest by both Particle Size Distribution (PSD) analysis methods which make agreement of results. Analysis of PSD of composite mixture provides a direction for selecting appropriate filler content and fabrication process.***

Keywords: ***Particle size distribution (PSD), hybrid nano-composite, Image analysis (IA), tensile strength, elastic modulus.***

I. INTRODUCTION

Epoxy resins are a promising polymer matrix to be used for structural applications due to its high strength to weight ratio [1] when it is reinforced with carbon nano-fillers. Excellent properties of carbon based nano-fillers such as graphene and carbon nanotube (CNT) makes it eligible to reinforce in epoxy polymer matrix in order to improve the applicability of epoxy based composite sample [2]. Reinforcement of both the fillers (graphene and CNT) simultaneously helps in producing positive synergetic effect of 3-D interconnected network thus improving microstructure and mechanical properties of hybrid composite [3]. The hybridization of graphene/ CNT has led to obtain efficient load transfer between fillers and matrix. Surface treatment of carbon nano-materials by functionalization can increase its dispersion in the pool of epoxy matrix [4][5]. Using graphene or CNT alone as a filler material tends to agglomerate faster and load transfer between filler and matrix becomes difficult.

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However if both the fillers are used at the same time can yield a strong interconnected structure at a low filler content. But the extent of dispersion of graphene/ CNT in the polymer matrix plays an important role in deciding final mechanical properties [2][6]. Furthermore varying the ratio of graphene and CNT affects the performance of hybrid composite [7]. Analyzing the Particle size distribution (PSD) helps in investigating the degree of homogeneity of composite mixture. Further the PSD can be correlated with the mechanical properties of composite. Dynamic light scattering (DLS) method is important method for analyzing PSD analysis for measurement of nano-size particle [8][9]. Though qualitative observation of homogeneity of composite mixture can be performed by analysis of SEM micrographs but the quantification of degree of homogeneity is less explored [10]. Numerical value of degree of dispersion and homogeneity of mixture is indicated by Poly Dispersity Index (PDI) [11]. SEM micrographs are analyzed by image analysis (IA) using Image J software [12]. Results obtained by DLS test can be compared with image analysis findings [13].

In the present research paper hybrid composite sample is fabricated constituting graphene and CNT fillers with 0 and 1 % weight percentage is loaded in epoxy resin matrix. The ratio of graphene and CNT is maintained 1:1, 1:3 and 3:1. The distribution of particles within composite is investigated. Extent of homogeneity of composite mixture is investigated by analysis of microstructure of fractured surface obtained through SEM image. PSD pattern analysis is performed by DLS test which is further compared by image analysis method. The combined effect of graphene and CNT 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 image J software. Thus determination of PSD and its correlation with homogeneity of mixture with respect to nano-fillers ratio and weight percentage is performed. Hence, current research will help in finding out suitability of fabrication process after computation of dispersion and homogeneity of mixture.

II. EXPERIMENTAL

A. Materials and Sample preparation

Functionalized graphene/ CNT and epoxy resin (diglycidyl ether bisphenol A (DGEBA)) were used for fabrication of composite.

The functionalized graphene/ CNT were mixed with epoxy resin in specified proportion as shown in Table 1. Epoxy resin was mixed with ethanol and sonicated in water/ ice bath at room temperature for 10 to 15 minutes followed by mixing pre-weighted quantity of filler.

The mixture is again sonicated and pouring in moulds to obtain the hybrid composite samples.

Table 1: Sample code corresponding to different composition of graphene/ CNT epoxy hybrid composites

Sample code	Epoxy resin (wt %)	Filler (wt %)	Filler composition	
			Graphene	CNT
A	100	0	0	0
D	99	1	0.5	0.5
F	99	1	0.25	0.75
G	99	1	0.75	0.25

B. Characterization

Dynamic Light Scattering (DLS) is used to analyze the particle size distribution (PSD) of fabricated composite sample. The scattered light was collected by probe to determine particle size. Pattern of distribution of particle and determination of hydrodynamic diameter of particle are performed [14]. Tensile test was used to evaluate the tensile properties of composites. Molded samples of 57× 14 × 5 mm dimension are subjected to tensile test at a displacement rate of 5 mm/min in room temperature. SEM (Scanning Electron Microscopy) was used to evaluate the morphology of fractured surface of the composite. The SEM micrographs depicting the microstructure of composite were used for qualitative analysis of homogeneity and dispersion of mixture. these SEM micrographs are further processed by using Image J software to investigate the quantitative analysis of homogeneity and dispersion of mixture [15].

Estimation of PDI by Image analysis [13]:

Equation 1, $$\boldsymbol{PDI} = \frac{\chi\,(16,i)}{\chi\,(84,i)}$$ (i: 0, 1, 2, and 3)

$$(\text{i}: \textbf{number} - \textbf{0}, \textbf{length} - \textbf{1}, \textbf{area} - \textbf{2}, \textbf{volume} - \textbf{3})$$

χ (n, i): where n is percentage at which particles are considered in total sample and i is particular parameter of particle considered.

III. Results and Discussion

A. Measurement of homogeneity by DLS

Cumulated volume distribution of particle of different hybrid composite samples measured by conducting DLS analysis is shown in the Figure 1. The PSD pattern indicates the minimum particle size arrangement for sample F, when the ratio of graphene is maintained lower as compared to ratio of CNT. However as the ratio of graphene is increased the particle size gradually increases as depicted by sample G in PSD pattern.

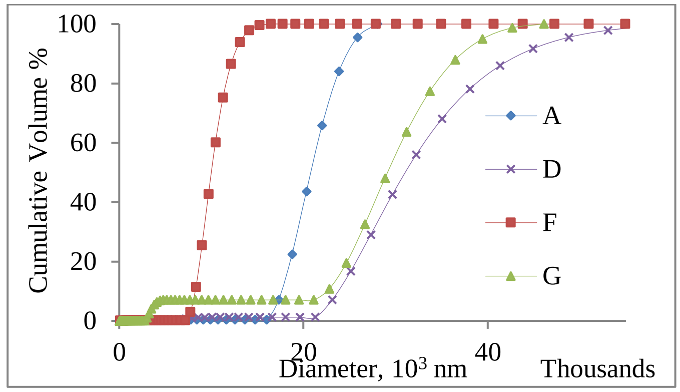

Figure 1: Analysis of PSD of hybrid epoxy nanocomposites based on their volume

Further analysis of PSD results are performed to investigate the extent of homogeneity of mixture which is indicated by the value of PDI. Among all samples, it is reflected from Table 2 that sample F has lowest value 0.513 of PI which indicates the best dispersion of nano-fillers. For sample with low graphene content homogeneity of mixture is better which is a prominent sample expected to yield best mechanical test results. Reason for this may be attributed to the well dispersion of graphene/ CNT in epoxy matrix. However highest value of PDI (0.918) in sample G indicates maximum agglomeration of the particles in epoxy matrix. Due to increased content of graphene in sample G, multiple layers of graphene tend to agglomerate, restricting formation of homogeneously dispersed composite mixture. This may also be attributed due to the maximum size of PSD indicated by Table 2.

Table 2: Cumulated results obtained using DLS

Sample	χ (16,3) µm	χ (50,3) µm	χ (84,3) µm	PDI
A	0.18	0.23	23.85	0.523
D	1.18	28.83	44.96	0.918
F	0.59	**10.26**	13.32	**0.513**
G	14.19	43.05	37.77	0.677

B. Measurement of homogeneity by image analysis

SEM micrographs of samples were processed for performing the image analysis in order to verify the DLS results. SEM images are further processed for obtaining PSD within the composite as shown in the Figure 2. SEM micrograph shown by Figure 2: a-1, b-1, c-1 and d-1 corresponding to sample code A, D, F and G respectively indicates the qualitative aspects of homogeneity of composite mixture. Pristine epoxy composite shown in Figure 2 (a-1) reflects smooth micrograph with no resistance to fracture. With incorporation of graphene/ CNT in epoxy resin, resistance to fracture is observed as shown for sample code D, F and G i.e Figure 2 (b-1, c-1 and d-1) with imprints of graphene/ CNT fillers. This may be due to the deep rooted fillers in epoxy matrix and also the enhanced resistance offered by epoxy to the fillers when being pulled-out from the surface.

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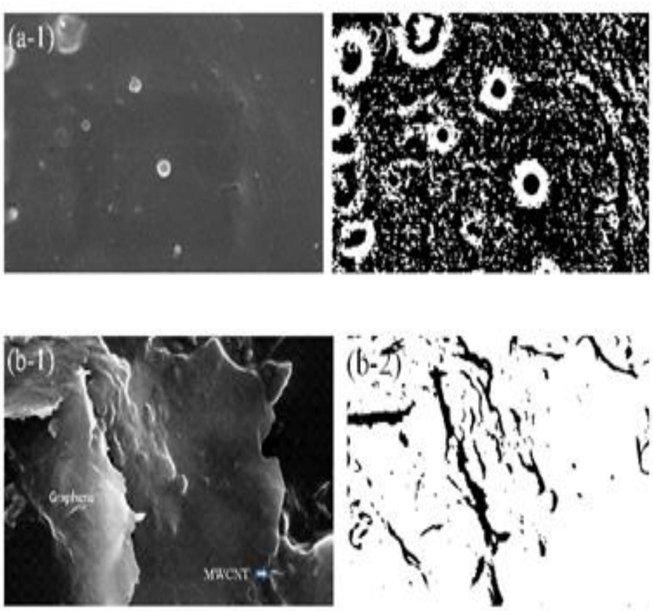
However for graphene/ CNT ratio 1:1, these particle are found to cluster faster at the grain boundaries thereby decreasing the homogeneity of their distribution in the mixture of composite results in poor load transfer capability of nano-fillers to the epoxy matrix. However the best composite micrograph is observed for sample code F. In order to obtain the PSD, SEM images are further analyzed in detail through IA software, which has been shown in Figure 2 (a-2, b-2, c-2 and d-2). IA is performed for obtaining PSD and measurement of homogeneity of composite mixture. Continuous black dark portion present in processed image shows agglomeration of particles occurred amongst the epoxy and nano-fillers. The qualitative observation regarding the change in homogeneity from visual observation of SEM micrographs are found to be consistent with results obtained from image analysis results.

PSD curve generated after IA is shown in Figure 3 verifies the similarity of pattern plotted in DLS test which confirm suitability of both methods. The curve shows uniform microstructure for sample code F and G as compared to sample D. In contrast microstructure of sample D shows evidence of disruption of network structure with partial distribution of particles.

Results of IA are summarized in Table 3. Minimum value of PDI is observed for sample F (0.1273) and maximum for sample G (0.200). Since a high value of PDI index indicates a poor distribution and high level of agglomeration whereas a low value of PDI index indicates vice-versa effect. It is observed that homogeneity of composite mixture decreases with increasing graphene content in the mixture and best homogeneous mixture is obtained for sample code F. Probably for further increase in dispersion for sample G and D requires better sonication process which indicates that further investigation is required on improving the mixing of composite mixture. It was presented that the proposed method is a useful tool for quantifying the degree of distribution with high accuracy by considering the PDI index as measures of the distribution of particles in the composite mixture.



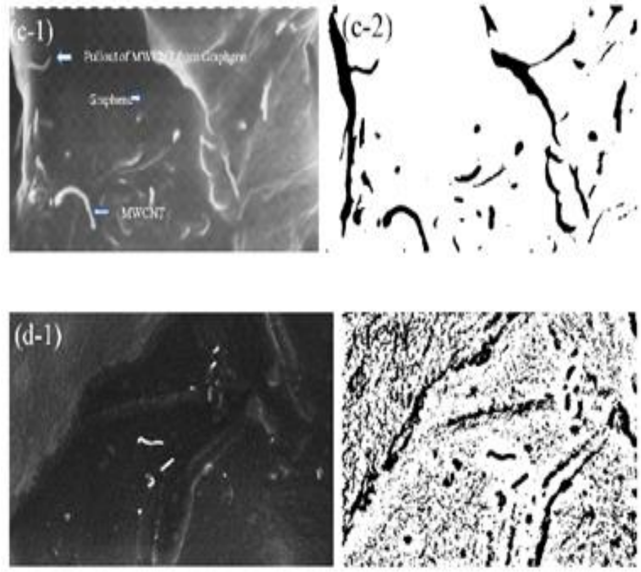


Figure 2: Image analysis of hybrid epoxy composite with sample code (a) A (b) D (c) F (d) G

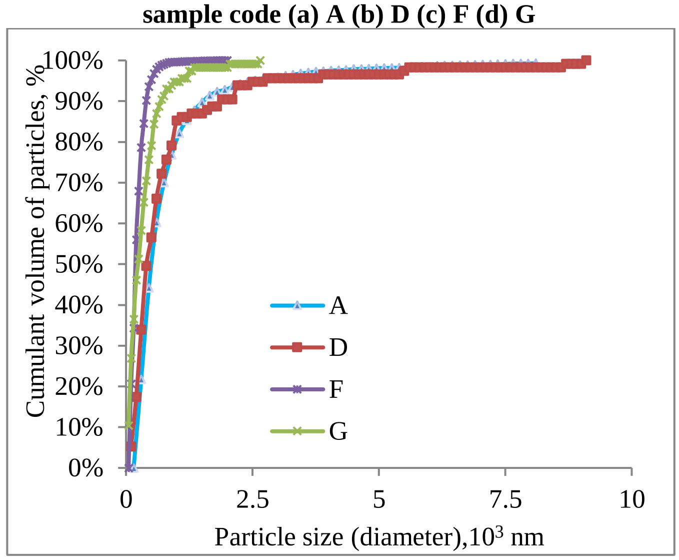


Figure 3: Image analysis showing PSD of graphene/CNT hybrid epoxy composite

Table 3: Cumulative result of image analysis

Sample	χ (16,3) nm	χ (50,3) nm	χ (84,3) nm	PDI
A	12	85.1	240	0.1176
D	5	84	190	0.1900
F	7	**22.5**	70	**0.1273**
G	7	33.9	40	0.2000

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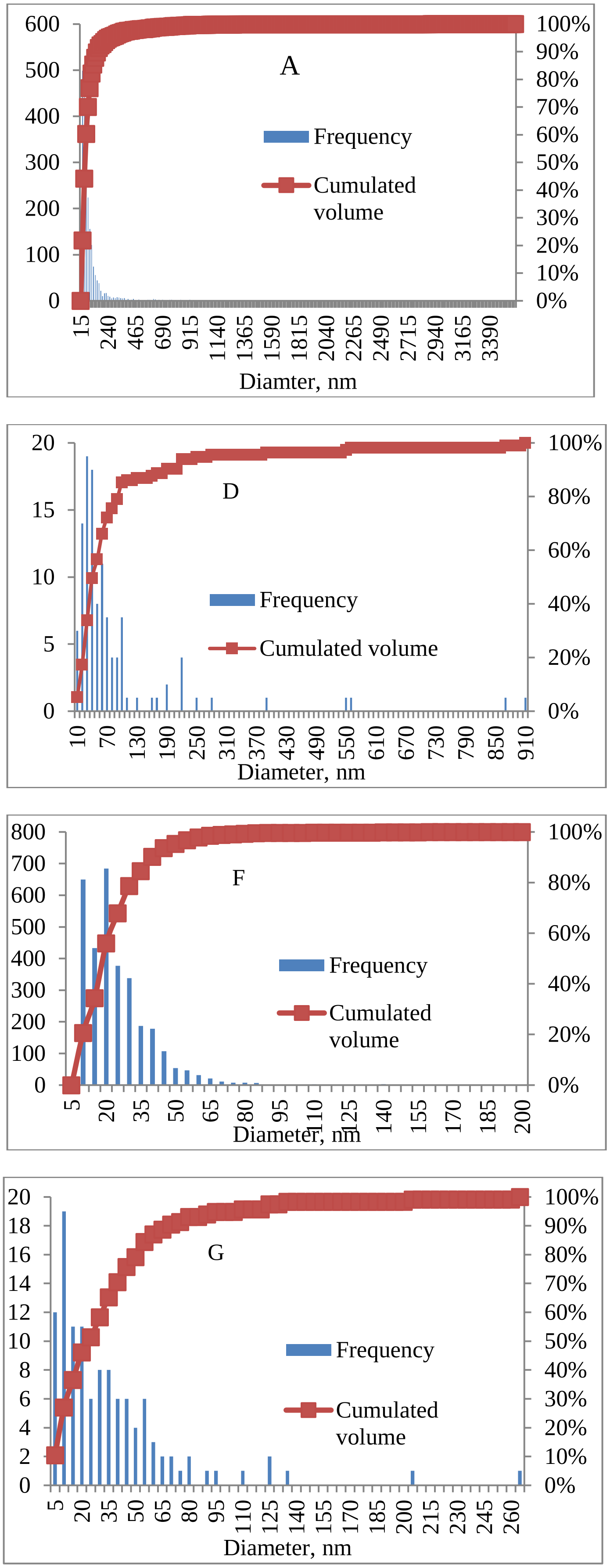

Figure 4: PSD of graphene/CNT hybrid epoxy nanocomposite

PSD with frequency distribution arrangement in terms of histogram is shown in Figure 4. Pattern of PSD obtained from image analysis resembles with DLS outcomes which confirm suitability of both methods.

C. Tensile properties of hybrid composites

Results of tensile test performed on composite samples are shown in Table 4 in order to examine the correlation of mechanical properties with the filler ratio. Noticeable increase in tensile stress and elastic modulus is observed for sample F. This is due to strong interconnected structure of graphene and CNT with epoxy resin. Increase in tensile strength and tensile modulus is noticed when ratio of graphene is less as compared to CNT content. Further for sample D with equal ratio of graphene and CNT fillers, tensile properties are degraded.

Furthermore comparative analysis of tensile stress and elastic modulus for different sample codes of hybrid composite has been compiled in Table 4 and it is correlated with PDI. The effect of filler ratio on tensile properties and PDI of hybrid composite is illustrated. Maximum improvement in elastic modulus and tensile strength is observed for sample F. For sample code F with graphene and CNT filler ratio as 1:3, an increase in tensile stress to 50.28 MPa (57.1 %) is noticed, similarly an increase in elastic modulus to 2848 MPa (39.9 %) is noticed for as compared with neat epoxy composite (sample A). Therefore Tensile strength is maximum when graphene filler content is lower as compared to CNT content. For sample G with filler ratio 3:1, tensile strength increased by 2080.16 MPa (2.2 %) and elastic modulus increased by 48.06 (50.2 %). Though the value of PDI differs from both PSD method but the pattern is observed to be same. Reason for this may be due to analyses performed with help of imaging processes indicate only mirror of certain sections. Reason for this lies in the basic principle of methodology and operation of both the methods. In DLS, 3-D environment is present whereas in IA 2-D image at particular section of fracture surface is analyzed. The lowest value of PDI is observed for sample F. Thus maximum tensile properties can be obtained when dispersion and homogeneity of graphene/ MWCNT is uniform.

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	0.1176
D	2039	46.08	0.918	0.1900
F	2848	50.28	0.513	0.1273
G	2080.16	48.06	0.677	0.2000

As expected the results indicates a relationship of particle distributions with mechanical properties of hybrid epoxy composite which can be verified by DLS and image analysis. The mechanical properties increases with decrease in inter particle spacing that occurs with increase in the homogeneity of reinforcement particle distribution.

IV. CONCLUSION

The synergy of graphene/CNT fillers ratio on epoxy resin is investigated. It was observed that filler ratio had an effect on PSD, morphology and homogeneity of the composite mixture. Uniform dispersion of graphene/ CNT filler in epoxy polymer matrix is important for obtaining improved tensile properties of composite material. Functionalization of filler, its content and ratio are some of the factors deciding homogeneity of mixture. Qualitative measurement of dispersion is illustrated, though quantification of dispersion is also required. Good dispersion and improved tensile properties are observed when graphene is lower as compared to CNT content furnishing good bonding and effective load transfer between filler and epoxy resin matrix. The maximum tensile stress and elastic modulus of 50.28 MPa and 2848 MPa respectively is noticed for graphene: CNT content of 1:3. Further lowest value PDI is observed for same sample by both DLS and SEM image analysis methods. Therefore a relation of filler ratio and PDI is established with the performance of polymer composite.

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