REAGGLOMERATION OF CARBON NANOTUBES DURING PROCESSING OF EPOXY NANOCOMPOSITES

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1 Introduction

One of the main applications of carbon nanotube (CNT) has been found in manufacturing polymer nanocomposites. Owing to its superior electrical and mechanical properties, CNT should theoretically enhance the properties of polymers drastically [1]; however, in practice, the degree of enhancement in properties is much lower than expected [2-5]. Besides, in the attempts that have been made in the literature to improve the properties of polymers by adding CNT, different reinforcing behaviours have been observed. For instance, both improvement and degradation in the mechanical properties of CNT-modified polymers have been reported [3]. A wide range of manufacturing techniques have been developed to overcome this problem and efficiently incorporate CNT into polymers; however, manufacturing CNT-modified polymer is still challenging because of the nanotubes nanoscale size [6].

Dispersion of CNTs is one of the most important challenges toward manufacturing CNT-modified polymers. CNTs have large aspect ratio and specific surface area because of which they entangle readily with each other when supplied at commercial scale. Mechanical reinforcement of polymer nanocomposites, however, requires disentanglement of nanotubes from the bundles and dispersing them uniformly within the polymer matrix. On the other hand, even when dealing with low CNTs weight fractions (less than 1 wt.%) an extremely large number of CNTs should be dispersed in the matrix. This makes the dispersion of CNTs extremely difficult and their reagglomeration almost inevitable during and after the processing steps.

Chemical and physical treatment of CNTs has been widely used to ease their disentanglement. Use of solvents, surfactants, functionalization, and polymer wrapping are just a few examples of different treatments used towards improved dispersion of nanotubes [3]. Regardless of the chemical treatment, the use of sonication or mechanical mixing is inevitable for obtaining an acceptable degree of dispersion.

Once a favorable state of dispersion is achieved through a controlled processing condition, the polymer may be heated to complete the synthesis of the final product. For epoxy resins, nanotubes are usually mixed with the resin first, and then, a curing agent is added to complete the chemical crosslinking reaction. Depending on the type of epoxy/curing agent system used, a cure cycle may be necessary to obtain a fully cross-linked network. Microscopic examinations performed on the cured CNT-modified epoxies revealed that the state of dispersion degrades when cured at temperatures higher than room temperature.

Several studies have postulated reasons behind the reagglomeration of nanotubes during the curing process. It has been discussed that at high temperatures, a reduction of the resin viscosity enhances the mobility of particles, which facilitates their movement towards each other and reagglomeration because of strong attractive van der Waals forces [7-9]. The state of dispersion can be aggravated further if the nanotubes have low affinity with the polymer matrix at high temperatures [7]. Another factor that influences the dispersion stability is the low shear forces caused by stirring or resin flow during processing [8, 10-12]. Although high shear forces are beneficial in breaking down the aggregates of nanotubes during the dispersion steps, low shear forces facilitate the local movement of particles, which can result in their reagglomeration [13, 14]. In a recent study [15], a direct relationship between the shear rate and the dispersion instability was observed for CNTs in an epoxy resin. In another
study by Pegel et al. [11] a similar trend was observed for CNT-modified polycarbonate melts. The nanotube concentration is another factor that affects the dispersion stability at high temperature. Ma et al. [16] discussed that there is a higher chance of reagglomeration at higher concentration because of the reduced inter-particle distance. Rosca et al. [17], on the contrary, reported a higher degree of reagglomeration at high temperatures for formulations containing low concentrations whereas the change in dispersion was not significant at high concentrations. Increased viscosity at higher concentration was explained as the reason for this observation. The addition of hardener and the cross linking reaction is also believed to alter the dispersion stability [8, 18].

In light of the above, the objective of this paper is to understand the dependency of CNT dispersion stability to heating rate, temperature, CNT concentration and addition of hardener to a CNT-modified epoxy system.

2 Materials and methods

2.1. Materials

Multiwall carbon nanotubes (MWNTs) supplied by Bayer Material Sciences (Baytubes C150) were used in this study. Baytubes C150, which are produced by chemical vapor deposition, have average outer diameter of 13-16 nm and length of 1-10 µm. AKD 2377 epoxy resin supplied by Axson (formerly Nanoledge Inc.) was used to prepare the nanocomposites. The epoxy system is semi-solid at room temperature, which is ideal for fabricating resin films and prepregs.

To prepare epoxy nanocomposite, epoxy was first heated at 70 °C to lower its viscosity to a suitable level at which it can be processed. CNTs were also preheated at this temperature to facilitate the mixing process. Then, weighted amount of CNTs was added to epoxy resin and mixed using a high shear mixer. Formulations containing 0.1 wt% and 0.3 wt.% of CNTs were produced using this technique. These formulations alone were used to study the stability of dispersion under different heating conditions. However, to examine the effect that addition of hardener may have on stability of dispersion, formulations mixed with hardener were also prepared. 3,3’-Diamino Diphenyl Sulfone (DDS) was used as an appropriate hardener for this epoxy system. DDS was heated at 70 °C before mixing with resin. The required amount of DDS (resin to DDS ratio of 100:16) was then mixed with the resin using a shear mixer for 10 min. The mixture was degassed in a vacuum oven at 70 °C for 30 min to remove any bubbles that was possibly formed during the mixing steps.

2.2. Methods

2.2.1. Rheological measurements

The rheological behaviour of various formulations was measured using a TA Instrument AR2000 Rheometer. A 25 mm disposable aluminum parallel-plate setup with a gap of 800-1000 µm was utilized. Rheological measurements were carried out in the oscillatory mode with a frequency of 1 Hz. Strain value of 10% was fixed as the controlled variable for all experiments. The initial temperature for the experiments was fixed at 70 °C to facilitate the flow of resin.

2.2.2. In-situ dispersion monitoring

The evolution of the CNT dispersion during the heating condition was monitored using a hot stage microscopy setup. A hot stage (Linkam THMS600) was mounted on a transmitted optical microscope capable of acquiring pictures of the sample under study. More information regarding this experimental setup can be found in [15]. For each experiment, around 1 mg of resin was placed on a cover glass and then, the temperature was raised to 70 °C to bring the resin to a viscous liquid phase. Then, another cover glass was placed on the top while maintaining the gap between two glasses at 25 µm using a metal spacer. Finally, the desired heating condition was applied.

Fig. 1a indicates a typical image of dispersion for the formulations consisted of epoxy resin and CNTs alone (without hardener). In this figure, the yellow background represents the resin whereas the darker spots denote aggregates of CNTs. Obviously, it is not feasible to observe the dispersion of individual nanotubes under an optical microscope, and only aggregates of CNTs can be detectable. On the other hand, because of nanoscale nature of CNTs, it is not practical to fully disperse all individual nanotubes within the polymer matrix making the presence of aggregates unavoidable. Therefore, dispersion of CNTs at microscale can be used as a useful
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representative of the overall dispersion. Fig. 1b shows the micrograph of a formulation mixed with hardener, which is a solid white powder at room temperature. Presence of hardener crystals is clear in this figure, which makes the evaluation of dispersion difficult. To solve this problem, before performing the experiments, samples were quickly heated to 110 °C and held for 1 min to dissolve the hardener in epoxy resin after which the samples were quickly cooled down to 70 °C.

Understanding the mechanisms by which the stability of dispersion is altered requires monitoring the state of dispersion during a given heating condition. This requires acquiring micrographs at small time intervals. Visual qualitative analysis of numerous micrographs is time consuming and inaccurate. Besides, it is difficult to compare the micrographs acquired for different heating conditions. To overcome this problem, a quantitative dispersion analysis method, which is capable of defining a dispersion index for a dispersion micrograph, can be applied. In this regard, an algorithm for quantitative analysis of dispersion degree in polymer composites, which was previously developed [19], is used here. A brief description of this algorithm is given in the following section.

3 Quantitative dispersion analysis method

In this algorithm, the state of dispersion is analyzed based on the spatial distribution of particles in a micrograph. For a system of particles, a “uniform dispersion” is defined as an even distribution of individual particles throughout the matrix such that the minimum distance between particles is maximized. On the contrary, an “agglomerated dispersion” occurs when all the particles stick together and form a large mass of particles. These two definitions are used to propose a criterion for quantifying dispersion.

For a given dispersion micrograph, first, the associated binary image is produced. In the binary image, on-pixels represent the particle elements while off-pixels are considered as matrix elements. Then, the distance between any matrix elements to the nearest neighboring particle element, \(d_i\), is computed. The mean value of this parameter for all matrix elements, \(\mu\), is calculated as

\[
\mu = \frac{\sum_{i=1}^{N_m} d_i}{N_m}
\]

where \(N_m\) is the number of matrix elements. The value of \(\mu\) represents how matrix elements are distributed around particle elements. In a uniform dispersion, the distance between matrix elements to their nearest neighboring particle elements is minimized where \(\mu\) finds its lowest value. As dispersion degrades towards an agglomerated one, particle elements fall at farther distances with respect to the matrix elements, in which case \(\mu\) increases towards its maximum value. Two extreme cases of dispersion are shown in Fig. 2 to visualize the distribution of nearest neighbor distances. In each case, 25 identical spherical particles with an areal fraction of 5 % in a 400 × 400 elements matrix domain are considered. The color assigned to each element indicates how far (in units of elements) that element is located with respect to its nearest particle element.

To quantify the state of dispersion, a dispersion index is defined by comparing the value of \(\mu\) for a given image with the corresponding values of \(\mu\) for two extreme cases of dispersion, i.e., uniform and agglomerated. To calculate \(\mu\) for these cases, associated dispersion images are first produced using the same areal fraction of particles, and then, the value of \(\mu\) is calculated using Equation 1. Dispersion index, \(DI\), is then defined as

\[
DI = \frac{\ln(\mu_a) - \ln(\mu_u)}{\ln(\mu_u) - \ln(\mu_a)} \times 100
\]

where \(\mu_u\) and \(\mu_a\) are the mean nearest neighboring distance for agglomerated and uniform dispersions, respectively. According to Equation 2, a uniform dispersion has a \(DI\) of 100 % whereas a zero value is expected for an agglomerated dispersion.

The applicability of the developed algorithm to real dispersion micrographs is shown in Fig. 3. Four different cases of dispersion for the CNT-modified epoxy resin are shown in this figure, and the corresponding values of \(DI\) are also indicated. This algorithm is used to quantify the dispersion micrographs of various formulations obtained from hot stage microscopy technique, which will be explained in details in the following section.
4 Results and discussion

Table 1 presents the details of different experiments performed. Case 1, which is considered as the baseline, contains 0.1 wt% CNT heated from 70 °C to 120 °C with a heating rate of 2 °C/min. For Case 2, the temperature was raised to 180 °C. The effect of heating rate was investigated in Case 3 by applying a heating rate of 10 °C/min while keeping the other parameters identical to Case 1. Finally, the effect of CNT concentration was examined in Case 4 by using the formulation with 0.3 wt.% CNT. In all cases, formulations with or without hardener are examined to study the effect of cross-linking reaction on the stability of dispersion.

4.1. Case 1: Baseline

Viscosity profile as well as dispersion monitoring results for Case 1 is shown in Fig. 4. Left and right vertical axes present variation in dispersion index and complex viscosity, respectively, versus time. Viscosity of both samples, i.e., with or without hardener, drops as the samples are heated from 70 °C to 120 °C. At 120 °C, the viscosity of the sample with no hardener remains constant as there is no driver to change the viscosity. However, the viscosity of the sample with hardener starts to increase gradually because of the chemical reaction that has begun inside the sample. The sample mixed with the hardener has a lower initial viscosity value than the sample with no hardener; this might have happened because the hardener lowers the viscosity of mixture by reducing the weight fraction of the epoxy resin.

The dispersion index also decreases as the temperature is increased until the temperature reaches 120 °C; at this point, no change in the dispersion of either samples is observed. A degradation of about 9 % in the state of dispersion is observed for both samples. It is evident from these results that the quality of dispersion follows a similar trend as viscosity, i.e., as viscosity decreases, quality of dispersion also degrades. This happens because resin can flow easier at lower viscosities providing more mobility to individual and aggregated nanotubes. As a result of increased mobility, nanotubes can come close to each other and reagglomerate. Besides, the resin cure seems to have no effect on reagglomeration behaviour since the change in viscosity, and consequently the flow of the resin, predominates the low degree of cross-linking reaction at temperatures below 120 °C.

4.2. Case 2: Higher temperature

Fig. 5 presents the results of dispersion analysis and rheological measurement for Case 2. For the sample with no hardener, the viscosity drops to its minimum value at the temperature of 180 °C after which it remains constant. The dispersion index also follows a similar trend by which the state of dispersion degrades by about 25 % until the temperature reaches 180 °C and then, remains unchanged. These results highlight the dependency of CNT dispersion degradation on changes of viscosity. As the temperature keeps increasing to higher temperatures, the viscosity decreases to lower values increasing flow and risk of reagglomeration. However, once the change in viscosity is halted, no significant change in dispersion is detectable. It is worth mentioning that at reduced viscosities, reagglomeration of individual nanotubes is quite possible because of Brownian motion, which cannot be recognized with the current setup. All dispersion measurements that are carried out are valid for aggregated nanotubes may not necessarily reagglomerate by Brownian motion in this viscous medium. Therefore, agglomeration is noticeable only when resin flows as a result of viscosity change.

The degradation of dispersion stops at an earlier stage when the resin is mixed with hardener. As the temperature approaches 130 °C, the degree of cross-linking starts to rise where a 3-D network is established within the polymer. Therefore, viscosity reaches a plateau even though the temperature is being increased. Formation of cross-linked structure restricts the mobility of resin as well as CNTs resulting in lower degree of reagglomeration compared with the sample with no hardener. It should be mentioned that dispersion index reaches a final value of about 75 % for this sample, which is lower than the similar sample in case 1.

4.3. Case 3: Higher heating rate

Fig. 6 shows the results of dispersion monitoring and viscosity measurements for Case 3. Since the temperature gradient was high, viscosity rapidly reaches its minimum value at 120 °C. This abrupt change in viscosity resulted in sudden and increased flow of resin compared to the case with lower heating rate. Consequently, degradation of the
dispersion was amplified where a reduction of about 20% was observed in the state of dispersion of either samples, i.e., with or without hardener. Addition of hardener into epoxy did not seem to result in a significant difference compared to the sample without hardener because the ultimate temperature is below the point at which chemical reaction becomes determining.

4.4. Case 4: Higher CNTs concentration

Fig. 7 illustrates the results of dispersion evaluation and viscosity measurements for Case 4. According to these results, the incorporation of higher loading of CNT into epoxy resin results in an increase in the viscosity profile. Let us consider the samples with 0.1 wt.% CNT (Case 1) and 0.3 wt.% CNT (Case 4) with no hardener embedded. Both samples have identical viscosities at 70°C since the rheological behavior is mainly governed by the viscous resin. As the temperature rises, presence of CNTs plays a more important role in controlling the viscosity. For instance, samples containing 0.1 wt.% CNT and 0.3 wt.% CNT have a viscosity of 0.75 Pa.s and 2.20 Pa.s at 120°C, respectively. This occurs because as the CNTs content is increased, higher shear forces are produced within the matrix, which enhances the resistance against the flow of resin. Therefore, higher viscosity is obtained for higher concentration of CNT. Moreover, viscosity gradient is lower for higher concentrations resulting in less flow rate in resin as it is heated up to desired temperature. As a result of increased viscosity along with reduced flow rate, slight changes in the state of dispersion is observed for sample with 0.3 wt.% CNTs. Similar behaviour was observed for the sample mixed with hardener as the degree of cross-linking was low in this temperature range.

5 Conclusions

The stability of CNT dispersion in CNT-modified epoxy resin was investigated by means of in-situ dispersion monitoring and rheological measurements. The effect of heating rate, heating temperature, concentration CNT and curing of resin was investigated. Four different scenarios were used to elucidate the influence of each parameter on the stability of dispersion. Results of different experiments suggest that stability of dispersion is highly affected by any factors that boost the flow of resin, and consequently, mobility of nanotubes. Higher heating temperature results in reduced viscosity and increased resin flow for the sample with no hardener; however, when hardener is added to resin, the material cures faster at higher temperature, which restricts the mobility of nanotubes. At high heating rates, viscosity changes faster making the resin to flow at a higher rate and giving nanotubes a greater chance to reagglomerate. Increasing the concentration of CNT counter intuitively resulted in a more stable dispersion during a heating condition. Increased viscosity and reduced flow rate is believed to be the main driver for this observation.

All dispersion measurements were performed in the absence of any external shear stress. Obviously, applying any external shear stress will amplify the degree of dispersion degradation. In addition, state of dispersion was estimated for aggregated nanotubes rather than individual nanotubes; therefore, the experimental results presented in this study do not necessarily include the nanoscale reagglomeration of individual nanotubes in overall system.

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References


Tables

<table>
<thead>
<tr>
<th>Samples</th>
<th>CNTs content (wt. %)</th>
<th>Heating rate (°C/min)</th>
<th>Hold temperature (°C)</th>
<th>Hardener inclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>0.1</td>
<td>2</td>
<td>120</td>
<td>no DDS with DDS</td>
</tr>
<tr>
<td>Case 2</td>
<td>0.1</td>
<td>2</td>
<td>180</td>
<td>no DDS with DDS</td>
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<td>no DDS with DDS</td>
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<tr>
<td>Case 4</td>
<td>0.3</td>
<td>2</td>
<td>120</td>
<td>no DDS with DDS</td>
</tr>
</tbody>
</table>

[72x688]
Figures

Fig. 1: A typical dispersion micrograph for: a) CNT-modified epoxy. Yellow background represents resin while dark black spots stand for aggregates of CNT; b) after mixing CNT-modified epoxy with hardener. Presence of hardener crystals does not allow for proper estimation of state of dispersion. To solve this issue, the mixture was heated at 110 °C for 1 min to dissolve the hardener crystals.

Fig. 2: Synthetic models showing two extreme cases of dispersion: (a) uniform dispersion; (b) agglomerated dispersion. Distribution of nearest neighboring distance is shown in (c) and (d) for the image in (a) and (b), respectively [19].

Fig. 3: Optical micrographs for different states of dispersion. Calculated value of dispersion index is shown in each figure.

Fig. 4: Results of dispersion monitoring and rheological measurement for Case 1: Samples with 0.1 wt.% CNT were heated from 70 °C to 120 °C with a heating rate of 2 °C/min. Samples with or without hardener were tested.
Fig. 5: Results of dispersion monitoring and rheological measurement for Case 2: Samples with 0.1 wt.% CNT were heated from 70 °C to 180 °C with a heating rate of 2 °C/min. Samples with or without hardener were tested.

Fig. 6: Results of dispersion monitoring and rheological measurement for Case 3: Samples with 0.1 wt.% CNT were heated from 70 °C to 120 °C with a heating rate of 10 °C/min. Samples with or without hardener were tested.

Fig. 7: Results of dispersion monitoring and rheological measurement for Case 1: Samples with 0.3 wt.% CNT were heated from 70 °C to 120 °C with a heating rate of 2 °C/min. Samples with or without hardener were tested.