



Dispersion control and characterization in multiwalled carbon nanotube and phenylethynyl-terminated imide composites

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ABSTRACT

The inherent multifunctional properties of carbon nanotubes provide an opportunity to create novel composites, but their dispersion into a polymer matrix is challenging due to nanotube dimensions, interparticle forces, and poor interaction with the polymer. In this study, we used melt mixing to disperse multiwalled carbon nanotubes (MWNTs) in a polyimide resin under various process conditions to understand the efficacy of the process and the energy required to achieve dispersion and distribution. Through controlled variation of process conditions, we achieved various degrees of nanotube dispersion and distribution. The different dispersion and distribution states were observed by microscopy and correlated with the magnitude of the changes seen in the glass transition temperature and viscosity when compared to the neat resin. The results of these studies will be used to assess the compatibility of nanocomposite resins with composite fabrication methods and predict appropriate processing conditions for producing multiscale composites.

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1. Introduction

Composites for use in high performance aerospace applications such as space exploratory vehicles, airframes, and propulsion require specialized properties in order to improve current designs. Potential improvements include increased strength and impact resistance, increased thermal stability, and environmental stability. Weight reduction could aid in energy conservation for propulsion performance, and enhanced electrical properties could help to shield vehicles through lightning strike mitigation and electromagnetic interference shielding. One way to achieve these properties is by using high temperature polymer systems with nanofillers creating multifunctional composites that exploit each component's properties. Carbon nanotubes offer inherent properties such as high mechanical strength and stiffness [1–6], thermal conductivity [7–9] and electrical conductivity [8,10,11] that can lead to a lightweight material with enhanced characteristics. In this study, we investigated the processing of multiwalled carbon nanotubes (MWNTs) with PETI-330, a phenylethynyl-terminated imide [12], using melt mixing. Analysis of processing variables identified energy requirements for obtaining both good dispersion and good distribution of MWNTs in PETI-330. Through the adjustment of filler concentration and processing conditions and measurements of thermal and rheological properties, data were obtained that could

be used in identifying a processing performance relationship and producing a system with appropriate viscosity for resin transfer molding (RTM).

Polyimides (PIs), which account for many high performance polymer systems, are noted for their thermal and mechanical properties; however, they are generally difficult to process [13] due to small windows between the melting and curing or degradation temperatures; PIs are also resistant to many solvents, making solution processing difficult. Polyimide oligomers incorporating phenylethynyl end groups lead upon processing to crosslinked materials with high thermal stability [14]. These phenylethynyl-terminated imides (PETI) have become a focus of aerospace research because of the combined properties resulting in thermo-oxidative stability, high mechanical properties, and large processing windows that are generally not identified with other PIs [13,15].

By adding nanotubes to a high performance polymer such as PETI, thermal and mechanical properties may be further enhanced. Producing a homogeneous dispersion of nanoparticles in polymer matrices, however, has proven to be more difficult than with larger particles due to strong interparticle forces that cause them to agglomerate. A number of studies have been performed to determine effective ways to achieve such a dispersion with nanotubes in thermoset polymers. Ghose et al. had success in preparing composites composed of a PETI resin and MWNT via dry mixing, *in situ*, and solution dispersion [14,16,17]. Choi et al. dispersed carbon nanofibers in an epoxy resin *in situ* using sonication in a solvent

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[18]. The composites exhibited a homogeneous dispersion at loadings up to 10 wt.% and increased the glass transition temperature (T_g). Zhu et al. achieved good dispersion and particle integration by using a multistep processing protocol with chemical functionalization [19]. The composite containing functionalized nanotubes exhibited better dispersion and mechanical properties than the corresponding composite containing pristine nanotubes.

The methods described above have been shown to be effective in dispersing nanotubes into thermosetting matrices; however, methods such as solution dispersion or ball milling may take hours or days to complete. In this research, we investigated a conventional thermoplastic polymer processing method, melt mixing, to reduce the processing time needed to produce nanoreinforced resins. Melt mixing is a desirable method for processing thermoplastic systems and has been successfully applied to the fabrication of thermoplastic nanocomposites. Andrews et al. [20] showed that melt mixing could be used to disperse MWNTs in a variety of matrices under relatively mild mixing conditions. Kasaliwal et al. [21] used a small scale twin screw extruder to prepare polycarbonate composites containing 1 wt.% MWNTs. Using electrical resistivity as a measure of dispersion, higher processing temperatures and motor speeds led to composites with the lowest resistivity and highest particle dispersion. Similarly, Krause et al. [22] varied the processing conditions for a small scale twin screw extruder mixing polyamide–MWNT composites and reported that improved dispersion was achieved with increasing energy. Shofner et al. [23] have shown that small ropes of single walled carbon nanotubes (SWNTs) may be dispersed by melt mixing to achieve improved mechanical properties. Zhang et al. [24] were able to achieve dramatic improvements in MWNT/nylon composites produced by melt mixing, achieving strength and modulus improvements of 120% and 115%, respectively, at 1 wt.% MWNT. However, melt mixing can be a challenge with thermosets due to the possibility of crosslinking during processing. Once polymerization is initiated, viscosity increases as polymer chains begin to extend and form networks, thus preventing further use of the system in fabrication methods that require low injection viscosities such as RTM or vacuum assisted resin transfer molding (VARTM). Because of the large processing window between the oligomer melting temperature and the gel temperature in PETI resins, there is an opportunity to use melt mixing with these systems [17].

In this research, we investigated the efficacy of melt mixing as a dispersion method of MWNTs in PETI-330. By studying the torque and energy applied to a system along with the resulting filler and polymer behavior, the minimum torque for homogenous filler dispersion could be established. These values can be used to establish optimal processing conditions to achieve a desired composite morphology and properties. Mixed and unmixed materials were characterized using electron microscopy as well as changes in glass transition temperature and viscosity to assess MWNT dispersion and distribution, differential scanning calorimetry (DSC) before and after curing, and dynamic rheology measurements to simulate RTM processing. The results of this study indicated that melt mixing may be used to disperse and distribute MWNTs in PETI resins, MWNTs increase post-cure T_g when a good dispersion is achieved, and the viscosity of the nanocomposite resin is acceptable for RTM processing with an appropriate choice of MWNT loading.

2. Materials and methods

Polymer nanocomposites containing PETI-330, from Ube Industries, Ltd., and MWNTs, Elicarb PR0940 from Thomas Swan & Company, were used for this study. Neat PETI-330 liquefies at

approximately 180 °C and has a post-cure T_g of 330 °C as well as a low and stable melt viscosity that makes it an excellent candidate for conventional composite manufacturing methods such as RTM or VARTM [25,26]. The uncured resin is an odorless, light-yellow powder with a density of 1.3 g/cm³ at room temperature. The Elicarb PR0940 MWNTs have diameters in the range of 10–12 nm and micron lengths with a bulk density of 1.7 g/cm³ and a purity of 70–90%. All materials were used as-received.

Two processing studies were performed to determine the effects of filler concentration and mixing energy on the morphology and properties of the resulting nanocomposites. In the first study, samples were prepared with 0.0, 0.5, 1.0, and 3.0 wt.% MWNTs at 188 °C using the same time and motor speed processing conditions. In the second study, three additional batches of 0.5 wt.% MWNT/PETI-330 resin were each processed at 200, 215, and 230 °C with the same motor speed, resulting in successively lower torque as the melt viscosity of the underlying resin decreased with increasing temperature.

The processing protocol involved initial mixing of 50.0 g of the dry materials by simple shaking, followed by melt mixing using an internal mixer with roller blades operated by a Brabender Intelli-Torque drive unit. In the first study, the materials were mixed at 188 °C for 12 min using a rotor speed of 60 rpm. In the second study, the residence time and rotor speed were 12 min and 60 rpm, respectively, while the temperature was adjusted to 200, 215, and 230 °C. In these studies, the mixer was charged with material during the first 3 min and after the material was fully liquefied, the mixing torque attained an approximately constant value referred to as the steady state torque. The steady state torque value was dependent on the mixing speed, mixing temperature, and concentration used. The entire mixing torque curve was used to calculate the mixing energy for each batch in order to compare the materials processed in both studies and correlate the processing data with the material morphology and properties. The mixing energy was obtained using the following equation:

$$\text{Mixing Energy} = \int (T * s) dt \quad (1)$$

where T is the torque, s is the motor speed, and t is the time.

The materials were characterized by electron microscopy, differential scanning calorimetry (DSC), and rheology after processing. A LEO 1530 scanning electron microscope (SEM) was used to image fractured surfaces in order to determine the distribution and dispersion of MWNTs in the uncured resin. The neat resin and 0.5 wt.% MWNT materials were sputter coated with gold to facilitate imaging. Higher MWNT loadings possessed sufficient inherent conductivity to be imaged without coating.

A TA Instruments Q200 DSC was used to measure the thermal behavior of 5 mg samples of each material processed. Two studies were completed to determine pre- and post-cure behavior. In the first study, several specimens from each batch were analyzed for pre-cure T_g with a temperature sweep from 40 to 420 °C at a rate of 10 °C per minute. In the second study, T_g was measured after fully curing the material at 371 °C for 60 min, cooling to room temperature, and completing another temperature sweep.

Rheology was used to understand the feasibility of processing the PETI-330/MWNT composites in methods such as RTM. Dynamic experiments were conducted using parallel-plate geometry with a TA Instruments AR-G2 rheometer. Samples were prepared by powdering the material and then pressing the material at 13,000 psi for 2 min at room temperature into a 25 mm diameter disk. A temperature sweep was performed on each sample with 20% strain at a constant frequency of 100 radians per second. These conditions were chosen to simulate RTM injection conditions. Laboratory testing has shown that material can be used in RTM if the viscosity is below 2.0 Pa s [27].

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