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Synthesis and characterization of thermotropic liquid crystalline polyester/multi-walled carbon nanotube nanocomposites

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ABSTRACT

Thermotropic liquid crystalline polyester (TLCP) was synthesized via low-temperature solution polycondensation from 1,4-Bis(4-Hydroxybenzoyloxy)butane and terephthaloyl dichloride. Polymer nanocomposites based on a small quantity of multi-walled carbon nanotubes (MWNTs) were prepared by in situ polymerization method. The wide-angle X-ray diffraction (WAXD) results suggested that the addition of MWNTs to TLCP matrix did not significantly change the crystal structure of TLCP. The interactions between the molecules of the TLCP host phase and the carbon nanotubes were investigated through Raman spectroscopy investigations. We detected a distinct wave number shift of the radial breathing modes, confirming the carbon nanotubes interacted with the surrounding liquid crystal molecules, most likely through aromatic interactions (π-stacking). The interactions between liquid crystal host and nanotube guests were also evident from a polarizing microscopy (POM) study of the liquid crystal–isotropic phase transition in the proximity of nanotubes. The thermal properties and the morphological properties of the TLCP/MWNTs nanocomposites were investigated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). TGA data demonstrated the addition of a small amount of MWNTs into TLCP matrix could improve the thermal stability of TLCP matrix. DSC results revealed that melt transition temperatures and isotropic transition temperatures of the hybrids were enhanced.

1. Introduction

Carbon nanotubes (CNTs) [1] have attracted a great deal of scientific interest as advanced materials for next generation because of its excellent electronic, mechanical, thermal, magnetic and structural properties [2–11]. Fundamental research suggests that CNTs are regarded as promising reinforcements in the polymer composites [12] due to the combination of their uniquely excellent properties with high aspect ratio [9] and the efficient load transfer from the host matrix to the tubes [13]. So far, much work has been done in the field of preparing polymer/MWNTs nanocomposites [14–17].

Thermotropic liquid crystalline polyesters have been intensively studied because of their potential applications as high performance materials in the last two decades [18,19]. Among them, the wholly aromatic thermotropic polyesters have generally received a considerable interest for technological applications due to their high use temperatures, excellent chemical resistance, relatively high glass transition temperatures, excellent processing and mechanical properties. Liquid crystals (LC) having the long-range orientational order can align carbon nanotubes using the self-organization effect of their host. The principal symmetry axis of the LC molecules (or molecule aggregates) spontaneously tend to align along a common direction defined as the director (n) which can be conveniently reoriented by the application of external fields termed the Freedericksz transition [20]. LC alignment should be possible with the CNTs, offering a general route for controlled assembly of organized nanomaterials and devices.

In order to control and optimize the aligning effect of the liquid crystalline matrix it is important to investigate the mechanism behind it. On the one hand the degree of orientational order of the host phase is obviously a most relevant parameter, a highly ordered liquid crystal phase being potentially more successful provided that the nanotubes are well incorporated in the phase [21–23]. On the other, the interactions across the liquid crystal–carbon nanotube interface are expected to play a crucial role. Even a highly ordered host phase will have no strong aligning effect if the nanotubes in it do not experience an energy penalty if their orientation differs from the preferred orientation of the liquid crystal [24]. The stronger the interactions between nanotubes and liquid crystal molecules, the greater this energy penalty should be. Hence, strong interactions between the guest and the host

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molecules should ensure an efficient transfer of order from the LC to the nanotubes. TLCP is a typical aromatic polymer and contains benzene ring on its backbone. Therefore, a strong interaction between TLCP and MWNTs is expected due to π–π stacking, which provides feasibility to explore TLCP/MWNTs composites.

Previous work in our laboratory [25] has demonstrated the feasibility of adding MWNTs to monotropic nematic LC (MPPB) to investigate the interactions between MWNTs and host matrix and study the electrical conductivity and thermal stability of the nanocomposite. But, no improvement in thermal stability was seen at the initial state of degradation. In this paper, we prepared TLCP/MWNTs nanocomposites by in situ polymerization method and further investigated the interactions between MWNTs and host matrix. Especially, we detected the thermal stability of nanocomposites as a function of the MWNTs content in the matrix polymer. We examined that adding carbon nanotubes into TLCP had effect on the properties of the TLCP, such as melt transition temperature (T_m), isotropic transition temperatures (T_i) and thermal stability. We expected that this study will be helpful in providing the understanding on the physical properties of the TLCP nanocomposites reinforced with a small quantity of MWNTs.

2. Experimental

2.1. Materials

MWNTs (diameters: 20–40 nm, purity: 95–98%) prepared by the catalytic decomposition of CH_4 were provided by Shengzhen Nanotech Port Ltd. Co. (China). In a typical experiment, MWNTs were added into concentrated HNO_3 and this mixture was refluxed at 85 °C for 8 h. Then the mixture was diluted with excess deionized water and then vacuum-filtered through millipore PTFE membranes until the pH of the filtrate reached approximately 7. The filtrate solid was dried in vacuo at 100 °C for 24 h.

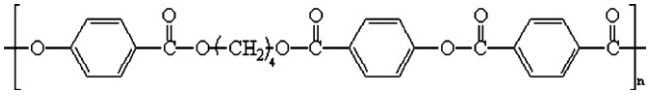
1,4-Bis(4-Hydroxybenzoyloxy)butane and terephthaloyl dichloride were used as received. Other reagents including triethylamine, 1,2-dichloroethane and acetone were AR grade and were used as supplied. The TLCP and TLCP/MWNTs nanocomposite were synthesized as follows.

2.2. Polymer preparation [26–28]

The TLCP was synthesized as follows, a solution of 1,4-Bis(4-Hydroxybenzoyloxy)butane 1.65 g (0.005 mol) and triethylamine (0.697 g, 0.012 mmol) in 1,2-dichloroethane (30 mL) was cooled to 0 °C. Then, terephthaloyl dichloride 1.02 g (0.005 mol) was added in one portion. The mixture was stirred at 0 °C for 1 h and at room temperature for 4 h under a nitrogen atmosphere, and then poured into acetone to precipitate the polymer. The white, powdery polymer was filtered off, washed carefully with water and dried at 80 °C in a vacuum oven. The yield was 94.0%. FT-IR (KBr): 2957 (CH_2), 1716 (C=O), 1603 and 1502 (aromatic), 1266–1113 (C–O) cm^{-1}. Elemental microanalysis (content %): N (0.00), C (66.74), H (4.57). T_m: 279 °C, T_i: 408 °C. The structure of thermotropic liquid crystalline polyester was showed in Scheme 1.

2.3. Preparation of TLCP/MWNTs nanocomposites

The TLCP/MWNTs nanocomposites were synthesized by the following steps, the MWNTs were added into the solution of 1,4-Bis(4-Hydroxybenzoyloxy)butane and triethylamine in 1,2-dichloroethane, followed by supersonic treatment for 2 h. The following procedure was the same as above by in situ polymerization method. In order to study whether the different content of MWNTs have effect on the properties of TLCP/MWNTs nanocomposites, we prepared a series of nanocomposites with different content. For simplicity, the composites were referred to as 0, 0.01, 0.1, 1% TLCP/MWNTs and so on, in which TLCP and MWNTs represented the components used to prepare the composites and the number denoted the MWNTs weight percent in the composites.



Scheme 1. Structure of thermotropic liquid crystalline polyester (TLCP).

2.4. Characterization

The Fourier transform infrared spectrum (FT-IR) of TLCP was recorded from 400 to 4000 cm^{-1} to identify the structure of the samples using a Nicolet Nexus 670 FT-IR from the Thermo Nicolet Inc, USA. Wide-angle X-ray diffraction measurements were performed at room temperature on a Rigaku (D/Max-IIIB) X-ray Diffractometer using Ni-filter Cu-Ka radiation. The scanning was 8°/min over a range of 2–60° at room temperature. The scanning type was continuous scan. Raman scattering spectrum was measured at room temperature using an excitation wavelength of 532 nm (JY-HR800) under the backscattering geometry. A polarized optical microscope (ECLIPSE 80i, Nikon) equipped with a THMSE 600 (LINKAM) hot stage was used to examine the liquid crystalline behavior, at a heating rate of 10 °C/min. The morphology of the surfaces of the samples was investigated using a JSM-6701 (Japan) Scanning electron microscopy (SEM). The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of TLCP/MWNTs was carried out under N_2 atmosphere on Netzsch STA 449C equipment. The samples were heated at 10 °C/min.

3. Results and discussion

The WAXD measurement plots are shown in Fig. 1 and some parameters are summarized in Table 1. It can be seen that both TLCP and TLCP/MWNTs nanocomposites had one group of low intensity diffraction peaks located at the range of 15–28°. These indicated that there were some crystal parts in these three kinds of products except the amorphous parts. Besides, the position of diffraction peaks and interplanar spacing (d) values of TLCP and TLCP/MWNTs nanocomposites were similar, illustrating that the three kinds of products attribute to one crystal systems. The *d* values of TLCP/MWNTs nanocomposites were bigger than these values of TLCP due to the crystal degree decrease little because of

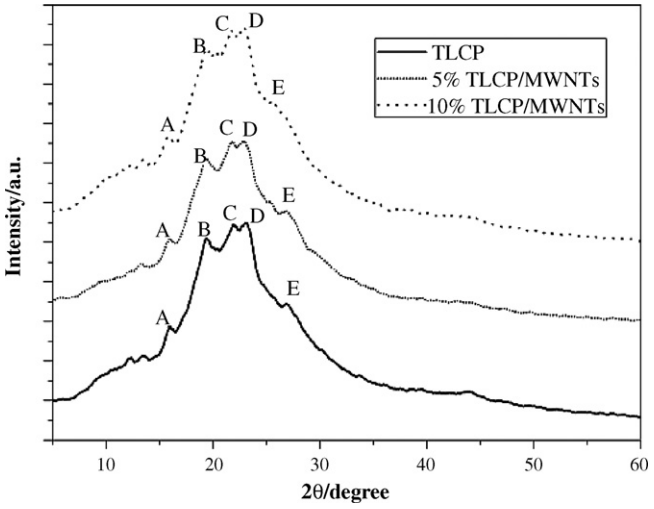


Fig. 1. WAXD of pure TLCP and TLCP/MWNTs nanocomposites.