Thermo-physical properties of epoxy nanocomposites reinforced by carbon nanotubes and vapor grown carbon fibers

Hiroaki Miyagawa [*], Michael J. Rich, Lawrence T. Drzal

*Composite Materials and Structures Center, Department of Chemical Engineering and Materials Science, College of Engineering,
Michigan State University, East Lansing, MI 48824-1226, USA*

Abstract

In this study, the thermo-physical properties of epoxy nanocomposites reinforced by fluorinated single wall carbon nanotubes (FSWCNT) and vapor grown carbon fibers (VGCF) were investigated. A sonication technique using a suspension of FSWCNT and VGCF in acetone was utilized to process nanocomposites in anhydride-cured epoxy. The viscoelastic properties of the nanocomposites were measured with dynamic mechanical analysis. The glass transition temperature decreased approximately 30 °C with an addition of 0.14 vol.% (0.2 wt.%) FSWCNT. The depression in T_g is attributed to non-stoichiometric balance of the epoxy matrix caused by the fluorine on single wall carbon nanotubes. The correct amount of the anhydride curing agent needed to achieve stoichiometry was experimentally determined by DMA measurements. After adjusting the amount of the anhydride curing agent for stoichiometry, the storage modulus of the epoxy at room temperature increased 0.63 GPa with the addition of only 0.21 vol.% (0.30 wt.%) of FSWCNT, a 20% improvement compared with the anhydride-cured neat epoxy. For VGCF, the storage modulus at room temperature increased 0.48 GPa with the addition of only 0.94 vol.% (1.5 wt.%) and then reached a plateau for larger amounts of VGCF. To understand the influence of VGCF on thermo-physical properties, the microstructure of the nanocomposites was interrogated using transmission electron microscopy (TEM). This study discusses the chemical effects of fluorine on matrix properties and the effect of stoichiometric balance on the thermo-physical properties of nanocomposites.
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1. Introduction

Owing to their splendid elastic modulus and strength, the utility of using carbon nanotubes (CNT) as reinforcements in organic polymers began when CNT were discovered by Iijima in 1991 [1–7]. One major concern affecting the usage of CNT for engineering applications is its high cost compared to other nano-reinforcements, such as clay nanoplatelets. Alternately, vapor grown carbon fibers (VGCF) are also attracting increasing atten-

tion as nano-reinforcements due to much lower cost, although some mechanical properties of VGCF may be inferior to those of CNT. In some cases the reinforcing effects of the CNT and VGCF have not been maximized due to the inhomogeneous dispersion of these materials in the polymer matrix.

In this study, epoxy matrix nanocomposites reinforced by fluorinated single wall carbon nanotubes (FSWCNT) and VGCF were prepared. The morphologies of FSWCNT and VGCF in the as-received condition and after incorporation in an anhydride-cured epoxy matrix were observed by transmission electron microscopy. The effect of FSWCNT and VGCF loading on the viscoelastic properties of the nanocomposites was determined by dynamic mechanical analysis (DMA).

2. Experimental

2.1. Materials

2.1.1. Fluorinated single wall carbon nanotubes
Fluorinated single wall carbon nanotubes (Carbon Nanotechnologies Inc., Houston TX) were blended in the epoxy using a

sonication technique [8]. The vendor reports a fluorination yield of at least 10 wt.% of fluorine, which equals a fluorine/carbon ratio of 0.08 [9]. FSWCNT retain much of their thermal conductivity and mechanical properties, since no carbon atoms are displaced during the fluorination, and consequently their structure is still defect-free. Kudin et al. [10] have concluded from the computed elastic constants that the stiffness of CNT is not affected by addition of large amounts of fluorine. Generally, untreated single wall carbon nanotubes (SWCNT) agglomerate via van der Waals forces to form a bundle that is extremely difficult to separate into individual SWCNT during the processing of SWCNT-reinforced nanocomposites. The supplier reports that SWCNT are typically about 100–1000 nm in length, whereas bundles are far longer than any individual SWCNT [11]. Mechanical characteristics of epoxy nanocomposites reinforced by untreated SWCNT report more than 1.0 wt.% SWCNT were used to improve the elastic modulus [12,13]. However, when the aspect ratio of SWCNT in these studies is considered, the theoretical reinforcing effect predicted by Tandon and Weng [14], Halpin and Tsai [15], and Hui and Shia [16] has not been achieved, which can be attributed to aggregation of the nanotubes. Fluorination disrupts the van der Waals forces between the nanotubes and increases the solubility of SWCNT in solvents such as alcohols and ketones, which leads to a greater degree of dispersion in these solutions. It is expected that the fluorine treatment will lead to greater bundle separation and dispersion of CNT in the polymer matrix and produce greater increases in the elastic modulus of the nanocomposites made with these materials.

2.1.2. Vapor grown carbon fibers

A commercially available VGCF [17], obtained from Applied Sciences Inc. (Cedarville OH), were evaluated in this study. PR-19-PS is pyrolytically stripped VGCF, in which polyaromatic hydrocarbons have been removed from the surface. PR-19-PS has a CVD carbon layer on the surface having a surface area of 20–30 m^2/g as measured by nitrogen adsorption. The outside diameter and the length of PR-19-PS are 100–200 nm and 30–100 μm, respectively. The density of VGCF was approximately 1.95 g/cm^3. The supplier reports that the elastic modulus is approximately 500 GPa.

2.1.3. Anhydride-cured epoxy

The epoxy resin was diglycidyl ether of bisphenol F (DGEBF), Epon 862 (Resolution Performance Products, Houston TX, epoxide equivalent weight = 172) processed with the anhydride curing agent methyltetrahydrophthalic-anhydride (MTHPA), Aradur^{TM} HY 917 (Huntsman Advanced Materials Americas Inc., Brewster, NY, equivalent weight = 159) and the accelerator 1-methylimidazole (DY 070, Huntsman Advanced Materials Americas Inc.). The mixing ratio for the neat epoxy was 100 parts by weight DGEBF to 92.7 parts MTHPA to 1.0 part imidazole. To fabricate the anhydride-cured FSWCNT/epoxy nanocomposites, up to 0.36 vol.% (0.5 wt.%) FSWCNT were sonicated in acetone for 5 h using a solution concentration of more than 1 L of acetone to 1 g of FSWCNT. Similarly for epoxy/VGCF nanocomposites, up to 2.5 vol.% (4.0 wt.%)

VGCF were sonicated in acetone for 2 h using a solution concentration of more than 100 L of acetone to 10 g of VGCF. DGEBF was then added to the solution and mixed with a magnetic stirrer for an additional hour. The acetone was removed from the mixture by vacuum extraction at 100 °C for 24 h, after which time MTHPA and imidazole were blended in the solution with a magnetic stirrer. Previous work on clay/epoxy nanocomposites demonstrated that the acetone is fully removed and has no chemical effect on the system [8]. The specimens were cured at 80 °C for 4 h followed by 160 °C for 2 h.

2.2. Transmission electron microscopy

As-received FSWCNT were sonicated in acetone for 5 h, and then deposited onto a lacey carbon film substrate grid for evaluation by TEM. The nanocomposite samples were sectioned at room temperature using an ultramicrotome fitted with a diamond knife having an included angle of 4°. Thin sections of approximately 100 nm thick were obtained for TEM observations. A JEOL 2200FS TEM with a field emission filament operated at 200 kV accelerating voltage or a JEOL 100CX TEM with LaB$_6$ filament at 120 kV accelerating voltage was used to collect bright-field TEM images of the epoxy nanocomposites.

2.3. Dynamic mechanical analysis

Dynamic mechanical properties were measured with a TA Instruments DMA 2980 operating in the three-point bending mode at a frequency of 1.0 Hz. The amplitude and the static force were 75 μm and 1.0 N, respectively. Data were collected from room temperature of 27 °C to 170 °C at a scanning rate of 2 °C/min. DMA specimens were cut by a wet diamond saw in the form of rectangular bars of nominal dimensions: 2.2 (±2.0) mm × 12 (±1.5) mm × 50 mm. A minimum of 3 specimens of each composition were tested.

2.4. X-ray photoelectron spectroscopy

The surface chemistry of the VGCF was determined by X-ray photoelectron spectroscopy (XPS) using a PHI 5400 ESCA spectrometer (Physical Electronics, Eden Prairie MN). All measurements took place at operating pressures of less than 5×10^{-8} Torr. The samples were irradiated with a non-monochromatic Mg X-ray source (1253.6 eV) operating at 300 W with a take off angle of 45°. A pass energy of 187.85 eV was used for survey scans (0–1100 eV) and elemental regional scans were acquired with a pass energy of 29.35 eV. The O1s spectral envelope was deconvoluted with a non-linear least squares curve-fitting program (Multipak, Physical Electronics, Eden Prairie MN) using a Gaussian–Lorentzian peak shape. Peaks were assigned based on the assumption of a 1.5 eV chemical shift per bond to oxygen. The main oxygen peak was fixed to a binding energy of 533.6 eV.