

EFFECT OF LATERAL SIZE ON DISPERSION STABILITY AND RHEOLOGICAL PROPERTIES OF GRAPHENE-BASED NANOCOMPOSITES

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ABSTRACT

There are many different graphene manufacturing processes resulting in a variety of grades with distinct purity, number of layers, lateral size, defects, etc. Thanks to the recent surge in the mass production of graphene powders, it is now possible to incorporate them in industrial applications. The first step toward this goal is understanding the effect of mass-produced graphene powders on the processing of composites. Literature shows that slightest change in the lateral size of the graphene particles can have direct impact on the composites' properties. In this study, the effect of lateral size of two industrial grades of multi-layer graphene powders on the dispersion stability and rheological behaviour of unsaturated polyester resins is investigated. A quantitative dispersion analysis method is employed to create a systematic and objective monitoring of dispersion evolution during curing of the resin systems. Both systems containing GB3X and GB0X saw a small delay in gelation, nevertheless, a comparison with the heating rates in pultrusion processes, shows that both systems would be fully cured upon exiting the die. On the other hand, the systems containing GB3X had more mobility and higher potential to reconfigure the particles dispersion during the curing.

1 INTRODUCTION

Composite materials are made up of two or more components with noticeably different properties which create a final material with different properties but proportional to the original constituents. Thus, the properties and performance of the final composite part correlates closely with the characteristics of the original components [1].

Graphene is a 2D materials with a honeycomb structure of single-layer carbon atoms [2] and is one of the most attractive nanofillers due to its exceptional mechanical, electrical and thermal properties. Since its discovery in 2004 by Geim and Novoselov [3], extensive research has been done on the applications and production of graphene powders resulting in numerous derivatives of graphene. In the agreed nomenclature among researchers, the *single layer* of carbon atoms is referred to as graphene. If the derivative consists of more than two layers (usually between 2-10 layers), then it is referred to as multi-layer graphene (MLG). Few-layer graphene (FLG) is a subcategory of MLG where the particles have 2-5 layers. Graphene oxide (GO) is another form of graphene where the oxygen contents are higher characterized by the C/O ratio of approximately 2. Reduction of GO results in a derivative with lower oxygen content as is referred to as reduced graphene oxide (rGO) [4], [5].

The main source of the variation in graphene type is the production process. Chemical vapour deposition (CVD) is one of the most recognized methods for production of high-quality monolayer–few-layer graphene. However, this graphene is not interesting for the industry as CVD is a small-scale production line and the equipment and experimental conditions are not expandable resulting in expensive price of the final product [6]. Top-down processes, such as mechanical exfoliation, chemical oxidation-reduction, and liquid-phase exfoliation are far simpler and cost-effective and have more potential for scaling up [6]–[8]. In these processes, an external force, physical or chemical, delaminates

the graphite flakes and breaks them down to graphene particles. Parameters such as exfoliation time, temperature, solvent, and surfactants can affect the final graphene powder properties. Research has shown that lateral size is an important characteristic of the graphene particles that directly impacts the thermal [9]–[11], mechanical [12]–[14] and electrical conductivity [15], [16] of the composites.

While the literature is very extensive with the effect of lateral size on the physical properties of nanocomposites, there is no research on the effect on *processing parameters* during curing of nanocomposites. Gel time is an important processing parameter defined as the time at which there is a sharp increase in the viscosity of thermoset polymers. Research has shown that nanofillers can accelerate or inhibit the curing depending on the resin and nanofiller type [17]–[19]. However, the question remains on the effect of lateral size in the case of two very similar graphene powders used as filler.

Nanoparticles dispersion in the polymer matrix is another critical factor influencing the composites properties. It is generally accepted that a uniform well-dispersed graphene results in superior properties while re-stacked agglomerated dispersion can cause slipping of graphene planes and act as source of stress concentration [20]–[22]. To evaluate the dispersion state, most of the literature suffice to a qualitative analysis using transmission electron microscopy (TEM), scanning electron microscopy (SEM) or optical microscopy images [23]–[26]. Moreover, the observations are only done either on a nano-modified resin in the liquid state (before curing) or on a cured composite part. These methods are quite subjective and cannot correlate the dispersion state in the liquid phase to the solid composite part. Furthermore, the small field of view in SEM and TEM images limits the sampling window and can result in misinterpreted observations.

Thus, in this study the effect of lateral size of two industrially available multi-layer graphene powders on the rheological and dispersion of an unsaturated polyester resin is studied. Rheology tests will provide information on the gel time of resin systems. An alternative image analysis method is introduced to quantify the dispersion state of graphene powders in the resin system. The effect of lateral size and particle loading is studied in both tests.

2 MATERIALS AND METHODOLOGY

2.1 Materials

The resin system used in this study is Dion 31520-03 which is an unsaturated polyester resin for pultrusion processes and contains 18.3% of calcium carbonate (limestone) filler. Two initiators are used for curing of this resin which are Trigonox KSM-C75 and Perkadox 16. The two different graphene powders used are commercially available as GrapheneBlack3X and GrapheneBlack0X and are referred to GB3X and GB0X in this text, respectively. Based on the manufacturer's data sheet, GB3X and GB0X have the same thickness of 6-10 layers and lateral size of 1-2 μ m and 0.5-1 μ m, respectively. Table 1 provides a summary of the two graphene powders properties. All materials were supplied by NanoXplore Inc.

 Table 1: Properties of the studied graphene powders [27]

Symbol	GB3X	GB0X
Primary particle size	1 - 2 μm	0.5-1 μm
Agglomerate size (D50)	38 µm	15 µm
Carbon content	96%	97%

Three different graphene contents of 0.25 wt%, 0.5 wt%, and 0.75 wt% were chosen for this experiment. Thus, seven batches (including a control sample of neat resin with no graphene) were

prepared by adding appropriate amounts of graphene to the resin. Afterwards, each batch was mixed using a mechanical mixer with increasing speed from 500 rpm to 1500 rpm for two hours. Then, for each test, appropriate amounts of initiators were mixed thoroughly with each batch.

2.2 Methodology

The dispersion stability of the nanocomposites was studied by monitoring the dispersion state after the batches were mixed at room temperature until gelation at 5 °C/min heating rate. For this purpose, the Linkam THMS600 controlled-temperature stage was coupled with the Nikon L150 reflective optical microscope to capture real-time in-situ images during curing. Figure 1 shows a picture of this set up.



Figure 1: The set up for capturing real-time images of microscopy samples

A drop of a freshly mixed resin system (containing initiators) was placed between two glass slides which had thickness of 0.17 - 0.25 mm to ensure minimal thermal lag between the stage and the sample. The slides were then placed on the heating element of the stage and were subjected to heating rates from room temperature to 100 °C/min and images with resolution of 1920 × 1200 were taken at 30 s time intervals to process later using the analysis explained in section 2.2.1.

Rheology tests were performed using an Anton Parr MCR 302 rheometer. First, a series of amplitude sweeps were done to determine the linear viscoelastic (LVE) range of the neat resin. Then, dynamic tests from room temperature until 100 °C at 5 °C/min were performed to capture the gelation time and temperature of the resin. The same protocol was followed for the graphene-modified resins.

2.2.1 Quantified Dispersion Analysis

A MATLAB code was developed based on the work of Yourdkhani et al. [28] to process the microscopy images and generate a dispersion index between 0 and 100. Firstly, each greyscale microscopy image is converted to a black and white image where the white pixels represent the resin matrix, and the black pixels represent the graphene particles. Then, the mean minimum distance between all white pixels and their closest black pixels is measured using the equation below:

$$\mu = \frac{\sum_{i=1}^{N_m} d_i}{N_m} \tag{1}$$

where d_i is the minimum distance between each white pixels and closest neighboring black pixel and N_m is the number of white pixels in the image. Using the same image, two extreme scenarios are created by

rearranging the pixels; an ideal case, where there are no black pixels next to each other, and an agglomerated case, where all the black particles are next to each other. The mean distance value is then calculated for the two extreme cases denoted by μ_a and μ_i for the agglomerated image and ideal image, respectively.

The dispersion state of the original image can be quantified by normalizing the mean distance values of the original image with those of the ideal and agglomerated cases using Equation (2).

$$DI = \frac{\ln(\mu) - \ln(\mu_a)}{\ln(\mu_i) - \ln(\mu_a)} \times 100$$
(2)

where DI is the dispersion index and can be number between 0 and 100%. For an ideal case, the DI is 100% and as aggregates start forming in the matrix, the DI would decrease until 0 which is the worst case.

3 RESULTS AND DISCUSSION

Figure 2 shows the microscopy images of resin systems containing 0.5 wt% GB3X and GB0X at two stages after mixing at room temperature and at gelation. A qualitative observation only reveals that the particles in Figures 3(c) and (d) are smaller in size. But it is difficult to comment on how dispersion state change during the curing of the systems or in which system dispersion has decreased more.



Figure 2: Microscopy images of Dion system for 0.5 wt% graphene content: a) GB3X room temperature, b) GB3X gelation temperature, c) GB0X room temperature after mixing, d) GB0X gelation temperature.

Figure 3 depicts the trend of dispersion stability with gelation of the systems containing GB3X and GB0X (same samples as Figure 2) using the results of the quantitative dispersion analysis. The calculated DI for the system containing GB3X is 64.4% after mixing at room temperature which

decreases down to 62.9% at gelation at 84.6 °C. The DIs for the system containing GB0X is calculated to be higher, at 68.7% after mixing and 67.9% at gelation, respectively.



Figure 3: Dispersion evolution during curing of resins containing 0.5 wt% of GB3X and GB0X.

The particle size distribution histograms in Figures 4(a) and 4(b) confirm this dispersion degradation by showcasing the increase in the number of larger particles after gelation. For instance, in the system containing 0.5 wt% GB3X, the number of particles smaller than 500 μ m decreases from 6336 down to 6327 after curing while the number of particles in the range of [500-1000] μ m and [1000-1500] μ m increase by 16% and 42% which indicates particle entanglement and agglomeration during the curing of the resin.

The particle size distribution histogram in Figure 4(b) also confirms the less-severe reduction in the DI of system containing 0.5 wt% GB0X. The number of particles smaller than 500 μ m decreases by 10% and the number of particles in the range of [500-1000] μ m increase by 11%.



Figure 4: Particle size distribution of the samples (a) containing 0.5 wt% GB3X and (b) 0.5 wt% GB0X after mixing and at gelation.

A summary of all graphene contents is provided in Figure 5. The systems containing GB0X have higher dispersion indices after mixing at room temperature compared to the systems with GB3X. This trend is consistent after curing of the samples, as well. Another important observation is the increase of DI with addition of graphene. This is validated by the basis of DI calculation methodology which is the minimum distance between white pixels and closest black pixels. As the graphene content increases, the

distance between white pixels and black pixels decreases and subsequently, a higher DI is calculated. Thus, when comparing samples with different nanofiller content, the particle size distribution histograms is crucial to make proper conclusion.



Figure 5: Comparison of DIs between the systems containing GB3X and GB0X at two stages (a) after mixing at room temperature and (b) at gelation

The results of the rheology tests are summarized in Figure 6. It is observed that the addition of both graphene types increases the gelation time of the nanomodified resins while this phenomenon is more pronounced for the GB3X system. This observation is justified by free radical scavenging activity of carbon-based nanomaterials in unsaturated polyester resins [18], [29], [30]. Another reason for the delay in gel time is linked to physical interception and steric hinderance of reactive sites of polymer chains in the presence of graphene particles [31], [32]. The smaller lateral size of GB0X causes less disruption of polymer chains which results in less delay compared to the systems containing GB3X.

It is important to note that the maximum delay observed in resin gelation is approximately 1.5 min for the system with 0.75 wt% GB3X at 5 °C/min heating rate. In pultrusion processes, the heating rates are much higher (>30 °C/min) [33], hence, the difference in gel time of the systems containing graphene would be in the order of a few second. Research has also shown that in a pultrusion die, the resin gels

between 36% to 77% of the die length depending on the pulling speed which corresponds to time exposed to high temperature. Thus, all resin systems would be fully gelled when exiting the die regardless of the graphene loading [34]. For instance, at a pulling speed of 5 mm/s, the gelation window would shift ~ 25 mm with the addition graphene.



Figure 6: Variation of gelation time of systems with addition of GB0X and GB3X at different contents with a heating rate of 5 °C/min.

A comparison between the dispersion stability of nanoparticles in this study and a similar study by Yourdkhani et al. [35] on an epoxy system with carbon nanotube loading can bring an insightful discussion about the parameters that affect the dispersion stability. The first parameter is the resin rheological behaviour. Unsaturated polyester resins, unlike epoxy systems, do not experience a substantial drop in viscosity with increasing temperature as shown in Figure 7. As lower viscosity resins facilitate particles mobility and re-agglomeration the dispersion degradation is greater in the epoxy system used by Yourkhani et al. since the viscosity drop is more significant. Furthermore, higher heating rates cause greater viscosity drops, hence, larger dispersion degradation.

Another important parameter affecting the dispersion stability is the gelation time. In systems with longer gelation times, nanoparticles have more time to re-arrange and re-agglomerate. In this study, the systems containing GB3X have higher gelation times (Figure 6) and consequently, experience greater loss in dispersion. Looking at the dispersion stability of the systems in Figure 3, the total loss in dispersion index of the system with 0.5 wt% GB3X is 1.55 % while this loss for the GB0X system is only 0.78 %. Thus, longer gelation times can deteriorate the dispersion stability.



Figure 7: Rheological measurements for the system containing 0.5 wt% GB3X with a rate of 5 °C/min.

4 Conclusion

Two similar industrial grade graphene powders with different lateral sizes were used as nanofiller in an unsaturated polyester resin to study the effect of lateral size on the gelation and dispersion of the nanocomposites. Both systems had a small inhibiting effect on the gel time of the resins, while this effect was more enhanced in the system containing GB3X. The delay is correlated with free radical scavenging activity and steric hinderance of graphene powders in the resin.

The real-time in-situ dispersion analysis methodology made it possible to control the nanofillers dispersion in the resin matrix at all stages after mixing at room temperature until resin gelation. Simultaneously, a quantitative dispersion analysis method was developed to achieve objective and consistent information about the dispersion of the graphene powders. The results were consistent with the qualitative observation of microscopy images but were able to provide systematic data throughout different graphene contents and types. The results showed that the systems containing GB0X had higher dispersion indices compared to the systems with GB3X. For the systems with 0.5 wt% GB3X and GB0X, particle size distribution histograms were created to provide a more in-depth analysis of dispersion indices. The histograms were in agreement with the quantitative analysis showing a decrease in the number of smaller particles and increase of larger particles.

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