Viscosity of CNT Loaded Epoxy Resin

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ABSTRACT

The processing of fibre reinforced carbon nanotube (CNT) loaded polymer composites (nanocomposites) requires that CNTs be mixed (or loaded) into the polymer prior to impregnating the fibres to fabricate a nanocomposite. The fabrication process uses vacuum-assisted resin transfer moulding (VARTM), which is complicated due to the increase in viscosity of CNT loaded resin. The goal of this paper is to experimentally characterize the viscosity of a CNT loaded epoxy resin, with different weight percentages and shear rates. The maximum viscosities measured for the samples were: 800 cP for 0.2 %wt., 750 cP for 0.4%wt., and 890 cP for 0.6 %wt. All samples exhibited shear thinning behaviour as the viscosity decreased with increased shear rates.

KEYWORDS: Carbon nanotubes, viscosity, epoxy.

1. GENERAL INTRODUCTION

Carbon nanotubes (CNTs) are a unique class of materials with measured mechanical properties approaching theoretical values; particularly tensile properties: tensile strength is in the range of 30 GPa to 150 GPa and elastic modulus is about 1.0 TPa, with exceptional resilience and large (albeit nonlinear) deformation before failure [1]. The source of these extraordinary properties is the fundamental structure of the material at the molecular level. The hexagonal graphitic form of carbon grows in such a way that it curls into a tubular shape of a few nanometres in diameter, with the basal planes oriented radially around the tube [2]. It is this preferential and regular arrangement of the individual graphitic molecules that gives the nanotubes their great tensile mechanical properties. These materials also possess superior electrical and thermal properties with thermal conductivity known to be twice that of diamond and electrical conductivity one thousand times greater than that of copper [3]. These enhanced properties make CNTs ideal fillers for polymers because they can significantly enhance the properties of such materials when used to form a nanocomposite, even at relatively low CNT filler loadings (i.e., concentrations).

Growing CNT using chemical vapour deposition (CVD) is most affected by reaction conditions such as furnace temperature, pressure of the vaporized carbon source (hydrocarbon), purity and flow rate of the carrier gas, and residence time of the thermal decomposition. Based on variations of these production conditions, two different types of CNTs can be grown: multi-wall carbon nanotubes (MWCNTs) and single-wall carbon nanotubes (SWCNTs). The first class of CNTs (MWCNTs) was discovered by Iijima in 1991 [4], and is the preferred filler for nanocomposites because its production costs are lower than those for SWCNTs [2]. MWCNTs have an ideal geometry, $10 - 15$ nm outside diameter, $2 - 4$ nm inside diameter, and $10 - 20$ μm length; their walls contain about 15 graphene layers (each being a single-atom in thickness). This geometry yields a high CNT aspect-ratio, which when coupled with the CNT's graphitic and defect-free structure gives CNTs their extraordinary mechanical (tensile strength and modulus), thermal (conductivity, glass transition temperature, and thermal decomposition temperature), and electrical (conductivity) properties. To transfer these extraordinary properties to nanocomposites, the CNTs must be evenly distributed throughout the polymer matrix; and must also provide adequate percolation and surface interaction with the polymer matrix [5,6].

Because of their high surface area and high aspect-ratio (length-to-diameter), as well as the strong attractive forces between the nanotubes, CNTs tend to intertwine and agglomerate easily, which result in large resin rich pockets in the nanocomposite. While geometry of the CNTs allows greater interface interaction and load transfer, the distance between the individually dispersed nanotubes becomes so small that the polymer molecules cannot pass between them [7,8]. Therefore, the most important factor in fabricating nanocomposites is uniform dispersion of the CNTs in the polymer matrix. To prevent CNTs from agglomerating, two approaches may be followed: i) use proper mixing techniques or ii) functionalize the CNTs (alter their surface chemical composition to enhance compatibility with the resin). Unfortunately, functionalization of CNTs destroys favourable electrical properties of nanocomposites. Also, conventional blending and mixing shearing forces are ineffective in dispersing unmodified CNTs. Therefore, innovative dispersion methods must be employed to uniformly disperse unmodified CNTs. These methods include microfluidizing, sonication, high shear mixing, surfactant addition, chemical modification and wrapping the nanofibers with polymer chains and solution casting, spin casting, melt spinning and extrusion processing; all of which affect the resin's viscosity. In this paper, we evaluate the viscosity of CNT loaded resins that have been mixed using the microfludizing process, which is the most effective process for uniformly dispersing CNTs.

2. OVERVIEW OF CNT LOADING (MIXING) PROCESS

The resin system used for this study was Part A SC-780 epoxy, which is a clear, two-phase toughened, low viscosity epoxy system developed specifically for the VARTM manufacturing processes. To conduct the viscosity measurements, the resin was loaded with multi-walled carbon nanotubes (MWCNTs) produced by catalytic chemical vapor deposition (CCVD) in powder form. This MWCNTs (or CNTs) were loaded (mixed) into the resin using a microfluiding apparatus (see **Figure 1**). This apparatus acts as a pump that forces material through a very small orifice creating shear forces, impact, and cavitation to deagglomerate and disperse CNTs into the resin. This high energy intensity process is the most effective approach to uniformly disperse CNTs throughout the resin. This process is also ideal because it is continuous, repeatable, and scalable. The apparatus is proprietary and has many components that maybe interchanged to optimize the dispersion of CNTs. The key component

for optimal dispersion is the interaction chamber; a z-chamber was selected for this study based on manufacturer recommendations. This chamber is a micro reactor that uses high flow velocities and shear to mix the CNTs into the resin. If the desired distribution of CNTs is not achieved during the initial pass, additional passes can be conducted to achieve the desire CNT dispersion. However, additional passes expose the CNTs to the energy of the system, which results in damage to the CNTs as they pass though the Microfluidizer, decreasing the mean tube length. In fact, the median particle size of CNTs can decrease from 0.892 µm to 0.254 µm, [9].

Figure 1. Modified M110-Y microfluidizer apparatus.

The required CNT loading (*CNT* wt%) can be determined using the following equation:

$$wt\% = \frac{CNT}{CNT + R + H}$$

Where,

CNT is the final weight of the CNTs,

R is the final resin weight, and

H is the weight of the hardener.

For this study, no hardener was used, so *H* is zero. One critical step in the preparation of the samples is loading the CNTs into the resin. In order to safely add powder CNTs to the resin, the loading process must be conducted inside a glove box, (see **Figure 2**). This is done by placing the required resin in a Nalgene container and adding the required CNTs. The CNTs must be stirred to prevent macroscopic agglomeration, which can settle or clog the microfluidizer. Also, the container must be sealed prior to removal from the glove box.

Figure 2. La Petite glove box used to safely load powder CNTs into resin.

3. RHEOLOGICAL (VISCOSITY) MEASUREMENTS

All testing was conducted using various samples of SC-780 epoxy Part A resin loaded with 0.0 to 0.6 wt.% CNTs. This epoxy component has a reported viscosity of 850 centipoises (cps) at 25°C. This material is considered a non-Newtonian fluid, with viscosity that is shear-rate and time dependent. Before the viscosity was measured, the CNT/resin mixture was prepared using two passes through the microfluidizer. Also, the material was degasified for thirty minutes to remove trapped air bubbles. Viscosity measurements then were conducted using a

Brookfield DV-E viscometer at a temperature of 25°C. To operate the viscometer, first an appropriate spindle is selected; for this case a 30-millimetre diameter parallel plate spindle was used. Different spindles correspond to different viscosities and must be selected based on the range of operation. With the spindle selected, a little bit of material is applied to the spindle to wet it. The required material amount is then poured on the bottom part; the parallel plate is then lowered until it makes contact (wets the entire sample) and has an appropriate meniscus; that is, when the sample thickness is exactly one millimetre, which is checked with a one-millimeter spacer that is provided with the viscometer. The viscosity calculations were then performed at different shear rates. The results are presented in the next section.

4. VISCOSITY RESULTS

The shear viscosity as a function of shear rate results for various mixing conditions of CNT loaded resin prepared using two passes through the microfluidizer are shown in **Figure 2**. The viscosity measurements were performed at a constant temperature of 25°C and different shear rates. The maximum viscosities measured for the samples are listed in **Table 1**; where the 1D indicates that the samples were stirred right before being tested after siting for one day. All samples exhibited shear thinning behaviour as the viscosity decreased with increased shear rates. Notice that the viscosity of 0.4 %wt. and 0.2 %wt. are lower than that for the neat SC-780 epoxy (unloaded resin) – dark blue line versus the red and green lines. Although this does not appear to be reasonable because one would expect an increase in viscosity as the particle content increases, it is speculated that the particle-to-particle interactions leads to a particle-to-polymer interaction that "lubricates" the material leading to a decrease in viscosity; at least until a critical loading where the particle-to-particle integration results in an increase in viscosity. The more important result is that based on these data, viscosity of resin is not drastically affected by small CNT loadings.
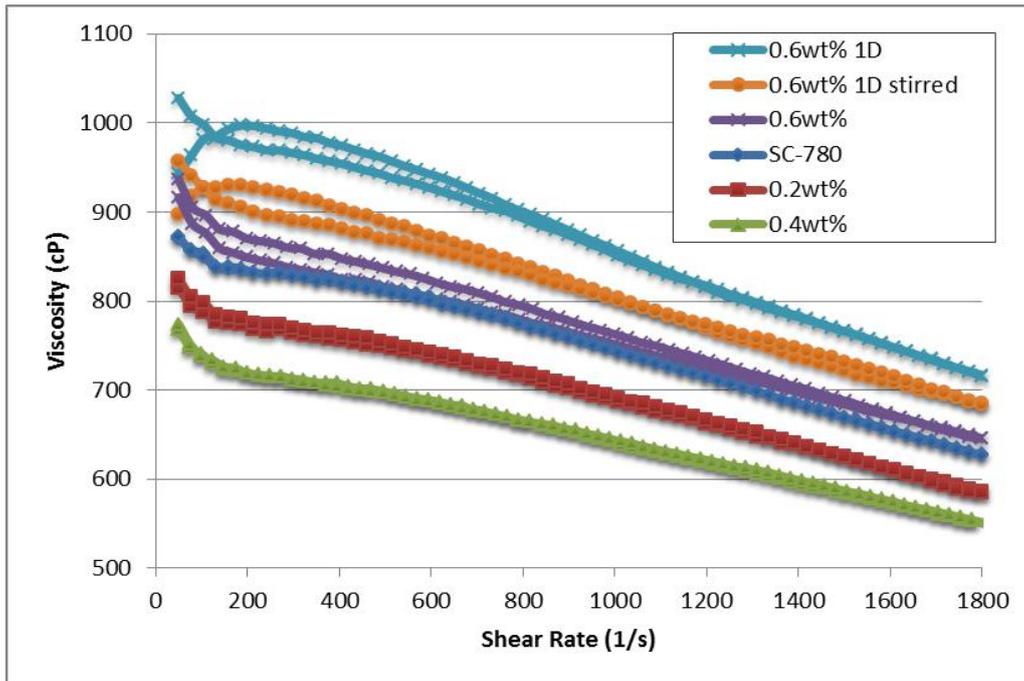
Figure 3. Viscosity vs. shear rate for MWCNT/SC-780 epoxy manufactured using two microfluidizing passes.

Sample	Viscosity (cP)	CNT load (%wt)	Comment
SC-780	870	–	Neat resin
1	800	0.2	–
2	750	0.4	–
3	890	0.6	–
3(1D)	1020	0.6	Sample sat for one day before being tested
3(1D stirred)	950	0.6	Sample sat for one day and was stirred right before being tested

Table 1. Viscosity for CNT/SC-780 epoxy manufactured using two microfluidizing passes.

5. CONCLUSIONS

An experimental program was conducted to study the effect of CNT loading on the viscosity of epoxy resins that are used in the fabrication of nanocomposite materials. The results appear to be very promising and elucidate some interesting characteristics of CNT loading. Following are observations that were made regarding the change in viscosity of epoxy resin as a function of CNT concentration and shear rate:

1) The viscosity of all samples increases as the shear rate increases, almost linearly.

2) The viscosities of the neat resin material and those of CNT loaded resins follow similar linear trends.

3) Interestingly, adding a small quantity of CNTs (up to about 0.4%) appears to "lubricate" the resin, causing it to become less viscous.

4) The viscosity of resin is not drastically affected by small CNT loadings.

5) Allowing the resin to sit for one day before being tested appears to increase the viscosity; the increase may be decrease if the CNT loaded resin is stirred right before testing.

REFERENCES

[1] E.T. Thostenson and T.-W. Chou, Carbon, 44 (2006): p3022-3029.

[2] K.G. Budinski and M.K. Budinski, Engineering Materials: Properties and Selection. 9th Ed. Prentice Hall, 2010, Columbus, OH.

[3] P.K. Mallick Fiber-Reinforced Composites: Materials, Manufacturing and Design. 3rd Ed. CRC Press, Florida, 2007.

[4] S. Iijima, Nature, 354 (1991): p56-58.

[5] J.N. Coleman, U. Khan, U.J. Blau, and Y.K. Gun'ko, Carbon, 44 (2006): p1624-1652.

[6] X.-L. Xie, Y.-W. Mai, and X.-P. Zhou, Materials Science and Engineering: R: Reports, vol. 49 (2005), no. 4: p89-112.

[7] F.H. Gojny, M.H.G. Wichmann, B. Fiedler, and K. Schulte, Composites Science Technology, 65 (2005): p2300–2313.

[8] B. Fiedler, F.H. Gojny, M.H.G. Wichmann, M.C.M. Nolte, and K. Schulte, Composites Science and Technology, 66(16) (2006), p3115-3125.

[9] T. Panagiotou, J.M. Bernard, S.V. Mesite, Deagglomeration and dispersion of carbon nanotubes using Microfluidizer^{TM} high shear fluid processors, NSTI-Nanotech 2008, ISBN 978-1-4200-8503-7, Vol. 1 (2008), p39-42.