VISCOELASTIC DAMPING PERFORMANCE AND RHEOLOGICAL BEHAVIOUR OF CUP-STACKED CARBON NANOTUBE MODIFIED EPOXY NANOCOMPOSITES WITH RE-AGGLOMERATION NETWORK

Xiao-Chong. Zhang¹, Fabrizio. Scarpa¹, Ronan. McHale² and Hua-Xin. Peng³

¹Advanced Composites Centre for Science and Innovation (ACCIS), Department of Aerospace Engineering, University of Bristol, Queen's Building, Bristol, BS8 1TR, United Kingdom. Email: joanne.zhang@bristol.ac.uk, f.scarpa@bristol.ac.uk, web page: http://www.bristol.ac.uk/composites/

²Thomas Swan & Co. Ltd., Rotary Way, Consett, County Durham, DH8 7ND, United Kingdom. Email: rmchale@thomas-swan.co.uk, web page: http://www.thomas-swan.co.uk/

³Institute for Composites Science Innovation (InCSI), School of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, PR China. Email: hxpengwork@zju.edu.cn, web page: http://www.zju.edu.cn/english/

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ABSTRACT

For over a decade, carbon based nanotubes have been considered as nano scaled fillers for potential reinforcement for polymers due to their exceptional mechanical properties. Re-agglomeration is a natural phenomenon in which the initially dispersed carbon nanotubes (CNTs) have the natural tendency to form a secondary agglomeration network during the subsequent curing process. Its morphological characteristics can vary for different filler content, processing time and temperature, thus influencing the physical and mechanical properties of cured nanocomposites. This work describes how to tailor the morphology of such re-agglomerations of cup-stacked carbon nanotube (CSNT) in an aerospace grade RTM6 epoxy. Loss and storage modulus of cured sample and the rheological behavior of uncured suspensions under amplitude sweep within the linear viscoelastic range were examined to identify the effects of the presence of a hierarchical filler network. Manufacturing parameters like the filler content, the melt temperature and the curing time have been studied. The results indicate that a controlled secondary re-agglomeration network may provide superior mechanical and viscoelastic properties in cured nanocomposites.

1 INTRODUCTION

The increased demand of high performance damping material for vibration and noise control in various industries has led to the evaluation of dissipation-efficient and light weight polymer-based nanocomposites for this type of applications[1][2, 3]. Among various nano-scale fillers, carbon nanotubes (CNTs) tend to exhibit Young’s modulus around 1 TPa and tensile strength over 100 GPa[4]. The combination of extremely large specific area and low mass density in CNTs allows efficient energy dissipation through interfacial sliding [2, 5-13], making CNTs a material of choice for potential vibration damping applications.

Experimental studies and numerical modeling have been carried out in recent years regarding the interfacial sliding mechanism for energy dissipation purposes. Suhr and co-workers [5, 14, 15] have demonstrated that polymer-nanotube interfacial sliding could be used for damping enhancement; a weight fraction of 1-2% nanotubes brought in several orders of magnitude increase in loss modulus of the composite system. In a common polymer/nanotubes material system, the three common interface
couplings that are considered responsible for energy dissipation are polymer-nanotube, nanotube-nanotube interfacial sliding [2, 5, 8, 11, 13, 16, 17], and coaxial sliding of tube walls within MWNT or DWNTs [18]. Polymer-nanotube sliding is determined by the CNT/polymer interfacial bonding, whereas nanotube-nanotube sliding within agglomerations is closely related to the dispersion quality of the CNTs [2, 19]. The damping mechanisms for polymer/CNTs composites with a homogeneous or heterogeneous dispersion can be therefore very different. In this context, it is widely believed that a homogeneous dispersion with a strong interfacial bonding between matrix and nanofillers would effectively maximize the potential enhancement of the composite mechanical properties. Following the foot step of pursuing a homogeneous dispersion, many studies have reported successful routes of CNT surface treatment in order to design a favorable interfacial bonding between CNTs and the matrix [20]. However, even at CNT contents of 1 wt%, the agglomerations are almost inevitable due to the low mass density of the nanotubes and strong mutual van der Waals attractions. Mechanical and chemical dispersion processes like sonication and surface functionalization can only bring the dispersion to an acceptable degree. Maintaining a stable dispersion stage is also another challenge because of the re-agglomeration tendency of CNTs, several studies have reported the re-agglomeration phenomena of CNTs under high temperatures and cumulated time during the curing process [21-23]. The re-agglomeration mechanisms is still not well understood, and very few studies have been directed towards the comprehension of how re-agglomeration affects the composites mechanical and rheological properties.

The present work focuses on the impact of CNTs re-agglomeration on the damping performance and rheological behavior of a new material system constituted of cup stacked carbon nanotubes (CSNT) in a RTM6 epoxy matrix. The results will show that the energy dissipation appears to be highly dependable not only on the filler-matrix bonding conditions but also their re-agglomerated filler network structures. The re-agglomerations shown in this study with resin well wetted inside revealed a high CNT concentration region forming a hierarchical structure that changed the uncured suspension rheological behaviour thus, significantly contributed to the energy dissipation in a cured composites, making agglomerations assisted damping performance more evident.

2 EXPERIMENTAL PROCEDURE

2.1 Materials and fabrication of CSNT/RTM6 nanocomposites.

Cup stacked carbon nanotubes (CSNTs) Carbere® were supplied by GSI Creos Corporation, Japan. Unlike single-wall nanotubes (SWNT) and multi-wall nanotubes (MWNT) which have continuous graphene wrapped tube walls, CSNT obtained by floating reactant Chemical Vapor Synthesis method revealed that the stacking morphology of truncated conical graphene sheets exhibits an angle to the tube axis, and large portion of the graphene sheet edges are exposed to the apparent tube surface. A Transmission Electron Microscopy (TEM) image of such CSNT is shown in Figure 1. In this study, the CSNTs with 95wt% purity were used in the as-received state with diameter ranging between 80nm to 100nm, and aspect ratio of ~50 [24]. RTM6 provided by HexFlow® is a mono-component epoxy resin already degassed, specifically developed for aerospace and space applications with service temperature ranging from -60°C up to 180°C [25].

![Figure 1: TEM image of CSNT showing a large hollow core and tube ends [24].](image-url)
CSNTs were added directly into the resin, followed by shear mixing using a Silverson high shear mixer at 6000rpm. Round bottomed heat stirrer was employed to maintain the resin operating temperature of 80 °C. This was followed by high-intensity ultra-sonication with various sonication time from 15min to 60min with the aim of controlling the re-agglomeration structure.

The 1wt% CSNT composite mixture was injected into a flat plate mold at 120 °C for optimal surface quality, and cured at 180 °C for 2 hours according to the RTM6 data sheet [25]. Five specimens for each sample batches have been fabricated for statistical purposes. All cured specimens have a thickness of 2mm (±0.1mm), length and width of specimens are according to ASTM 5023-07 (DMA in flexural) test standard. Uncured CSNT/RTM6 suspension with CNT content varying from 0.1wt% to 1wt% have been fabricated for rheological tests.

2.2 DMA and rheological measurement.

Our previous study[3] have shown that nanocomposite with re-agglomerations revealed higher loss factor than that of the relatively uniform dispersed samples. To prove the superiority of re-agglomerates in damping, specimens undergone different sonication time (15min, 30min and 60min) were fabricated.

The amplitude dependency of the viscoelastic properties (storage modulus E’, loss modulus E”) of cured CSNTs/epoxy nanocomposites were evaluated using a Dynamic Mechanical Analyzer (DMA+/NUT/022/B-Metravib) under flexural testing mode. Specimens were subjected to dynamic strain at constant frequency of 1Hz over an amplitude range between 0.05% and 1.5% under 50°C.

Malvern Kinexys Pro+ rheometer were used in this study with a 4° cone angle 40mm diameter measuring geometry and 0.15mm working gap. The fabricated composites melt were cooled down to -20°C to “freeze” the initially dispersed filler structure. Each sample batch were tested under two environments: room temperature and 80°C (working temperature of RTM6) to form two kinds of filler structures (originally dispersed, and re-agglomerated). Samples to be tested under room temperature were initially undergone a continuous shear to destruct any existing microstructure and left at rest for 10 min to allow the polymer chain and CSNTs to be settled. Then a oscillatory test with shear strain sweeping from 0.01% to 1000% where conducted under frequency of 1Hz. Samples to be tested under 80°C were initially undergone a continuous shear and then left under 80 °C for 30min to allow the re-agglomeration network to form, then cooled down to room temperature before the strain sweep. Same oscillatory strain sweep were then conducted to determine the LVE range. Unmodified RTM6 resin were also tested under same temperatures for control purpose. Each sample batch were tested for 5 times under the same conditions for statistical reason. Determination of sample LVE range was based on the ISO 6721-10 standard.

3 RESULTS AND DISCUSSION

3.1 Viscoelastic damping performance with amplitude sweep

Figure 2 shows numerous large re-agglomerates in 15min-sonicated samples. As expected, agglomerates with diameter of ~10 to 20μm were observed (Figure 2a). It can be seen that, resin are well wetted between the adjacent tubes, demonstrating a good wettability. There could be two possible origins of the agglomerates: one came from the undispersed dense CNT bundles, the other is caused by the re-agglomeration phenomena at low resin viscosity when the temperature rises[22]. Figure 2 b and c serves as an evidence of the existence of the second type in the samples produced according to the fabrication method used in this study, proving that re-agglomeration is a thermally activated process. The higher energy gained during the ultrasonication and the curing processes, together with a significant reduction in resin viscosity due to temperature build-up have enhanced the mobility of the CNTs,
facilitating the re-agglomeration[26]. Long pull-out grooves are visible from Error! Reference source not found. 2c, indicating a weak bonding between the filler and the matrix.

Figure 2: SEM images of 15min-sonicated sample fracture surface.

Figure 3: Storage modulus (a), loss modulus (b), and loss factor (c) as a function of dynamic strain amplitude for samples contain 1wt%CSNT with different sonication time.
Figure 3 (a), (b) and (c) show the dynamic strain dependence of the storage modulus, loss modulus and loss factor, respectively. Figure 3(a) revealed that the elastic modulus of nanocomposites shows a marked decrease with increasing strain amplitude, indicating that the enhancing mechanism from load transfer is degrading at large strain level. This suggests that the critical shear stress had been reached and the CNT interfacial sliding had been activated thus degraded the load transfer [2]. This interfacial sliding is gradually facilitated with increasing strain, those tube aligned with the loading direction tend to fail first [2]. Corresponding to the storage modulus, the loss modulus (Figure 3 (b)) shows a significant increment with increasing dynamic strain. At the lower strain of 0.05%, both the pure epoxy and the CNT modified samples exhibit similar loss modulus, indicating that the stick-slip mechanism was not activated and all the specimens behaved alike. With the strain increased to 0.2%, the critical shear stress between filler and matrix has been reached, thus the stick-slip mechanism had been activated, and therefore a large jump in loss modulus was observed. At this point the specimens started to behave differently. With further increase in dynamic strain, pure epoxy and 60min-sonicated samples revealed a plateaus region at ~133MPa and ~123MPa, respectively. One similarity between these samples is that they both can be considered as homogeneous (here we consider the 60min-sonicated sample with few small agglomerates as homogeneously dispersed). This suggests that, at ~0.3% strain, the polymer chains in pure epoxy, and all the CNTs in 60min-sonicated sample have been activated for interfacial sliding, energy dissipation capability have reached the limit.

The 15min-sonicated and 30min-sonicated samples containing re-agglomerates behaved differently with a continuous increase in loss modulus within the 0.2%-0.5% strain range. After that, modulus of both samples dropped to ~128 GPa, at a comparable value with pure epoxy and 60min-sonicated samples. Figure 3 (c) shows the loss factor of all samples with increasing strain. With a lower storage modulus and the highest loss modulus, the 15min-sonicated sample with numerous large re-agglomerates revealed the highest loss factor, thus the best energy dissipation capability throughout the dynamic strain range. At 0.5% dynamic strain, it has a loss factor about 40% higher than that of the 60min-sonicated sample which has a fairly uniform dispersion.

3.2 Rheological Properties

Figure 4 shows the variation of storage modulus G’, loss modulus G” and loss factor tanδ with increasing shear strain. Both the original melt and the re-agglomerated melt revealed very similar storage modulus, loss modulus and hence loss factor, with G” > G’, indicating the polymer chain were unlinked, polymer rheological properties was unaffected by 30min heating. As the arrows pointed, the permissible maximum strain[27] (defined as the limiting value of the LVE range in terms of the shear strain) are very similar at ~500%. This result eliminates the possibility of resin curing during heating affecting nanocomposites rheological properties.
Figure 5: Strain amplitude sweep of 0.1wt% CSNT modified RTM6 resin under room temperature (a) and 80°C (b).

Figure 6: Strain amplitude sweep of 0.5wt% CSNT modified RTM6 resin under room temperature (a) and 80°C (b).

Figure 7: Strain amplitude sweep of 1wt% CSNT modified RTM6 resin under 80°C.

Figure 5, 6 and 7 shows the variation of storage modulus G’, G” and tanδ with increasing CSNT content from 0.1wt%, 0.5wt% to 1wt% respectively. These three concentration revealed 1900% increase
in storage modulus with increasing CNT content. Comparing the room temperature plot with the 80°C plot for each figure, one can easily observe that the suspension with re-agglomeration network (plot (b)) presents a ~50% higher storage modulus. This reinforces our previous findings that a re-agglomeration network with entangled nanofillers provides higher composites stiffness than a uniformly dispersed filler structure[3]. By comparing plot (a) and (b) in each figure, we observed that melt with re-agglomeration networks revealed a lower permissible maximum strain than that of the original melt at room temperature. This serves as another proof of the existence of the re-agglomeration network in the suspension. This re-agglomerated filler network is more sensitive to strain than that of a uniform dispersion causing storage modulus to drop at a lower strain. This finding can be further proved by comparing Figure 5(b), Figure 6(b) and Figure 7. With increased CSNT content the interparticle distances between dispersed CSNTs are reduced significantly making the re-agglomeration more remarkable with increasing entanglement and hence the permissible maximum strain shifted to a lower value.

4 CONCLUSIONS

This study demonstrated a successful route for the fabrication of CSNT/RTM6 nanocomposite with controlled heterogeneous CSNT dispersions (re-agglomeration in the present case). Increasing re-agglomerates number and size was observed with reduced sonication time and increased heating time. Unlike conventional nanotube agglomerates, re-agglomerates formed in this study have resin well infused within which is likely to be the cause of the pronounced contribution to the composite damping performance and rheological behavior. It is also suggested that a tailored heterogeneously dispersed re-agglomerations network could be more effective in enhancing overall mechanical and damping performance of nanocomposites.

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