Rheological and Electrical Properties of Multiwalled Carbon Nanotube – Epoxy Composites

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Introduction

In recent years, a great deal of interest has been focused in the area of composite materials prepared with carbon fibers and with carbon nanotubes, both single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs).[1-3] Carbon nanotubes posses both mechanical and electrical properties[1-6] that make them an obvious candidate for composites, however significant impediments exists in the use of MWCNTs in epoxy resins. Specifically, the addition of even small amount of these high aspect-ratio materials leads to a dramatic increase in the viscosity, quickly rendering the mixture extremely difficult to mold and process.[7] Here we present our results of studying the viscosity and electrical properties of MWCNT-epoxy mixtures in an effort to establish the limits to processing.

Experimental

The epoxy resin system used in this study was EPON 826 with NMA curing agent, both obtained from Miller-Stevenson. The accelerator was EMI-2,4 which was obtained from Sigma/Aldrich.

MWCNTs, produced in-house[6] were blended into the complete resin mixture using a Thinky planetary mixer. The resulting suspension was then further processed with a 3-roll mill (EXAKT 80E) to fully disperse the nanotube filler.

Table 1. The Specific Milling Conditions

Pass	Roller Speed (rpm)	Gap#1 (microns)	Gap#2 (microns)
1	200	50	40
2	200	25	20
3	200	10	5
4	200	5	5
5	200	5	5

Rheological characterizations of the fully-mixed, MWCNT filled composite epoxy resins (without EMI-2,4 accelerator), were carried out on a TA Instruments AR-G4 rheometer using a 25 mm parallel plate system with a 1 mm gap space. Temperature control was accomplished with a Peltier plate.

Results and Discussion

To determine the effect that mixing had upon the length of MWNTs, numerous individual MWCNT lengths were measured by SEM before and after milling in an epoxy resin composite as shown below.

Table 2. Effect of 3-roll milling on the length of MWNTs in MWNT/epoxy mixtures.

Sample	Length[a] (μm)	σ[b] (μm)	N
Raw MWCNTs	19.01	11.94	276
0.1 vol%[c]	6.43	5.52	137
3 vol%[c]	3.95	2.32	642

[a] average length calculated from the log normal fit.
[b] standard deviation calculated from the log normal fit.
[c] MWNTs recovered from milled epoxy/MWNT mixtures at the loadings given

Not surprisingly, the viscosity of epoxy-nanotube composites rises rapidly as the loading of nanotubes increases. Also not surprisingly, these mixtures exhibit strong shear thinning behavior. In experiments with a decreasing shear rate (**Figure1**) (immediately preceded by an increasing shear rate), nanotube alignment was achieved within a short period of time, showing a smooth decrease in viscosity with increasing shear rate. At all loadings and sweep directions, viscosity drops significantly at higher shear rates, presumably due to alignment of the nanotubes in the shear field. This is particularly evident when MWCNT-filled epoxy resin is compared to the Newtonian, small molecule neat resin.

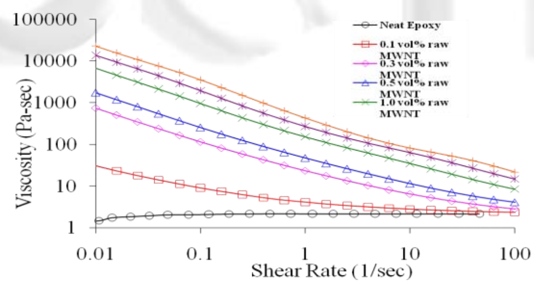

Fig 1. Viscosity measured as function of decreasing shear rate

The viscoelastic properties were measured at different temperatures (25, 35, 45, 55, 65 and 75°C) in an angular frequency sweep from 1 - 500 rad/s along with a controlled strain of 0.1 %. The 0.1 % strain was found to be in the linear visco-elastic region in an oscillatory stress vs. oscillatory strain curve for all MWCNT loadings. There was a progressive increase in the complex shear modulus with increasing MWCNT loading as seen in **Figure 2**, which suggests a loss in frequency dependence as shown in **Figure 3**. This suggests that there is an increasing solid-like or elastic character of fluid with increasing loading. As shown in **Figure 4,** the material's viscosity dependence on temperature decreases with increasing loading.

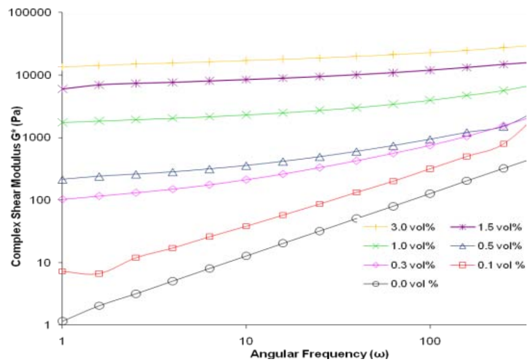

Fig 2. Modulus (G*) vs. Angular Frequency (ω) at 25°C for all loadings.

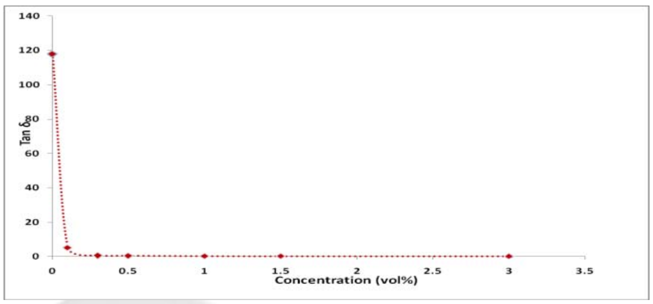

Fig 3. Tan δ vs. MWCNT Concentration (vol %) at ω= 10 rad/s & 25°C

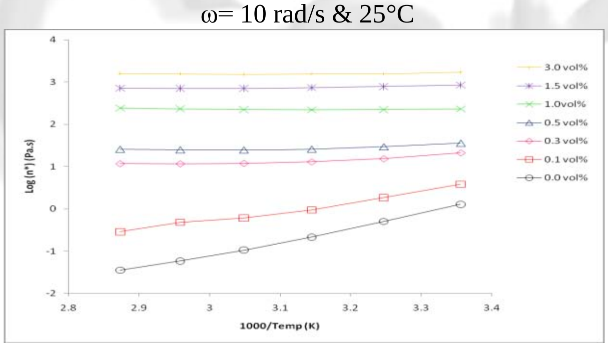

Fig4. The complex viscosity n*(Pa-s) vs. 1000/Temperature (K) at ω= 10 rad/s for loadings of 0, 0.1, 0.3, 0.5, 1.0, 1.5, and 3.0 vol % MWCNTs in epoxy

Rectangular samples (1 cm x 4 cm x 2mm) were cut from cured samples and the electrical conductivity was measured in a typical 4-point experiment. Electrical leads were attached to the ends and surface (spacing of approximately 30 mm) with silver filled-epoxy adhesive and a voltage (typically ~5V DC) was applied to the outer leads. The current was recorded as well as the voltage drop across the inner leads. The resistance was calculated as the ratio of the voltage drop to the current. The resistivity was calculated as the resistance per spacing multiplied by the specimen cross-sectional area.

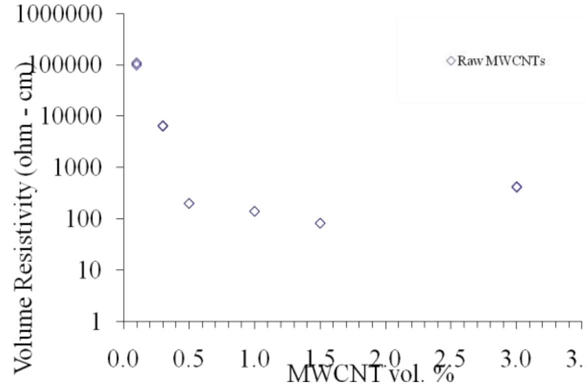

Fig 5. Resistivity of Epoxy- raw MWNT Composites

As one might suspect the resistivity of these samples drops as the MWCNT content increases, consistent with the high conductivity of MWCNTs and the low percolation threshold for these high aspect ratio materials. At a loading of only 0.1 vol. %, percolation had already occurred.

Conclusions

At all loadings and sweep directions, viscosity drops significantly at higher shear rates, presumably due to alignment of the nanotubes in the shear field. The fluid becomes more elastic in character and its viscosity has less temperature dependence with increasing filler loadings. The benefit of increased electrical conductivity conductivity occurs simultaneously with significantly increased viscosity. We found the percolation threshold for MWCNT-filled epoxy to be between 0 and 0.1 vol%,

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