Silane functionalization effects on dispersion of alumina nanoparticles in hybrid carbon fiber composites

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Hybrid carbon fiber reinforced polymer composites are a new breed of materials currently being explored and characterized for next generation aerospace applications. Through the introduction of secondary reinforcements, such as alumina nanoparticles, hybrid properties including improved mechanical properties, such as fracture toughness, and stress-sensing capabilities can be achieved. However, problems with manufacturing can arise resulting from the inherent variability of the manufacturing techniques along with the tendency for the nanoparticles to agglomerate. Photoluminescence spectroscopy is used in order to investigate the effects of adjustments to manufacturing processes and silane functionalization on particle dispersion and sample consistency between samples of the same type. This work finds that application of surface treatments on the nanoparticles improved their dispersion, with the reactive treatment providing for the most consistency among samples. Improvements to dispersion and increased consistency resulting from specific changes in manufacturing processes were shown numerically. Findings provide manufacturing recommendation to achieve optimum dispersion and mechanical properties of the composite. © 2018 Optical Society of America

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1. INTRODUCTION

Carbon fiber composites are highly suitable materials for aerospace applications due to their high strength to weight ratio [1]. However, limitations to the improvement of carbon fiber composites exist resulting from the two-component nature which forces trade-offs between properties of the fiber and matrix [2]. For next-generation applications, the usage of multiple reinforcements for the creation of hybrid carbon fiber composites are necessary in order to provide for a greater spectrum of selectable material properties. Carbon fiber composites with additional reinforcements have been explored in various configurations including the usage of multiple fiber types [3], the addition of carbon nanotubes [4], and the use of various other particulate inclusions [5-8]. Alumina (Al₂O₃) particles are promising as a hybrid reinforcement as they improve mechanical properties such as elastic modulus and fracture toughness. Higher volume fractions of nanoparticle inclusions provide greater improvements to mechanical properties such as fracture toughness [9], crack initiation toughness [10], elastic modulus [11] among others [12, 13]. However, these improvements are highly dependent on the successful dispersion of the inclusions as a homogeneous distribution of reinforcement provides better mechanical performance [14]. Poor filler dispersion results in the presence of agglomerations which act as stress concentrators [15]. To fully maximize the benefits of added reinforcements it is necessary to address the issue of particle agglomeration.

Silane coupling agents originated as a surface treatment are used to strengthen the interface between fiber and matrix in glass fiber reinforced polymer composites [16]. Recent work has shown improvements in the dispersion of alumina nanoparticles within a polymer matrix, improving elastic modulus and tensile strength, through surface modifications with silane coupling agents [17]. The improvement in dispersion of particles arises from the reduced particle to particle interactions that contribute to agglomeration [18]. In addition to providing for improved particle dispersion, the chemical bonding of the particulates to
the matrix can also provide for a higher particle-matrix interfacial strength when compared to unmodified particles [14]. Another type of particle surface treatment known as non-reactive coupling agents are also explored due to their benefits to particle dispersion through decreasing particle surface tension which in turn decreases particle interactions at the potential cost of a weakened particle/matrix interface [19].

Traditional methods for dispersion characterization in various materials involve the development of quantities which describe dispersion based on microstructural analysis [20]. These values can result from quantifying relative particle size [21, 22], comparing distances between features [23], and others [24–28]. For atomic force microscopy (AFM), the surface of the sample needs to be flat and smooth which is difficult to achieve in carbon fiber composites. Besides this, micrographs provide characteristic of a very small area whereas the dispersion may vary significantly from place to place across the structure. While these values provide for robust dispersion characterization, it is still necessary to characterize the effects of non-homogeneous reinforcement distributions on the mechanical response of those materials. This characterization is possible using the photoluminescent properties of the alumina particles embedded within the examined hybrid carbon fiber composites. The stress response of the photoluminescent emissions of chromium-doped alumina has been extensively explored and characterized [29–34]. The same photoluminescent response allows for the local particle concentration to be compared across the surface of the sample through relative emission intensities. The comparison of local particle dispersion along with local mechanical response will provide better understanding of composite behavior under load.

Photoluminescence spectroscopy for dispersion characterization has previously been used to explore particle dispersion in polymer nanocomposites [35, 36] and was further developed for the characterization of dispersion in hybrid carbon fiber composites [37]. As a technique, photoluminescence spectroscopy is highly desirable due to the possibility of capturing high spatial resolution measurements combined with the ability to scan large areas [38, 39]. This results in extremely large datasets which can more easily provide statistically significant and representative information. Analysis methods for quantitatively comparing these large datasets require further refinement. This work introduces analysis of photoluminescence contour maps for the effects of particle surface treatment.

2. EXPERIMENTAL PROCEDURE

A. Sample Preparation

A1. Hybrid carbon fiber reinforced polymer composite samples

To allow for measurements based on photoluminescence, alumina nanoparticles were included as a secondary filler in the carbon fiber composites. The nanoparticles used were α-alumina with an approximate grain size of 40 nm and an average particle size of 150 nm [40]. These were supplied as a powder by Inframat Materials LLC, Connecticut, USA. The epoxy matrix was Epikote 862 (a Bisphenol F and epichlorohydrin based resin) cured with a stoichiometric quantity of Epikure 3402 (an aromatic di-amine based curing agent) supplied by Momentive Materials, Bolton, UK.

Silane coupling agents were applied as surface coatings to the nanoparticles in order to improve the dispersion. Two different types of silane coupling agents were used, supplied by Sigma-Aldrich, Gillingham, UK. γ-glycidoxypropyltrimethoxysilane was used as a reactive silane coupling agent (RSCA) and γ-glycidoxypropyltrimethoxysilane was used as a non-reactive silane coupling agent (NRSCA). The reactivity of the surface treatments relates to their interactions with the epoxy matrix. The RSCA reacts chemically with the matrix via its amino groups and the epoxide groups of the matrix. The NRSCA treatment does not have the compatible organofunctional groups needed for matrix bonding. Both treatments contain the necessary silanol groups to react with hydroxyl groups in order to bond covalently with the surface of the alumina nanoparticles (Figure 1).

Fig. 1. Schematic for bonding mechanism between silane coupling agent (SCA) and epoxy

The alumina nanoparticle-resin mixture was prepared in an as-required batch process whereby the necessary quantity of nanoparticles was weighed into a large beaker. The silane coupling agent was then added directly to the particles and the mixture was stirred by hand until complete wetting of the particles was observed. The epoxy resin was then added to the system and stirred for 15 minutes at 150 rpm at a processing temperature of 50°C. Following the mixture was homogenised using an ultrasonic processor (Cole Parmer, London, UK). This process improves dispersion of particles suspended in a liquid solution through ultrasonic vibrations. These vibrations cause cavities to form in the mixture and upon their collapse provide a force which is capable of breaking up large particle agglomerations and dispersing particles more evenly throughout the solution [41]. The samples were sonicated for 1 hour in batches of 250 ml. The process generates significant levels of heat and thus the sonication was carried out with the mixture partially submerged in an ice-bath to prevent excessive temperature rises, which would degrade the resin. The particles in the sonicated mixture were observed to remain in suspension over a number of days. Following the sonication, the nanoparticle-resin mixture was thoroughly degassed in a vacuum chamber at a temperature of 50°C. Finally, a stoichiometric quantity of hardener was added, mixed mechanically for 15 minutes and degassed.

Unidirectional carbon fiber sheets (UT-C400, Marineware, UK) with a tow size of 12k were used for all composite manufacture [42]. As described in Figure 2, the samples were manufactured using resin infusion under flexible tooling (RIFT) with the fiber direction parallel to the direction of flow of the polymer [7]. Eight plies of carbon fiber were laid up and this produced a carbon fiber plate with a nominal thickness of 3 mm. RIFT is an effective method that allows for the infusion of the nanoparticle-resin mixture and provides for a relatively void-free composite. Alumina weight fractions of the matrix were maintained at values of either 6, 9, or 12 wt% in the resin were used. The samples were cured for four hours at 120°C with a post cure for a further
four hours at 170°C. Three particle loadings, 6 wt%, 9 wt% and 12 wt% with RSCA, NRSCA or untreated surface nanoparticles are studied in this work. Two samples from each of nine categories were tested providing a total of 18 samples. Each set was cut from different locations from the same composite sheet using a waterjet cutter. The fiber volume fractions of the composites were measured using optical microscopy of cross-sections. Carbon fiber volume fractions of 57 ± 3% were obtained for the finished composites.

A.2. Alumina-epoxy compression test samples

Bulk polymer plates were manufactured, by preparing the mixture of resin, hardener and 9 wt% of alumina (with RSCA or NRSCA) as for the fiber composite samples. The resin mixture was then poured into a pre-heated steel mould coated with release-agent (Frekote 700-NC, Loctite, UK) and cured using the composite cure cycle. The bulk polymer plates were removed from the mould, and cut to size for testing. Three samples from each configuration were prepared for plane-strain compression test.

B. Experiments

B.1. Photoluminescence Measurements

The photoluminescent properties of alumina arise from the chromium (Cr$^{3+}$) substitutional impurities within the crystal structure [34]. When the material is excited with a light source, two distinct spectral lines, known as R-lines, are emitted at approximate wavenumbers of 14403 cm$^{-1}$ and 14433 cm$^{-1}$ corresponding to R1 and R2 [43]. The intensities of these emissions are then related to the concentration of alumina particles at each collection point [37]. By comparing local intensity across the surface of a sample, it is possible to measure the homogeneity of particle dispersion. As the ratio of R2 intensity and the total intensity of both R-lines are almost constant (0.3-0.4), either of the intensities can be used to characterize the dispersion (see Visualization 1). In this work, the intensity value for each local point is characterized by the R1 intensity, the higher intensity of particle dispersion. As the ratio of R2 intensity and the total intensity of both R-lines are almost constant (0.3-0.4), either of the intensities can be used to characterize the dispersion (see Visualization 1). In this work, the intensity value for each local point is characterized by the R1 intensity, the higher intensity of particle dispersion. The portable piezospectroscopy system [44] used in the experiments described here, combines a Princeton Instrument Pixis 100 charged coupled device (CCD), Acton SP2150 spectrometer, and an InPhotonics Inc. RPB Raman probe. The light source used was a 532 nm diode-pumped solid-state (DPSS) laser and outputted approximately 14 mW from the end of the spectroscopic probe. In order to provide the intensity maps, an X-Y-Z stage was used in conjunction with the CCD to collect measurements in a snake scan pattern. Photoluminescence data were collected in a 10x40 mm$^2$ rectangular region with a spatial resolution of 200 μm on the surface of the sample resulting in 10,000 total datapoints per photoluminescence map. Collection parameters were adjusted between samples in order to maintain the emissions at an intensity below the CCD saturation intensity and to maintain a signal to noise ratio (SNR) above a minimum threshold. All resulting emission spectra were processed using a least squares fitting algorithm explained elsewhere [38]. Processed spectra were normalized to the experimental parameters through the laser fluence [45]. The laser fluence, $F$, is defined as:

$$F = \frac{\text{Laser power} \cdot \text{Collection time}}{\text{Laser spot size}}$$

(1)

As a result of the constant power of the laser, some data points had spectral emissions with low signal to noise ratios resulting in inaccurate results from the least squares processing. The criterion for establishing what constituted unsatisfactory data was based on a minimum R-squared threshold where the minimum value was found through inspection of the R-line spectra. Figure 3 shows the maximum and the minimum signal quality for 6 wt% RSCA and NRSCA samples for side A. Five percent of total data points fall below this threshold value and appear as black regions in the contour maps.

![Fig. 3. Maximum and minimum signal quality R-lines for 6 wt% RSCA and NRSCA samples (side A)](image)

B.2. Plane-strain compression test

Plane-strain compression tests were performed on bulk polymer samples to understand the yield behavior, since the materials fail before yield in uniaxial tension. The method described by Williams and Ford [46] was followed, using 3 x 60 x 40 mm$^3$ samples. These samples were loaded in compression between two parallel, 12-mm-wide platens at a constant displacement rate of 0.1 mm/min. The results were corrected for the compliance of the test machine and test rig. The yield stress, $\sigma_{yc}$, was defined as the first region of the true stress versus true strain response with a zero gradient.

3. RESULTS AND DISCUSSION

The results for the previously explained experiments are presented in the following sections. In the first section, the pho-
Photoluminescence measurements are used to construct intensity contour plots. These plots are used to qualitatively as well as quantitatively make conclusions on the dispersion of the alumina particles in the different samples. Findings are presented in these sections regarding the effects of the particle surface treatment on the dispersion of particles. In the compression test results, particle dispersion characteristics were compared with the compressive yield stress results.

A. Representative photoluminescence results for examined specimens

Figures 4 and 6 show the dispersion maps for one set of samples from the combinations of RSCA, NRSCA and untreated surface alumina nanoparticles with 6, 9 and 12 weight percentage in the composite. Each pixel represents the normalized RI intensity of the photoluminescence emissions (R-line) at the examined location. A homogeneous dispersion of particles results in a photoluminescence contour map where there is low variation in the intensities measured across the surface of the sample. Alternatively, samples with a poor dispersion of particles result in a photoluminescence contour map where there is high variation in the intensities, usually coupled with large intensity gradients separating particle-rich zones and particle-depleted zones. The following section will outline the dispersion patterns for the sample with the untreated particles. Afterwards, the effects of the surface treatments will be explored utilizing the sample with untreated particles as a baseline.

A.1. Characteristics of dispersion in samples with untreated particles

The samples with untreated particles (Figure 4) tend to provide the largest amount of agglomerations among all weight percentages, except in the 9 wt% sample. This is seen through the large intensity variations which dominate the surfaces in the 12 wt% and 6 wt% samples. By examining these particle dispersion contour maps, it can be observed that, the 9 wt% sample has the best dispersion of particles for the untreated set. The samples also exhibit low concentration lines which run diagonally in both directions. These low concentration lines are also seen in the surface treated samples, presented in future sections, and are artefacts of the manufacturing process. They share the same pattern as the distribution media used in the RIFT process; and as such, points where the fibers of the distribution medium impinged on the sample show lower concentrations of particles due to a reduced thickness of resin on the surface of the fiber composites. This seems to be unaffected by the presence of surface treatments, future work will consider testing several distribution media in order to improve the dispersion of particles.

A.2. Surface treatment effects on the dispersion of particles

For dispersion characterization, it is also necessary to address how the particles distribute through the thickness of the samples as a result of the manufacturing process. One rough measurement of the through-thickness distribution of particles is by the comparison of the difference in overall intensity between the faces of the samples. It is expected that the bottom face (side B) of the sample will have a higher overall intensity due to particle sedimentation. Similar intensities on both sides of the samples indicate that this settling is mitigated, which is preferred in order to maintain constant material properties through the material. Examining the photoluminescence contour maps for the sample with untreated particles, it is evident that there exists a significant overall intensity mismatch in the 12 wt% and 6 wt% samples with a majority of intensity on side B, see Figure 2. The 9 wt% sample does not show this behavior as clearly. The differences in particle dispersion and sedimentation can be explained by varying flow properties of the particle-loaded resin with different particle loadings. The 9 wt% particle loading represents a potentially optimal flow property that resulted in more homogeneous dispersion and lower sedimentation. Figure 5 shows bright-field optical microscope images of different spots at through thickness cross-section of 12 wt% untreated sample where black spots represent alumina nanoparticles. These images were taken using an optical microscope (‘AXIO Scope’ from Carl Zeiss, Germany) at 20x magnification and provides information on the presence and sedimentation of alumina nanoparticles through thickness. The effects of surface treatments on this behavior are also examined in future sections.

Fig. 4. Dispersion maps for set 1 of samples with untreated particles at all weight percentages.

Fig. 5. Bright-field optical microscope images from 1 to 6 corresponding top to bottom through thickness cross-section of 12 wt% untreated sample. Black spots represent alumina nanoparticles.
This indicates that the adjustments to particle surface treatment mitigate the sedimentation effects and help to maintain a better distribution of particles through the sample.

It is noticed that the trend between weight percentage and dispersion is different between the samples with treated and untreated particles. In the samples with untreated particles, the most homogeneous sample is the 9 wt% which is significantly better than the 6 wt% and 12 wt%. Alternatively, the treated samples are the most homogeneous with 6 wt% of particles. It is again hypothesized that the differing trend for homogeneity between the untreated and treated samples results from differing flow properties [47] of the particle-loaded resin which can impact the infusion rate [48] along with the specific flow media used [49] ultimately affecting particle dispersion. It is worthwhile to develop a method for quantifying the dispersion, to isolate the effects of the manufacturing parameters on it. Initial work on such a method is presented in the following section.

B. Quantitative analysis of photoluminescence data

Photoluminescence spectroscopy collects data on the concentration of particles across the surface of the sample in a grid pattern where the size of each grid is related to the spatial resolution of the scan. As a result, it is possible to convert the spatial particle concentration data, which takes the form of the previously presented contour maps, to a probability density function. The variance to mean ratio (VMR) of each probability density function is then calculated as a way to compare the spread of data around the mean of each distribution similar to statistical methods previously developed [50]. The equation for the variance to mean ratio is shown in equation 2, where \( \sigma^2 \) is the variance and \( \mu \) is the mean:

\[
VMR = \frac{\sigma^2}{\mu}
\] (2)

Distributions with smaller VMRs have a more random distribution of species across the investigated region [51]. An example of this is shown in Figure 7, where the 12 wt% NRSCA has a larger VMR in plot b which corresponds to greater inhomogeneity of the photoluminescence emissions as seen in Figure 6. The random standard for the distribution is based on the Poisson’s distribution which has a VMR of 1 and is used to model randomly-distributed data. A VMR of 0 indicates a variance of 0 which is representative of a homogeneous distribution of examined parameter. Calculating these values for each distribution and plotting them allows for quick numerical comparisons of the dispersion of nanoparticles within large numbers of samples. The VMRs for the tested samples are plotted in Figure 8. With point-by-point scanning process, photoluminescence data of 10,000 points was collected for each side of a sample, which implies that, a dataset of 40,000 data is considered for this VMR study concerning each configuration.

**Fig. 7.** Comparison of intensity distributions to representative random distribution. a) 9 wt% NRSCA and b) 12 wt% NRSCA

**Fig. 8.** VMR plotted for set 1 and set 2 of hybrid carbon fiber composite samples. RSCA sample shows the most consistency between weight percentages and sets (VMR = 0 is desired).
dispersion with the application of either surface treatment. For untreated 6 wt% and 9 wt% samples, though the photoluminescence contour maps show better homogeneity for the 9 wt% sample, in VMR study, they fall in the same range. In the case of the 9 wt% samples, the samples with untreated particles actually report the most homogeneous distribution of particles with the VNR analysis in Figure 8. The dispersion of the treated particles showed no significant differences to that of the untreated particles when the experimental variation is taken into account. It is also noted that the RSCA treatment provides for the most consistent dispersion of particles independent of weight percentage. The non-reactive surface treatment will cap off some of the residual functional groups on the particles that would cause agglomeration, thus reducing the effect. The length of the chains stops the particles getting close enough together for the residual groups to be able to interact. Hence it reduces particle to particle interaction. This effect is further reduced with the reactive surface treatment. This form of bonding does not occur in the non-reactive surface treatment, which could be an explanation for why the dispersions of the NRSCA treated particles are not as independent of weight percentage.

C. Compressive yield strength of alumina-epoxy

The values of the compressive yield stress for the bulk polymer samples, measured in plane strain compression, are shown in Table 1. Numbers presented in the table are mean values and rounded to zero decimal places. A value of 102 MPa was measured for the unmodified epoxy, and this value was not significantly changed when 9 wt% of alumina treated with RSCA was added. However, when the NRSCA was used the yield stress decreased to 94 MPa. The work of Víróos and Pukánszky [52, 53] has shown that when there is low interfacial stress transfer the compressive yield stress of particle-modified epoxy polymers decreases. This was confirmed by Hsieh et al. [54], who measured the yield stress of a range of epoxy polymers containing 20 nm diameter silica nanoparticles and correlated debonding of the particles during fracture, due to poor matrix to particle adhesion, with the decreased yield stress. This corresponds to the dispersion results presented here which shows that NRSCA has poor dispersion and which has been attributed to lower matrix to particle adhesion.

Table 1. Effect of silane on compressive yield stress of alumina-modified bulk epoxy polymers

<table>
<thead>
<tr>
<th>Functionalization</th>
<th>Alumina content (wt%)</th>
<th>$\sigma_{yc}$ MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control epoxy</td>
<td>0</td>
<td>102 ± 0</td>
</tr>
<tr>
<td>RSCA</td>
<td>9</td>
<td>101 ± 0</td>
</tr>
<tr>
<td>NRSCA</td>
<td>9</td>
<td>94 ± 3</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

This work examines the effects of silane coupling agents on the dispersion of particles in hybrid carbon fiber composites. Nine sets of samples were manufactured using resin infusion under flexible tooling (RIFT) with differing weight percentages of particles and differing particle surface treatments. These samples were then analyzed utilizing photoluminescence spectroscopy for the creation of photoluminescence contour maps. Comparisons of these contour maps result in three primary findings.

The first finding is that the relationship between weight percentage and particle dispersion is affected by the surface treatment. The samples with untreated particles have a maximum homogeneity at a particle loading of 9 wt% where the samples with treated particles have a maximum homogeneity at a particle loading of 6 wt%. This difference in behavior may result from the effects of the surface treatments on the flow properties of the resin. In each weight percentage, surface treatments improved the dispersion of the particles and reduced sedimentation.

The second finding of this paper relates to the effects of the particle surface treatment on the overall dispersion of the particles. It is found that in the 6 wt% and 12 wt% samples, the application of a surface treatment results in significant improvements to particle dispersion. The final finding from the contour maps relates to the sedimentation of particles. Through comparisons of both sides for each set of samples, clear sedimentation can be seen in the 12 wt% and 6 wt% samples with untreated particles. The improved dispersion resulting from the application of the surface treatment is coupled with decreased particle sedimentation.

A method to numerically quantify the dispersion of particles for each sample was conducted using the data from photoluminescence contour maps and the calculated dispersion values showed similar findings. Regardless of weight percentage, the reactive treatment results in very similar dispersions of particles throughout the sample. Compression strength measurement validates the findings of dispersion in regards to NRSCA showing poor dispersion due to poor matrix to particle adhesion. The results of these tests have applications in the systematic improvement of composite manufacturing processes for the reduction of the inherent variability in order to maintain the homogeneity of material and mechanical properties of hybrid nanocomposites and consequently the integrity of components manufactured from them.

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