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Bottom-up synthesis of PS–CNF nanocomposites

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Abstract

Polystyrene–carbon nanofiber (CNF) nanocomposites have been synthesized by a ‘bottom-up’ method through electrostatic assembly. First, a cationic polystyrene (PS) latex was synthesized by conventional emulsion polymerization. The latex was mixed with an aqueous suspension of oxidized CNF. PS–CNF nanocomposites were obtained by heterocoagulation due to the electrostatic interaction between cationic PS latex and anionic CNF. Thermal properties were characterized by DSC and TGA, while morphologies of the nanocomposites were studied by SEM. Electrical resistivity results showed that the percolation threshold in our PS–CNF nanocomposites was below 2 wt% (1 vol%). This low percolation threshold is related to the dispersion, and thus a superior network formation of CNF in PS matrix.

Keywords: Polystyrene–carbon nanofiber nanocomposites; Emulsion polymerization; Heterocoagulation

1. Introduction

Since the initial work of Iijima [1] for producing carbon nanotubes (CNTs), considerable research has been done in the field of polymer–CNT nanocomposites due to their superior mechanical and electrical properties [2–6]. Vapor grown carbon nanofibers (VGCFs), which typically have diameters in the range of 50–200 nm, are also referred to as multiwall CNTs. Compared with CNTs, especially with single wall carbon nanotubes, VGCFs can be produced today in higher volumes and at lower cost using natural gas or coal as the feed stock [7,8]. Their good thermal and electrical conductivity, excellent mechanical properties, high aspect ratio (up to 1000) and low cost have attracted attention from both industrial and academic areas [9–11].

One important application of CNF in polymer composites is mechanical reinforcement. Both thermoplastic and thermosetting polymers have been reinforced with CNFs: polypropylene (PP) [12–17], polycarbonate [18–20], poly (ether ether ketone) [21], nylon [17,22], ABS [23], and epoxy [24]. Conventional mixing methods such as a twin-screw extruder, high shear mixer and two-roll mill have been used. Another main application of CNFs exploits good electrical conductivity. An increasing number of components are being made from fiber reinforced composites. For example, aircraft radomes and the leading edge of the vertical stabilizers are generally made from glass fiber reinforced composites using an insulating polymer matrix. For these applications, some electrical conductivity is required to provide electrostatic dissipation (ESD) and electromagnetic-radio frequency interference (EMI/RFI) protection. Currently, a highly conductive filler such as carbon black is added to the matrix in order to ensure electrical conductivity above the required level; this approach reduces the manufacturing and maintenance costs of components as compared with those previously coated with an anti-static paint [25–27]. In order to obtain a conductive path throughout a component, a 3-dimensional network of conductive filler particles is required, which is known as percolation. The percolation threshold is the filler loading at which the electrical resistance of the composite sharply drops. Both theoretical and experimental results indicate that the percolation threshold strongly depends on the particle shape, the higher the aspect ratio, the lower the percolation threshold [28,29]. Due to a high aspect ratio (up to 1000) and good electrical conductivity, CNFs are a good choice among carbon fibers for applications in ESD, EMI and RFI [30,31]. For the preparation of PP–CNFs

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nanocomposites, the first step was melt mixing PP and CNFs followed by compression or injection molding. By compressing molding, Lozano et al. [32] reported a 9–18 wt% percolation threshold. Using injection molding, Gordeyev and coworkers [33] obtained PP–CNF nanocomposites with a percolation threshold around 4% in volume (given that the specific gravity is about 2 g/cm^3, this is equivalent to 8 wt%). In Andrade's work [34], a percolation threshold as low as 1% in volume (about 2 wt%) was reported, but there was no description about the preparation method. We cannot reconcile these differences at this time, but the difference might be due to the alignment during injection process or the surface chemistry of CNFs. In the preparation of epoxy-CNF nanocomposites, Prasse et al. [35] reported a percolation threshold as low as 0.75 wt% with the help of electric field induced alignment during curing and the nanocomposites were electrically anisotropic. Enomoto and coworkers [36] prepared CNF–polystyrene (PS) nanocomposites by injection molding; the percolation threshold is about 3–4% in volume (6–8 wt%). In polymer blend-CNF systems, the Sumita group [37] found that CNF selectively locates within one polymer phase and forms a network structure at a rather low concentration. In a poly(methyl methacrylate) (PMMA)/high density polyethylene (HDPE)–CNF system, the percolation threshold of PMMA–CNF reduced from 8 to 4 wt% with the addition of 1% of HDPE, and this threshold further reduced to 1.5 wt% after the specimens were annealed at 220 °C for 30 min. In all the systems reviewed above, high shear and relatively long mixing times were used in order to separate CNFs and disperse CNFs in the polymer matrix. One result of the high shear mixing is that the CNFs are broken and thus the aspect ratio is reduced which directly affects the percolation threshold and load transfer [18,28].

In this paper we report the 'bottom-up' synthesis of PS–CNF nanocomposites by a heterocoagulation method. Heterocoagulation is a general method which is widely used in preparing organic/organic, organic/inorganic and inorganic/inorganic hybrids [38–43]. Recently we have successfully synthesized polymer–clay nanocomposites with fully exfoliated morphology by this method [44,45]. The mechanism of this route is ion exchange between cationic PS latex and oxidized CNF; the PS latex particles deposited onto the surface of CNF due to ionic bonding. The merits of the present method include: easy regulation of CNF loading, no shear (cost-effective and maintains high aspect ratio), and no solvent (environment friendly).

2. Experimental section

2.1. Materials

2, 2′-Azobis (2-amidinopropane) dihydrochloride (V-50), provided by Wako Pure Chemical Industries Ltd., was used without further purification. Cetyltrimethylammonium bromide (CTABr) and sodium hydroxide were obtained from Aldrich and used as received. Styrene (St) from Aldrich was purified by distillation under vacuum before use. Deionized water was used in all the experiments. The vapor grown carbon nanofiber (VGCNFs) is Pyrograf III® PR-19-PS from Applied Sciences, Inc. (ASI) with diameters of about 200 nm and length of 100–200 μm. This CNF was oxidized by ASI with approximately 5% surface oxygen content; the oxygen functionality is a mixture of carboxylic, carbonyl, lactonic, hydroxyl and ether-type groups.

2.2. Preparation of cationic polystyrene (PS) latex

Into a four-necked 500 mL Pyrex reaction kettle, which was equipped with a mechanical stirrer, argon inlet, refluxing condenser and a dropping funnel for the addition of St monomer, were placed 250 mL of deionized water, 15 g of purified St, 1 g of CTABr, and 0.76 g of V-50. The reaction contents and St in dropping funnel were purged with argon for 45 min. The polymerization was commenced by heating at 60 °C while stirring at 300 rpm. 35 g of St monomer was added dropwise to the reaction kettle over 3 h. After the addition of St, the polymerization temperature was maintained at 70 °C for 100 min and then the mixture was cooled to room temperature. Some latex was taken out to determine monomer conversion by a gravimetric method.

2.3. Cation exchange of CNFs

To convert the carboxylic acid groups on the CNF surface into sodium carboxylate groups, the oxidized CNF was treated with sodium hydroxide. A typical procedure is as follows. 0.5 g of CNF was dispersed in 100 mL of 1 M aqueous NaOH solution and sonicated for 1 h, then CNF followed by filtration and repeated washing with deionized water. Finally the cation exchanged CNF was redispersed in deionized water and sonicated before mixing with cationic PS latex.

2.4. Heterocoagulation of PS latex with CNFs

A predetermined amount of cationic latex and CNF suspension were mixed together in a beaker with stirring. The mixture was stirred for 3 h and then allowed to stand overnight. The colloidal mixture was demulsified by freezing at −20 °C; after thawing to room temperature, the mixture was filtered and thoroughly washed with water. The nanocomposite was collected and dried at 70 °C in vacuo until constant weight was obtained. For scanning electron microscopy (SEM) studies, the colloid mixture was collected at different times after mixing and diluted with deionized water; a drop of the diluted colloid was deposited on an aluminum foil and allowed to dry for SEM examination.