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Synthesis and characterization of carbon nanotube-reinforced epoxy: Correlation between viscosity and elastic modulus

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ABSTRACT

We report the synthesis and characterization of nanocomposite thin films consisting of single-walled carbon nanotubes with different functionalization schemes dispersed in an epoxy matrix. The thermal, rheological, and mechanical properties of nanocomposite thin films were experimentally characterized to establish a relationship between processing and performance. The results from the rheological analysis confirmed that the nanotube type and functionalization strongly affect the resin viscosity during cure. A correlation between the rheological behaviour and the measured elastic properties was established. Nanotubes produced by plasma and functionalized with carboxyl group had the lowest influence on viscosity and led to the highest improvement in elastic properties. The measured increase in elastic modulus was consistent with predictions based on Mori–Tanaka micromechanics.

1. Introduction

Research on the synthesis and characterization of carbon nanotube (CNT)-reinforced polymer structures has produced a large and rich literature; several recent articles contain an excellent overview of these developments [1,2]. Much of the earlier work focused on the direct incorporation of the nanotubes as reinforcement fillers in the resin. These resins were then processed to fabricate films, fibres, or bulk composites with enhanced mechanical and other multifunctional properties. However, the measured enhancements in properties are significantly less than expected due to the difficulty of processing nanocomposites (especially in controlling alignment and dispersion, and in ensuring strong matrix–CNT interfaces). This difficulty is due, in part, to the effects of the nanotubes on the rheological and curing behaviour of the polymer. Specifically, the viscosity of the matrix can increase by orders of magnitude upon the addition of carbon nanotubes with large aspect ratios (length/diameter >500). The degree to which the viscosity is affected is highly dependent on the type and aspect ratio of the nanotubes [3], dispersion state [4], and functionalization [5]. Epoxy with functionalized nanotubes can exhibit a high degree of shear thinning behaviour compared to the neat resin [6]. Carbon nanotubes have shown to affect the cure behaviour of resin systems as well, and single-walled carbon nanotubes (SWCNT) in epoxy act as strong catalysts even at a loading of 5 wt.% [7]. The presence of CNT has led to an increase in the initial rate of reaction [8] and in the time to the maximum rate of reaction [9]. Thus, these effects cannot be ignored if one aims to have a full understanding of the processing of polymers in the presence of the nanotubes. As a step in that direction, this work presents a systematic experimental study that provides a foundation for developing chemistry-process–structure-property relationships for nanocomposite thin films. The focus of this work will be the investigation of the relationship between the rheological and mechanical properties of epoxy resins modified with SWCNT using different synthesis and functionalization methods.

2. Materials synthesis

2.1. Synthesis of single-walled carbon nanotube (SWCNT)

SWCNT were prepared using a highly efficient double-laser-oven technique [10] and a high throughput induction thermal plasma process [11]. For the laser-oven technique, an inert environment of flowing Argon (250 sccm) was maintained inside a 45 mm diameter quartz tube fitted with a Brewster window. A gas-inlet was positioned at one end, while a water-cooled collector (or an environmental sample chamber) and a pumping port were placed at the other. The pressure and temperature inside the

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quartz tube were maintained at 67 kPa and 1450 °C, respectively, throughout the process. Two types of lasers were employed in this process. The first was a nanosecond-pulsed Nd:YAG laser (Spectra-Physics Pro290–30) operating at 1064 nm (or 532 nm) and 30 Hz with a fluence of approximately 2 J cm^{-2}/pulse (and 1 J cm^{-2}/pulse), respectively. This laser was setup for the purpose of vaporizing the targets (graphite doped with 0.6 at.% each of cobalt and nickel). The second laser used in this process was a Nd:YAG laser (Spectra-Physics Tornado S240-TN50–106Q), operating at either continuous wave or 20 kHz, at a wavelength of 1064 nm and measured average powers of 50 W and 48 W, respectively. This laser was used to alter the rate of cooling of the condensing plume generated by the vaporizing laser. The product of this process contained SWCNT (70 wt.%), metal catalyst contamination (6 wt.%), and other impurities including amorphous and graphitic carbon particles. Subsequently, the as-produced SWCNT were subjected to a purification process to remove these impurities. Briefly, this process relies on cycles of solvent extraction, floatation and precipitation. Besides its simplicity and scalability, an important feature of the procedure was that it did not damage the SWCNT, as will be shown later. The specific details and techniques of the purification procedure are in preparation and will be published elsewhere.

2.2. SWCNT and epoxy integration

The carbon nanotubes manufactured by the laser process were functionalized using 4-aminobenzyl alcohol through diazonium reactions following the procedure shown in Scheme 1 [12] in Fig. 1 (designated as "Alkoxy Laser"). Alternately, carboxyl groups were introduced using the rapid functionalization method developed in our laboratory, shown in Scheme 2 [13] in Fig. 1 (designated as "Carboxyl Laser"). The underlying motivation for functionalization was to aid in the debundling and dispersion of the nanotube during composite processing. For the plasma produced SWCNT, only carboxyl functionalization was used (designated "Carboxyl USP").

The matrix used in this study was a standard aerospace grade epoxy, Araldite® MY0510 epoxy (Huntsman), which was cured with 4,4-Diaminodiphenyl Sulphone (DDS) as the hardener. The integration of hydroxy-functionalized SWCNT into MY0510 is described in Scheme 3 (Fig. 1). Briefly, the hydroxy group was first deprotonated with sodium metal in THF under nitrogen atmosphere to form an alkoxy group, a strong nucleophilic agent. Following nucleophilic attacks on the epoxy groups, C–O covalent bonds are formed between the epoxy resin and the SWCNT. In the absence of moisture, the reaction would continue and cross-link the resin until all the epoxide groups are transformed. For this study, the cross-link reaction was stopped after 2 h by sparging air until most of the solvent was removed. Finally, the viscous resin mixture was placed in a vacuum oven at 100 °C and <100 kPa overnight to complete removal of the solvent. Carboxyl-functionalized SWCNT can be covalently anchored to the MY0510 resin through esterification reactions between the carboxylic and epoxide groups, as shown in Scheme 4 (Fig. 1). Here, a well-dispersed sus-

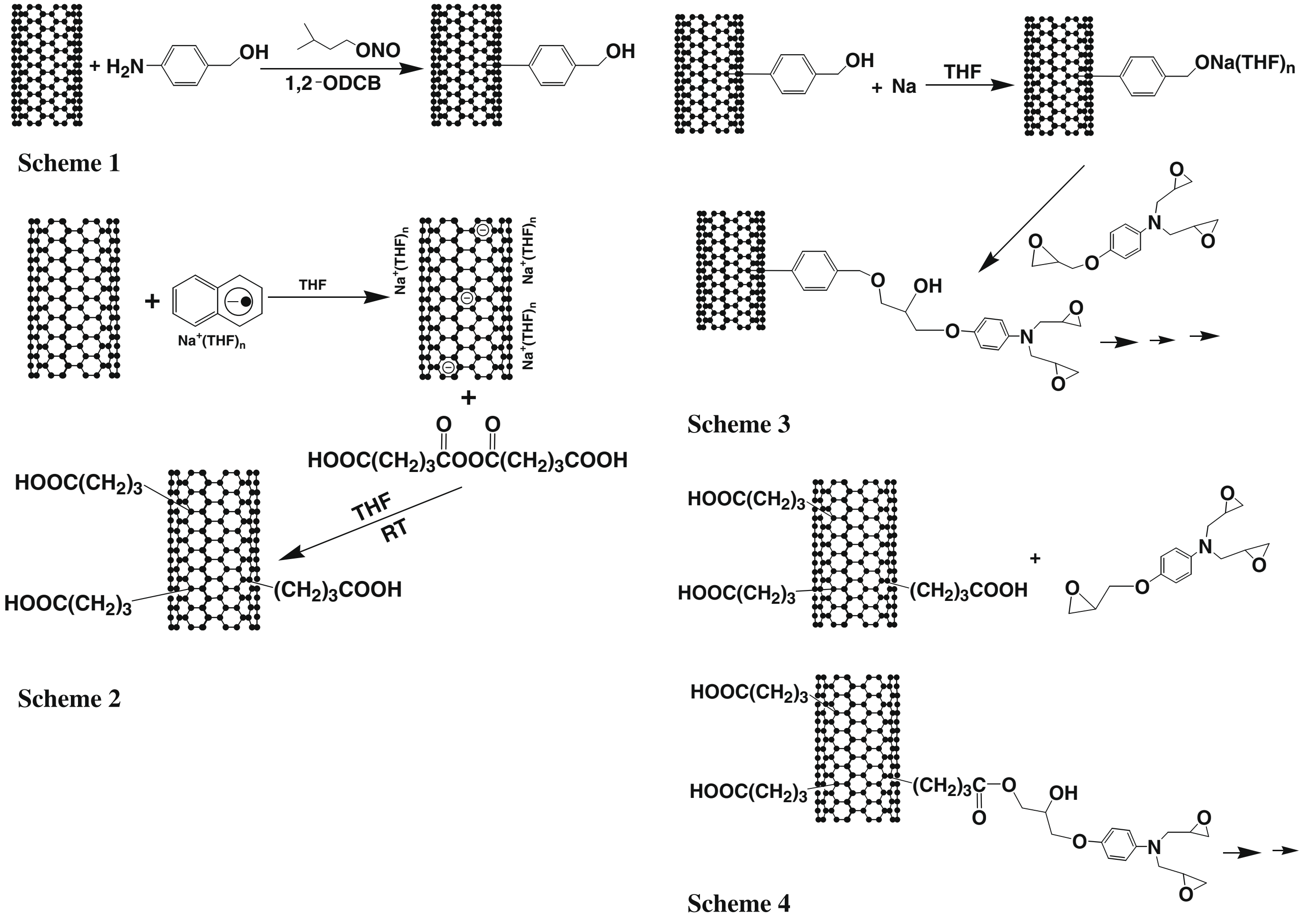

Fig. 1. Different schemes for chemical integration of epoxy and SWCNT. Scheme 1: Alkoxy functionalization of SWCNT through diazonium reactions. Scheme 2: Carboxyl functionalization of SWCNT by the rapid functionalization method. Scheme 3: Anchoring of MY0510 onto the alkoxy-functionalized SWCNT. Scheme 4: Anchoring of MY0510 onto carboxyl-functionalized SWCNT through esterification.