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Quantitative optical analysis of filler dispersion degree in MWCNT–epoxy nanocomposite

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ABSTRACT

Recently developed methodology of quantitative analysis based on optical analysis of filler particles' area distributions is applied now to estimate the dispersion efficiency of multiwall carbon nanotubes in nanocomposite prepared by solution intercalation method. Experimental parameters of dispersing (temperature, duration and power level of ultrasonication) were optimized and the most effective experimental procedure was determined. The methodology of determination of dispersion parameter is proved by indirect method of light transmittance experiments. The nanocomposite specimens having lower dispersion parameter represented the highest transmittance over the nanocomposite specimens.

1. Introduction

The behavior and properties of polymer nanocomposites (NCs) are dependent not only on properties of its structural components but also on the material microstructure: the dispersion and orientation of filler particles, and the interactions between filler particles and polymer matrix [1]. The complete dispersion of nanoparticles in a polymer optimizes the number of available reinforcing elements for carrying an applied load. Therefore one of the main parameters that affect the behavior of the material is the effectiveness of filler particles' dispersion in the material [1–4]. The formation of nanoparticles' agglomerates within a polymer system surely influences detrimentally the final nanocomposite performance such as strength, stiffness, fracture toughness, electrical/thermal conductivity, transparency, etc.

Depending on the demanded scale different microscopy methods such as transmission electron microscopy [5–8], scanning electron microscopy [5,8] and atomic force microscopy [9,10] are amongst the most spread techniques to evaluate dispersion of different types of nanoparticles.

In addition dispersion of carbon nanotubes (CNTs) can be estimated indirectly by light transmittance experiments. Several investigations [11–14] on transmittance of different solvents containing CNT showed that they were good candidates for effective optical limiting over broad temporal and laser energy ranges. Scattering processes prevail for the case of CNT having huge surface area because of the interpenetration of CNT among the homogeneously dispersed polymer chains. Accordingly the for case of better dispersion of CNT within the polymer resin the amount of scattering centers in the specimen of the same filler content should increase. Thus, more light was scattered and, as a result, optical transmittance of the NC specimens decreased [15].

The high surface energy of certain nanoparticles causes them to agglomerate in the synthesis and post-synthesis processes. As a result the obtained materials contain filler particles in the nanometer scale, which form variable and complex networks, shapes, and morphologies, all of which can influence properties and behavior of the NC. The actual morphology of certain nanoparticles in polymer resin varies with the synthesis process and can have large batch-to-batch variations [15].

Therefore making samples of polymer matrix NC with good and repetitive dispersion is a challenging area that demands considerable efforts [16]. The commonly used methods to break up agglomerated nanoparticles are ball milling, high shear mixing and ultrasonication [15]. Nevertheless each polymer system requires a special set of processing conditions to be formed, based on the processing efficiency and desired product properties.

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Thus the effectiveness of experimental mixing parameters was being revealed through the indirect effect on electrical [17], mechanical [17,18] thermophysical [16,19] and barrier [20] properties of NC applying different methods of investigation.

For the case of ultrasonication method the breakage of agglomerates is controlled predominantly by specific energy input (power, time, dispersion volume and temperature of the solvent). Since there are several experimental parameters affecting the mixing procedure the choice of their combination is not evident and should be arranged experimentally.

One way to estimate difference between experimental parameters for the dispersing effectiveness of nanoparticles within a polymer resin is to apply recently developed method of quantitative analysis [21]. According to the method dispersion of filler particles is associated with their area and the dispersion parameter D is defined as the probability to fall in a certain range of the particle area distribution. The method has been applied to both model and real composite systems characterized by different dispersion levels and various filler contents. Application of the method to model composite systems has shown that the dispersion parameter increases with the decrease of clusterization degree (relative cluster size) for all the investigated composite systems. Filler particle dispersion also becomes worse with the increase of filler content since higher quantity of clusters appear with the increase of filler content.

Therefore the objective of the current paper is to match the optimal experimental parameters for the manufacturing of CNT–epoxy nanocomposite at constant filler content performed by ultrasonication method. It was done with application of recently developed quantitative method to estimate the effectiveness of CNT dispersion in NC using optical images. The alternative method such as light transmittance was applied in order to corroborate the results obtained by the quantitative optical analysis.

2. Material and methods

The multiwall CNT with average diameter 9.5 nm and average length 1.5 μm used as nanofiller were provided by *Nanocyl Ltd*. CNT were produced via the catalytic carbon vapor deposition process. A monocomponent epoxy resin RTM6 was provided by *Hexcel* and is developed to fulfill the requirements of the aerospace and space industries in advanced resin transfer molding process. The viscosity of RTM6 is about 1×10^3 Pa s at room temperature and follows almost linear decrease till about 1×10^{-1} Pa s under heating till 120 °C when the polymerization reaction starts to proceed [17].

The same composition of CNT and RTM6 resin (NC with filler content 0.1 wt.%) was used in six dispersion procedures with various experimental parameters (temperature, time and power) given in Table 1. As it is clear from Table 1 three stages of NC processing could be selected.

For the first stage CNT were ultrasonically dispersed in acetone using ultrasonicator *Misonix 3000* at power 18 W for 1 h. This procedure was chosen to be the most effective basing on the investigation of histograms of particle area distribution in acetone for the ultrasonication time from 15 min till 3 h. In order to get clear comparison between experimental parameters of the second stage the first stage was kept constant for all the NC specimens.

For the second stage the obtained solution was then mixed with the RTM6 resin and ultrasonicated according to chosen experimental procedure with the sonicator probe inside the material or acting through the oil bath. It was assumed that there is a linear dependence of experimental factors (duration, temperature and power of the ultrasonication) on the filler dispersion within the polymer resin. Finally for the third stage the mixture was placed in the aluminum mold, degassed for 30 min and cured for 1 h 30 min at $T = 180$ °C.

The specimens were prepared for optical microscopy by cutting the specimen of size 20 × 20 × 0.5 mm with the blazer. The specimens' surface was finished by polishing it with a paste containing aluminum particles of size 1 μm. Five images were obtained for each procedure and then used for the analysis. The obtained images provided information about dispersion degree in the area of about 3 mm^2 for the lowest magnification (×50) of optical microscope *OLYMPUS BX51*.

The light transmission experiments were performed using *Analytik Jena* UV VIS spectrophotometer Specord 210 in the spectral interval 200–1100 nm. The light transmission for NC specimens was measured using pure epoxy resin as a reference. All the light transmission and optical microscopy measurements were made at room temperature.

3. Brief description of quantitative analysis

For the quantitative estimation of the filler dispersion the recently proposed methodology was used [21]. According to the method the dispersion of filler particles is associated with their area. It is considered that if two or more neighbor particles are in contact they form a cluster. Consequently, the more equal is the particles' area the more homogeneous is the system obtained.

In order to determine the area of individual filler particles of the given systems the original images obtained from optical microscope were binarized and filler particles separated from the background in freely available *ImageJ* program [22] setting a brightness threshold between particles and background by isodata algorithm. Thus the area of individual filler particles is defined through the number of pixels in each specific case, and is used for the subsequent analysis. It is assumed in the method that the distribution of individual filler particle area obeys Gaussian law. The area under the distribution curve is defined as the probability of filler particles to fall in a certain range of the particle area distribution, represents dispersion parameter D [21] and includes two independent parameters – average area μ and standard deviation σ of the particles' area. The dispersion parameter D is defined in the linear range of probability function $\mu \pm 0.1\mu$ and is calculated according to formula [21]:

$$D = \frac{0.2}{\sqrt{2\pi}} \cdot \frac{\mu}{\sigma}. \quad (1)$$

As it was stated and proved in the previous paper [21] for better dispersion of filler particles within hosting matrix, the value of dispersion parameter, D, should be the highest achievable for all the overall experimental procedures.

Table 1
Experimental dispersing procedures for processing multiwall CNT-RTM6 NC.

Dispersing procedures	First stage	Second stage				Third stage
		t (h)	T (°C)	P (W)	Type	
1	Sonication of CNT in acetone for i = 1 h, p = 18 W	2	90	24	Oil bath	Degassing for t = 30 min at T = 80 °C; curing for t = 90 min at T = 180 °C
2		3	90	24	Oil bath	
3		2	55	20	–	
4		2	55	36	–	
5		3	80	36	Oil bath	
6		3	90	36	Oil bath	

4. Application of the quantitative analysis to multiwall CNT-epoxy nanocomposite

According to Table 1 six different dispersing procedures were applied for processing of NC and then analyzed using quantitative analysis described above. The obtained original optical images of each dispersing procedure are shown in Fig. 1. Analyzing these images it is difficult and not objective to choose between the dispersing procedures according to just visual observation.

Fig. 2 shows the binarized image (*a*) and typical cluster area probability distribution (*b*) obtained for procedure number *2* e.g. It could be observed that experimentally obtained histogram could be well approximated with normal distribution at $\mu = 16\ \mu m^2$, $\sigma = 14\ \mu m^2$. Analogously one-mode distributions were obtained for all the procedures and it means that after the phase analysis remained only clusters and the individual CNT were neglected.

5. Results and discussion of quantitative optical analysis as applied to multiwall CNT–epoxy nanocomposite

Final results of the quantitative analysis are given in Figs. 3 and 4. Fig. 3 shows the dispersion parameter evaluated by Eq. (1) according to the applied dispersing procedures. The indicators are put for the comparison between procedures having two equal factors and one different in the direction of the factor amplification. Each data represent the mean value over 5 images taken in different locations from the same NC specimen. The increase in duration, power and temperature during the ultrasonication process leads to a higher dispersion parameter which corresponds to a higher effectiveness of filler dispersion.

In order to get more correct comparison among all the factors the contributions of the factor $\Delta F/F_0$ and dispersion parameter $\Delta D/D_0$ – the relative change with respect to factor's and dispersion parameter's minimal values (F_0 and D_0) were calculated for each factor independently. This action allows analyzing the contribution of each factor influencing the CNT dispersion efficiency in NC. While the rest factors' parameters are kept constant.

It could be found from Fig. 4 that though temperature and duration of the ultrasonication has lower contribution they reveal almost twice higher effect on dispersion parameter. Obviously this could be caused by the rapid lowering of the polymer viscosity. According to the results obtained in [17] the viscosity of RTM6 within the temperature interval 80–90 °C decreases app. by the order of magnitude. As a result it leads to improvement in effectiveness of CNT dispersion within the polymer system.

Nevertheless some drawbacks of the proposed analysis should be considered. The obtained distributions of CNT agglomerates' area are unimodal. One the one hand it is appropriate for the analysis and proves the accuracy of the determination the characteristic coefficient *D*. But on the other hand it means that the individual CNT are neglected by the analysis since there should be bimodal distribution of the particle area. In such way the concentration of CNT could be different among the images and it can influence

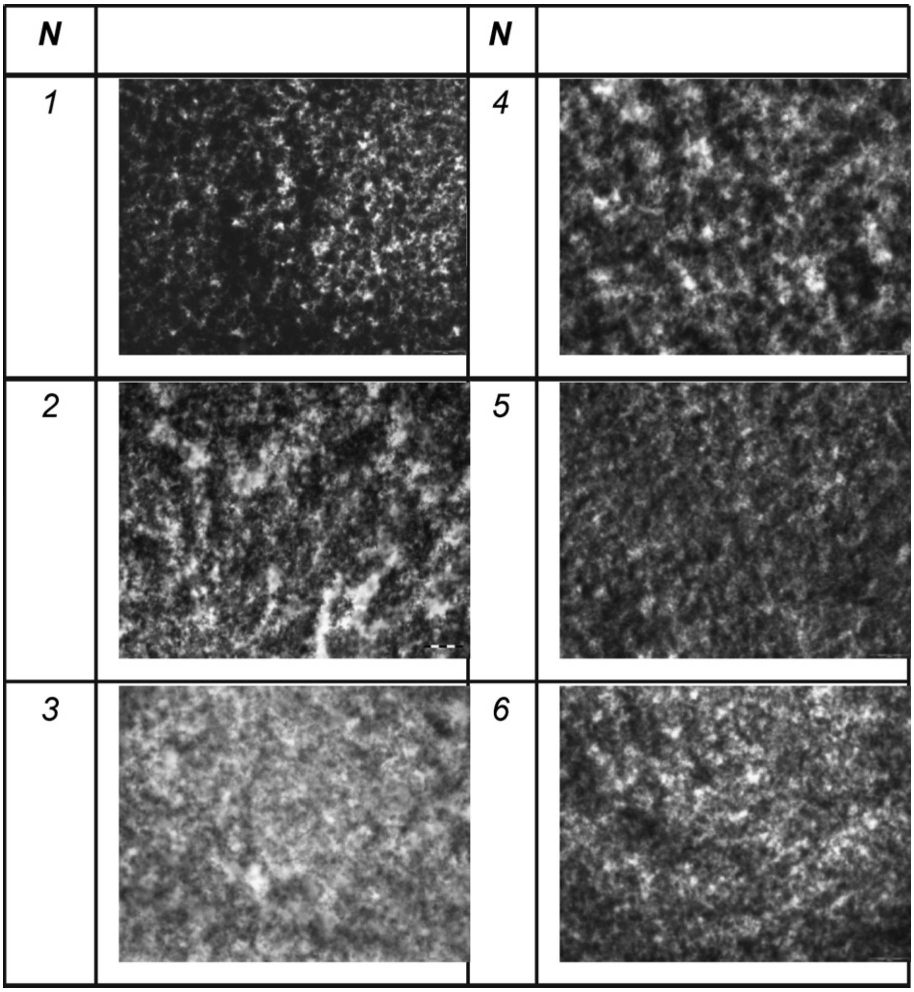

Fig. 1. The optical images listed according to the procedure described in the Table 1 (magnification – 50×, area size – 1.30 × 1.65 mm).

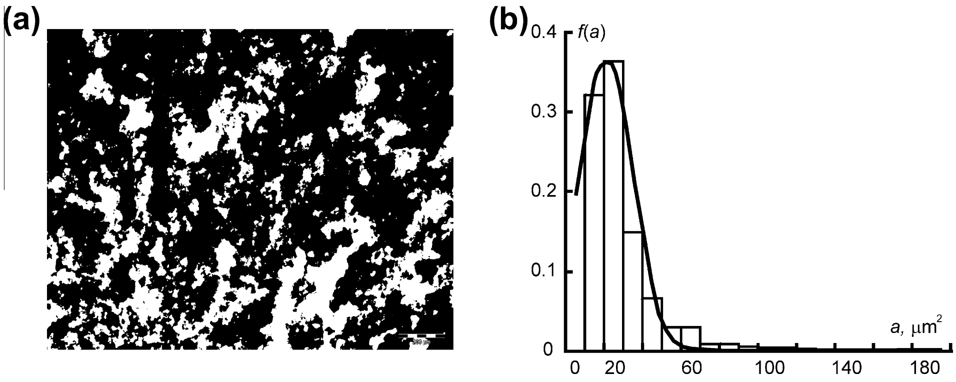

Fig. 2. Binarized image (*a*) and typical cluster area probability distribution (*b*) for procedure number *2* (bars – result of histogram analysis, curve – approximation with normal distribution at $\mu = 16\ \mu m^2$, $\sigma = 14\ \mu m^2$.

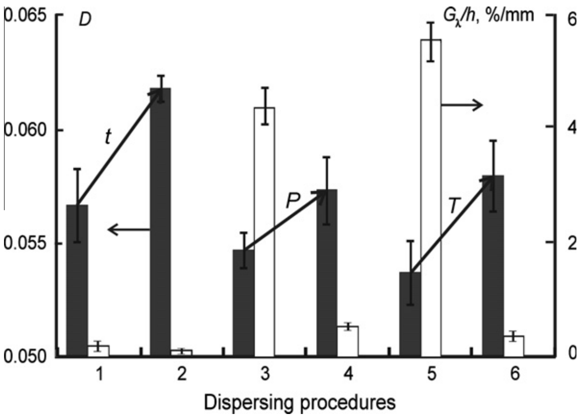

Fig. 3. Dispersion parameter *D* (■) and light transmittance G_λ (□) normalized to NC specimen's thickness *h* (at $\lambda = 760$ nm) for different dispersing procedures listed in the Table 1.

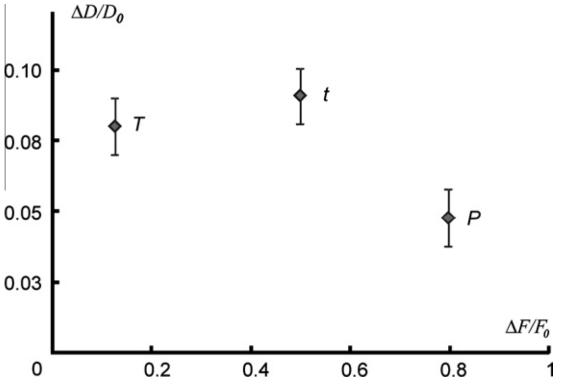

Fig. 4. Effect of dispersion parameter increase vs. contribution of the factor.

the results of comparison between different dispersing procedures. That's why it is advisable to keep relative content of filler particles, evaluated as relation of the total area of filler particles divided by the area of the image, constant carrying out the analysis.

The second drawback is that there is no difference between initial agglomerates of CNT and the agglomerates that can appear due to Van der Waals attraction forces during the dispersing procedures. The point is that the distribution of the initial individual filler particle areas could be more or less different for each dispersing procedure. This can affect the further distribution of the filler particles after the processing of composite material and prevents possibility to evaluate effectiveness of dispersing CNT in the proper way.

The last drawback to be mentioned is that the shape of CNT and their agglomerates cannot be spherical as it is assumed in the method proposed. Due to different orientation of the particles having shape with orientational asymmetry their projection on the image plane will be different under different angles. Furthermore the overlapping of dispersed particles is possible and thus they can appear as agglomerates. That is why the section thickness in relation to filler particle size is important for this method and should be kept the same for all the investigated specimens.

Therefore the results regarding the distinction among the dispersing procedures of multiwall CNT–epoxy NC provided by the method should be proved by the alternative method for example by light transmittance experiments in which the contribution of all the CNT either individual and agglomerated is taken into account.

6. Investigation of light transmittance for multiwall CNT–epoxy NC specimens

In order to get indirect comparison for the effectiveness of filler dispersion between the dispersing procedures the light transmission experiments were performed. The results of light transmission are given in Fig. 6. The light transmittance is defined as

$$G_\lambda = I/I_0 \qquad (2)$$

where I_0 and I represent, respectively, the intensities of the incident and transmitted light. Since CNT absorb and scatter the light energy, the lower value of light transmittance should indicate that the efficiency of the filler dispersion is higher at the same filler concentration. Obviously the formation of the agglomerates should result in higher light transmittance through the NC specimens. This could be explained by the high surface area of CNT. If CNT are dispersed in epoxy resin in scale of nano-sized particles, the composite samples should evince lower light transmission because of the intense light scattering and absorption on the interfaces between CNT and epoxy matrix.

From Fig. 5 it could be revealed that the results of quantitative estimation are in good correlation with light transmittance results. The NC specimens with the most effectively dispersed CNT which were prepared by procedure *1,2, 4* and *6* show the lowest transmittance of the light trough the specimen. Moreover, the NC specimens having lower dispersion parameter *D* (procedures *3* and *5*) represented the highest transmittance over the NC specimens. The above mentioned results for normalized to NC specimen's thickness light transmittance at wavelength 760 nm (an approximate limit of visible light wavelengths) are given also in Fig. 3

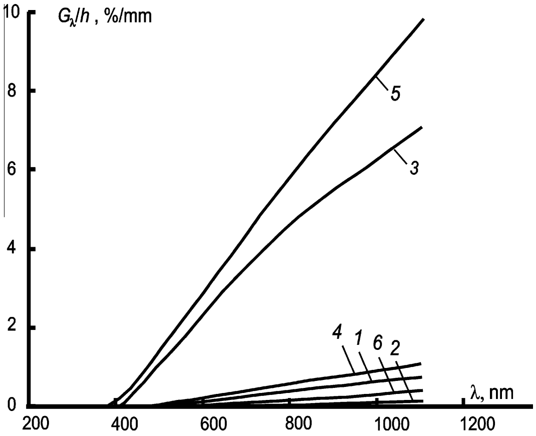

Fig. 5. Normalized to NC specimen's thickness light transmittance spectra for NC specimens prepared by different dispersing procedures (numbers on the curves) as listed in the Table 1.

together with the results on evaluation of dispersion parameter *D* for different experimental procedures.

Due to high surface area of CNT and interpenetration of CNT among the homogeneously dispersed polymer chains intense scattering processes occur. Accordingly for case of better dispersion of CNT within the polymer resin the amount of scattering centers in the specimen of the same filler content should increase. Thus, more light should be scattered and, as a result, the light transmittance of the NC specimens should decrease. Consequently the proposed methodology of the determination of single dispersion parameter was proved by the indirect method of light transmittance.

7. Conclusions

The recently developed quantitative method to estimate the dispersion of filler clusters in polymer resin was applied to MWCNT–epoxy nanocomposite at constant filler content of 0.1 wt.%. These NC specimens have been produced by six different dispersing procedures.

Experimental parameters (temperature, duration and power of ultrasonication) have been changed in order to define the most effective procedure. The optimization was undertaken using optical analysis which includes investigation of filler particles' area distributions. This methodology provides a suitable way to estimate the dispersion of CNT in RTM6 resin at micro-level.

It was concluded that among three experimental parameters such as duration of the ultrasonication, temperature and power level during the ultrasonication process, the temperature and duration of the ultrasonication play the dominant role. Obviously it was caused by the rapid lowering of the polymer viscosity and as a result improvement in effectiveness of CNT dispersion within the polymer system.

The results obtained by quantitative optical analysis have been confirmed by indirect method of light transmittance experiments. The nanocomposite specimens having higher dispersion parameter *D* represented the lowest light transmittance over the nanocomposite specimens since the amount of scattering centers for light transmittance is growing up for better case of CNT dispersion.

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