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Synthesis and characterization of thermotropic liquid crystalline copolyester/multi-walled carbon nanotubes composites via *in situ* polymerization

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ABSTRACT

We present a novel approach for the preparation of thermotropic liquid crystalline copolyester (TLCP)/multi-walled carbon nanotubes (MWCNTs) composites via *in situ* polymerization. A two-stage polycondensation procedure was employed in our process, where carboxylic acid modified MWCNTs were dispersed in acetic anhydride via ultrasonication prior to being charged to a prepolymerization reactor together with monomers and catalysts for esterification reaction at 130 °C–200 °C. The esterified mixture was then fed into a polycondensation reactor at 280 °C–320 °C. In this way, fully exfoliated MWCNTs were dispersed in the TLCP matrix at concentrations up to 0.3 wt%. Systematic studies show that well dispersed MWCNTs acted as "pseudo nucleation sites" for the nematic ordering in the adjacent TLCP melt. Thus the extrudates show a smaller core region and higher overall orientational order. Consequently, the addition of MWCNTs is not only effective in improving the mechanical stiffness but also toughness of the composites. For example, the 0.3 wt% TLCP/MWCNT composite shows a 62%, 135% and 145% increase in Young's modulus, tensile strength and toughness, respectively, in comparison with the pure TLCP.

1. Introduction

Main chain TLCPs have attracted extensive interest both academically and industrially since the early 1970s [1–4]. The low shear viscosity and strong shear-thinning characteristics enable the TLCPs melt to fill long and thin mold sections. The low thermal expansion coefficient makes them ideal for the molding of high precision, complex parts such as high-density computer cable connectors, pin-grid arrays, fiber optic connectors, etc. Due to their molecular rigidity, they also possess strong mechanical properties, isotropic TLCPs show tensile modulus ~5–20 GPa.

Carbon nanotubes (CNTs) are considered to be perfect whiskers with exceptional mechanical properties. It is generally accepted that the tensile strength and modulus of individual CNTs are up to 11–52 GPa and 0.32–1.47 TPa, respectively [5]. CNTs are also known to have extremely high resilience with an ultimate strain at break greater than 5%. It is believed that the incorporation of CNTs in polymer matrix may lead to ultimate reinforcement composites with significantly enhanced mechanical properties. However, realization of the full potential of these materials is limited because the effectiveness of the CNTs as reinforcement fillers relies not only on their intrinsic properties but also on the dispersion and interfacial load transfer.

Generally, three methods have been employed to fabricate the polymer/carbon nanotubes composites in the literature. They are solution mixing, melt compounding and *in situ* polymerization, respectively. Solution mixing is the most common method used on a laboratory scale since it is effective and amenable to small sample sizes [6,7]. However, this method is not suitable for making TLCP/CNTs composites because most TLCPs have poor solubility in organic solvents. Even in some aggressive and highly toxic solvents like pentafluorophenol their solubility is typically below 1 wt% at high temperatures [8]. In the melt compounding method, CNTs are dispersed in a polymer matrix using either a static mixer or twin-screw extruders [9,10]. This method is most compatible with current industrial practices. However, the high melt viscosity, caused by the incorporation of CNTs may produce very high shear stresses. This may cause shear-induced degradation of polymers. The most effective method for a homogeneous dispersion of CNTs is via the *in situ* polymerization process [11–14]. In this process, CNTs are usually dispersed in the low viscosity monomers via a combination of mechanical agitation and ultrasonication. Strong interfacial bonding can be achieved if the CNTs surfaces may be functionalized to induce covalent bonding with the polymer matrices [15]. Wang et al. [16] synthesizes the TLCP/MWCNT

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composites by *in situ* polymerization and they found the π–π stacking between MWCNTs and TLCP increased the thermal stability of the composite. Lafuente and Martinez [17] prepared TLCP/single-walled carbon nanotubes (SWCNTs) composite by the *in situ* method, and found that the SWCNTs are covalently bonded with the matrix, which improved the tensile modulus and strength moderately. Zhao and co-authors [18,19] fabricated a series of MWCNTs and TLCP composites by *in situ* solution polycondensation and found that the MWCNTs improved the thermal stability and expanded the nematic temperature range of TLCP. As most reported literature for *in situ* polymerization utilize solution polymerization, the method is not readily scaled up. Additionally, CNT sedimentation and aggregation may also become an issue due to the phase separation when the molecular weight of TLCPs reaches certain level.

In this study, the TLCP/MWCNT composites were prepared via a two-stage melt polycondensation process. As depicted in Fig. 1, in the first stage, functionalized MWCNTs were dispersed in the esterified monomers via a combined mechanical agitation and ultrasonication. The homogeneously dispersed MWCNT-esterified monomers were then transferred to a melt polycondensation reactor at high temperatures under continuous agitation. Dispersion of the MWCNTs was maintained with the increase in melt viscosity. It is expected that the covalent bonding can be formed between TLCP and MWCNTs based on multi-functional reactive sites on the surface/in the end of MWCNTs.

2. Experimental

2.1. Materials

All chemicals used in this study were of analytical grade. 4-hydroxybenzoic acid (HBA), 2-hydroxy-6-naphthoic acid (HNA), terephthalic acid (TA), acetic anhydride, potassium acetate, and dimethyl sulfoxide (DMSO) were bought from Sigma–Aldrich. Acetic anhydride was purified by refluxing for 4 h in the presence of CaH_2 before use. MWCNTs with diameters of 20–40 nm and lengths of 5–15 μm were purchased from Shenzhen Nanotech Port Co., Ltd, China. Pentafluorophenol was purchased from Chemlin (Nanjing, China) and used as received.

2.2. Acid treatment of carbon nanotubes

The as-received MWCNTs were modified by the following procedure: the as-received MWCNTs were added to the mixture of concentrated HNO_3 and H_2SO_4 with a volumetric ratio of 1:3 and this mixture was stirred at 80 °C for 30 min to create the carboxylic acid groups on the MWCNTs surface [20]. This mixture was diluted with excess deionized water and then vacuum filtered through 0.20 μm millipore polycarbonate membrane until the pH value of the filtration reached 7. The filtrate solid was dried in a vacuum oven at 120 °C for 12 h, yielding the modified MWCNTs.

2.3. Preparation of TLCP/MWCNT composites

2.3.1. Synthesis of the pure TLCP (C-0) [21]

In a glove box under N_2 protection, HBA (800.0 g, 5.79 mol), HNA (403.1 g, 2.14 mol) and TA (1.5 g, 0.009 mol) were charged into a 3 L glass reactor. A catalytic amount of potassium acetate (0.18 g, 150 ppm) in 2 mL acetic acid was added, followed by acetic anhydride (840.0 g, 8.23 mol). The reaction temperature was set at 130 °C for 1 h and raised to 200 °C for another 2 h to complete the esterification. Afterwards, the mixtures were transferred to a 2 L stainless steel reactor. Before the transfer, 3 cycles of vacuum/N_2 purge were carried out to exclude any traces of air and moisture in the reactor. The temperature of the reactants was then raised to about 280 °C–320 °C, where the polymerization occurred, around 95% acetic acid of the theoretical amount was distilled out for the following 3 h. The N_2 purge was closed and the reactor was evacuated for 2 h in order to get a high molecular weight of TLCP. Then the high pressure N_2 was filled back in the reactor to extrude the polymer.

2.3.2. Synthesis of TLCP/0.3 wt% MWCNT composite (C-3)

HBA (800.0 g, 5.79 mol), HNA (403.1 g, 2.14 mol) and TA (1.5 g, 0.009 mol) were charged into the 3 L glass reactor. A catalytic amount of potassium acetate (0.18 g, 150 ppm) in 2 mL acetic acid was added to the mixture. In another flask, 3.6 g surface modified MWCNTs were added, followed by acetic anhydride (840.0 g, 8.23 mol). Prior to introduction of MWCNTs in the glass reactor, a sonication tip was used to disperse the MWCNTs in the acetic anhydride inside the flask for 15 min. Thereafter, the MWCNTs suspension was poured into the flask containing monomers under N_2 protection. The batch was set at 130 °C for 1 h and raised to 200 °C for another 2 h to complete the esterification. A similar procedure to the synthesis of pure TLCP described above was used in the subsequent polymerization process at high temperatures. Composites containing 0.1 wt% (C-1), 0.3 wt% (C-3), and 0.5 wt% (C-5) MWCNTs with respect to the TLCP were prepared. The inherent viscosity of C-0, C-1, C-3, and C-5 in pentafluorophenol at 60 °C is 5.36, 5.29, 5.21 and 5.12 dL/g, respectively. During the polymerization, the reaction was stopped at the same torque. The melt

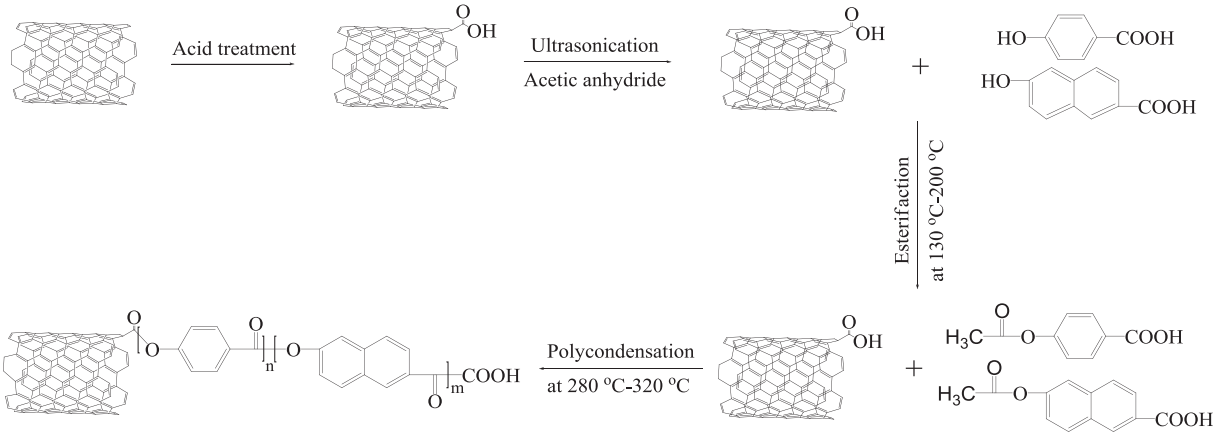

Fig. 1. Schematic representation of the preparation of TLCP/MWCNTs composites.