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Enhanced electrical properties of polycarbonate/carbon nanotube nanocomposites prepared by a supercritical carbon dioxide aided melt blending method

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ABSTRACT

Polycarbonate/carbon nanotube (CNT) nanocomposites were generated using a supercritical carbon dioxide ($scCO_2$) aided melt blending method, yielding nanocomposites with enhanced electrical properties and improved dispersion while maintaining the aspect ratio of the as-received CNTs. Baytubes® C 150 P CNTs were benignly deagglomerated with $scCO_2$ resulting in 5 fold (5X), 10X and 15X decreases in bulk density from the as-received CNTs. This was followed by melt compounding with polycarbonate to generate the CNT nanocomposites. Electrical percolation thresholds were realized at CNT loading levels as low as 0.83 wt% for composites prepared with 15X CNT using the $scCO_2$ aided melt blending method. By comparison, a concentration of 1.5 wt% was required without $scCO_2$ processing. Optical microscopy, transmission electron microscopy, and rheology were used to investigate the dispersion and mechanical network of CNTs in the nanocomposites. The dispersion of CNTs generally improved with $scCO_2$ processing compared to direct melt blending, but was significantly worse than that of twin screw melt compounded nanocomposites reported in the literature. A rheologically percolated network was observed near the electrical percolation of the nanocomposites. The importance of maintaining longer carbon nanotubes during nanocomposite processing rather than focusing on dispersion alone is highlighted in the current efforts.

1. Background and motivation

The production of polymer-multi walled carbon nanotube (CNT) nanocomposites has been the focus of studies in the past two decades due to the potential for CNTs to transfer their impressive thermal [1], electrical [2] and mechanical properties [3,4] to composites. These nanocomposites have become relevant in industry over the past several years, especially in applications of electromagnetic interference shielding [5] and electrostatic dissipation [6].

Commercially available CNTs are typically provided as large agglomerates on the order of several hundred microns in diameter resulting from chemical vapor deposition synthesis [7]. The agglomerates are held together by relatively strong van der Waals forces and physical entanglements of carbon nanotubes, making them difficult to separate.

A method of mixing polymer and CNTs must be chosen so that sufficient energy is applied to destroy the agglomerates and distribute the carbon nanotubes homogenously. Typical methods include *in-situ* polymerization, solution blending, and melt compounding. Melt compounding nanocomposites is of particular interest due to its scalability, flexibility, and lack of processing solvents compared to solution blending and *in-situ* polymerization [8,9].

Significant effort has been directed at understanding and improving the dispersion of CNTs in polymer melts to produce nanocomposites with superior electrical properties [10–13]. However, recent studies suggest that dispersing the CNTs from their initial bundles during melt processing leads to significant reduction in the nanofiller aspect ratio [14–16]. The damage to CNTs may occur when high external stresses are applied to unwetted agglomerates, resulting in rupture of the dry agglomerate core [17]. Reduction in carbon nanotube lengths during processing may result in decreased electrical properties for melt compounded

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nanocomposites, as the aspect ratio scales inversely with the theoretical percolation threshold [14]. Therefore, care must be taken in choosing processing conditions that mitigate damage while dispersing the CNT during nanocomposite generation.

A multitude of recent literature has investigated melt processing conditions to determine the effect of input mixing energy on CNT lengths, agglomerate dispersion and subsequent nanocomposite electrical properties [11,14–17]. In melt compounding, mixing energy is a quantity used to relate the external stresses on CNT agglomerates to the mixing variables which are dependent on screw speed, residence time, the applied torque, and other variables. This allows one to effectively relate dispersion mechanisms, processing conditions, and shortening of the CNTs to the properties of melt compounded polymer nanocomposites [14,16,17].

Although the dispersion of CNTs is generally improved with increasing mixing energy, the extent of shortening has also been related to increased values of mixing energy. Guo et al. [15] melt compounded polycarbonate nanocomposites in a twin screw micro compounding device using CNTs with very high aspect ratios (474). The authors observed decreased percolation thresholds when mixing times were doubled, from concentrations of 0.07 wt% to 0.2 wt%. The CNTs were shortened by 89% of their initial length to 550 nm after melt compounding at longer residence times, indicating that gentler mixing led to improved electrical properties. Pötschke et al. [16] investigated the effect of mixing speed on electrical properties of poly (caprolactone) (PCL)/CNT nanocomposites prepared with a twin screw micro compounding device. Increasing mixing energies, controlled by mixing speeds, resulted in better dispersion of the CNTs in the PCL. However, both rheological percolation and electrical percolation decreased at the highest mixing speeds studied where the CNTs were shortened to 70% of their initial length. Socher et al. [11] investigated the effect of matrix viscosity on the dispersion and electrical properties of polycarbonate (PC)/CNT nanocomposites. Greater dispersion was observed in higher viscosity nanocomposites due to increased input energies, but the electrical properties were diminished. It was reported that nanocomposites prepared with a higher viscosity matrix reduced the CNT lengths compared to a low viscosity matrix, where lower stresses were applied. In summary, these findings suggest that intermediate mixing energies which partially maintain the CNT aspect ratios while providing sufficient dispersion are desired to achieve low percolation thresholds. This issue may be avoided if alternative nanocomposite generation methods are developed which retain the aspect ratio of the CNTs during dispersion.

Supercritical carbon dioxide ($scCO_2$) deagglomeration of CNT bundles followed by melt blending has been suggested as a benign way to generate CNT/ polymer nanocomposites while retaining the aspect ratio of the nanofiller [18,19]. Gulari et al. [19] obtained a patent in 2008 for the processing of nanotubes with $scCO_2$, followed by melt compounding to generate nanocomposites. However, few specifics were provided for the $scCO_2$ processing of the CNT and the melt compounding step of nanocomposite generation was not described in any detail. A method has been developed by Chen et al. [18] to process CNT aggregates with $scCO_2$ followed by single screw melt compounding, known as the $scCO_2$ aided melt blending method. In applying this method, the authors observed improved mechanical properties in polyphenylsulfone nanocomposites, but limited morphological analysis was conducted and the effect of the process on the aspect ratio of the CNTs was not investigated. Furthermore, the work by Chen et al. [18] was not concerned with the formation of electrically conductive networks in CNT nanocomposites. More recent work has focused on the deagglomeration of CNT aggregates using $scCO_2$ processing while retaining the aspect ratio of the CNT [20]. It was found that the rapid expansion of the supercritical suspension resulted in varying degrees of deagglomeration for CNT bundles without damaging the CNT aspect ratio. The varying extents of $scCO_2$ processing yielded CNTs with significantly reduced bulk densities. The potential exists to generate nanocomposites possessing improved dispersion and electrical properties.

The aim of this work is to determine the effect of $scCO_2$ processing of CNT agglomerates on the morphology and surface conductivity of CNT/polycarbonate nanocomposites prepared with the $scCO_2$ aided melt blending method using single screw mixing. Nanocomposites were generated using direct melt blending and varying extents of $scCO_2$ processing, as reported in work elsewhere [20]. Following nanocomposite generation, it is desired to define the extent of damage to individual CNTs in the nanocomposites. Furthermore, it is desired to determine whether the deagglomeration of CNT bundles by $scCO_2$ treatment before melt mixing leads to an improvement in the electrical conductivity in polycarbonate/CNT nanocomposites. Nanocomposite morphologies are investigated by means of optical microscopy, rheological measurements, and transmission electron microscopy to determine the state of CNT dispersion and distribution throughout the polymer. Some comments are offered as to the effect of the $scCO_2$ processing on the mechanical CNT network in the nanocomposites as well.

2. Experimental

2.1. Materials

2.1.1. Carbon nanotubes

The multi walled carbon nanotubes (CNTs) used in the current study are Baytubes® C 150 P from Bayer MaterialScience (Leverkusen, Germany), which are delivered as large agglomerates in the form of powder with a bulk density of approximately 150 kg/m^3. The properties of the CNTs and their agglomerates are reported in detail elsewhere [7,20]. The CNTs are generated through fixed bed chemical vapor deposition (CVD) synthesis and were used as-received from the supplier.

2.1.2. Polycarbonate

A medium viscosity polycarbonate (PC), Makrolon 2608 from Bayer MaterialSciences, was chosen as the polymer matrix. The melt flow index is 13 g/10 min under a load of 1.2 kg at 300 °C. Makrolon 2608 possesses a number average molecular weight of ~10,500 g/mol with a polydispersity index of 2.54 as determined by GPC.

2.2. Methods

2.2.1. Composite processing

It was desired to determine the effect of benign $scCO_2$ deagglomeration of CNT bundles on the electrical properties and morphology of nanocomposites prepared by melt compounding. The $scCO_2$ deagglomeration of CNT bundles was thoroughly investigated and is reported elsewhere [20]. The extent of deagglomeration was found to correlate to the bulk density of the $scCO_2$ processed CNT which is measured using the EN DIN 60 standard. Degree of expansion refers to the factor by which the bulk density of the as-received CNT is reduced after $scCO_2$ processing. Increasing degrees of expansion correspond to increasing extents of deagglomeration. For example, a 15 fold (15X) degree of expansion describes a reduction in bulk density from 150 kg/m^3 to 10 kg/m^3 for the Baytubes® CNT after $scCO_2$ processing, corresponding to agglomerates on the order of 9 μm in diameter. Samples are referred to as direct blended (DB) and $scCO_2$ processed with a modifier (10X, 15X, etc.) for their reported degree of expansion. The DB samples