

Properties of Thermotropic Liquid Crystalline Polyester Nanocomposites Derived from Multi-Walled Carbon Nanotubes

Wen-Feng Zhao, Ji-Xin Liu, Zhen-Kai Cui, Wu-Quan Hu, Jian Jiang, Shi-Jun Da*, and Rong Li*

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China

A series of nanocomposites containing multi-walled carbon nanotubes (MWNTs) and terephthalovldi-p-oxybenzoyl chloride-triethylene glycol copolyester (T-T) were prepared by in-situ hightemperature solution polycondensation. The liquid crystalline properties and thermal stability of the resulted MWNTs/T-T nanocomposites were investigated by wide-angle X-ray diffraction (WAXD), polarized optical microscopy (POM), differential scanning calorimetry (DSC), and thermogravimetric analyzer (TGA), respectively. The results showed that MWNT doping at a low concentration improved the thermal stability of T-T matrix and expanded the nematic temperature range without largely changing its conformation, making it more suitable for processing. The dispersion of MWNTs and interfacial interactions between the thermotropic liquid crystalline polymer (TLCP) molecules and the carbon nanotubes (CNTs) were investigated by scanning electron microscopy (SEM) and optical spectroscopies. The UV-vis spectroscopy and fluorescence spectra supported a strong $\pi - \pi^*$ interaction between the polymer and the nanotube-ster University

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1. INTRODUCTION

During the last several decades, a new branch of polymer science, i.e., the synthesis and study of thermotropic liquid crystalline polymers (TLCPs), appeared and has received intensive studies.¹⁻³ TLCPs could form a thermally stable nematic mesophase due to their excellent mechanical properties, such as superior chemical resistance, low controllable coefficient of thermal expansion, low gas and liquid permeability, excellent dimensional stability under high temperature or other adverse environments, and easy to process with high precision by extrusion and injection molding.⁴⁻⁷ Therefore, TLCPs have received considerable attention both in the neat state and as reinforcing fillers of thermoplastic polymers. TLCPs have also been used to displace conventional thermoplastic polymers and to develop commercial TLCPs and their composites such as high performance engineering plastics or fibers.⁸ Among these, main chains TLCPs have become useful structural materials, either as high precision mouldings, or as high performance fibres.

The discovery of carbon nanotubes9 has attracted a great deal of scientific interest because of their excel-

lent electrical, mechanical, thermal and magnetic prop-

erties, such as low density, high surface area and high

chemical stability. CNTs have been envisioned as promis-

ing materials for potential applications in many fields.^{10,11}

Intensive research has focused on CNTs composite mate-

rials with enhanced mechanical,¹² electrical¹³ and thermal

properties,¹⁴ which suggests that CNTs are regarded as

effective reinforcements in the polymer composites¹⁵ due

to the combination of their unique properties with high

aspect ratio¹⁶ and the efficient load transfer from the host

matrix to the tubes.¹⁷ Recently, much work has been done

erties of nanometer materials (e.g., quantum size effect,

small size effect, surface and interface effect),²¹ Poly-

mer nanocomposites have become the object of intensive

research during the last decade. TLCPs with rigid-rod-

like molecules have the long range orientation order and can be preferentially orientated to form fibrils under elon-

gational or shear flow during melt processing, termed as the Freedericksz transition.²² While carbon nanotubes are

Because of their special physical and chemical prop-

in preparing polymer/MWCNTs nanocomposites.¹⁸⁻²⁰

^{*}Authors to whom correspondence should be addressed.

order of nanometers, their lengths range from microns to centimeters.²³ Furthermore, it was expected that the aromatic structure of the TLCP could interact strongly with the graphene sheet of the nanotube surface through intermolecular overlap of π -orbitals (π -stacking).²⁴ So it is very interesting for carbon nanotubes in combination with liquid crystals to form a new research area.²⁵ Recently, Kim and coworkers²⁰ demonstrated that the thermal, mechanical and rheological properties of aromatic polyester PEN/carbon nanotube nanocomposites were strongly dependent on the homogeneous dispersion of CNTs and the interactions between CNTs and PEN, which could be enhanced by slight chemical modification of CNTs. Kim et al.²⁶ also reported that a very small quantity of CNTs could remarkably improve thermal stability and mechanical properties of the TLCP nanocomposites. Jyongsik Jang et al.²⁷ reported that surface oxidation of CNTs could improve the mechanical durability and thermal stability of LCE-CNT comoposites. The selforganizing properties of anisotropic, calamitic nematic liquid crystals have been exploited to align a minute number of CNTs.²⁸ Evidence of MWNT alignment was found in the studied polyazomethine/MWNT composites.²⁹ Wern-Shiarng Jou et al.³⁰ reported that the electromagnetic shielding effectiveness of CNTs/LCPs was higher than that of CNTs/melamine formaldehydes (MF) composites. Similarly, electromagnetic interference shielding effectiveness of carbon nanofiber/liquid crystal polymer (LCP) composites was also discussed.31

In the present work, efforts were made to study thermal properties and liquid crystalline behaviors of the TLCP/MWNTs nanocomposites. We first prepared the TLCP nanocomposites with various concentrations of MWNTs by *in-situ* polymerization and then investigated the interactions between MWNTs and host matrix, as well as the profound effects of MWNTs on the nanocomposites properties.

2. EXPERIMENTAL DETAILS

2.1. Materials

MWNTs (diameters: 20–40 nm, purity: 95–98%) prepared by the catalytic decomposition of CH₄ were provided by Shenzhen Nanotech Port Co. Ltd. (China). In a typical experiment, raw MWNTs (1 g) were added to a mixture (160 ml) of concentrated sulfuric acid and nitric acid (3:1 volume ratio) and sonicated in a water bath at 50 °C for 12 h to remove mineral and catalyst additives and to increase some –COOH or –OH groups on the CNTs surface, which may decrease the $\pi - \pi$ stacking effect among the aromatic rings of the nanotubes, leading to the formation of their agglomeration.³² After filtration, the remaining black power was washed with deionized water until the pH value reached neutral. 4-Hydroxybenzoic acid, terephthaloyl dichloride and triethylene glycol were used as received Diphenylether and thionyl chloride were AR grade and used as supplied. The TLCP and TLCP/MWNTs nanocomposite were synthesized as follows.

2.2. Preparation of TLCP and the Nanocomposites

The terephthaloyl-di-p-oxybenzoyl chloride (TOBC) was synthesized according to Bilibin et al.³³ A solution of TOBC (0.885 g, 2 mmol) and triethylene glycol (0.300 g, 2 mmol) in diphenylether (20 mL) was purged with nitrogen and then stirred at 180 °C for 10 h under a slow but steady nitrogen flow. After being cooled to the room temperature, the mixture was poured into large methanol to precipitate the polymer. The white powdery polymer was filtered and washed carefully with acetone and water. The final product was dried at 80 °C in a vacuum oven. The steps are shown in Scheme 1. IR (TOBC): 1778.14 cm⁻¹ (COCI), 1738.05 cm⁻¹ (COOR), 1597.69 cm⁻¹, 1409.46 cm⁻¹ (C=C), 1266.41 cm⁻¹ (C=O); IR (T=T): 2891.16 cm⁻¹ (-CH-), 1731.28 cm⁻¹ (-COO), 1271.34 cm⁻¹ (-O=C=C), 1603.30 cm⁻¹ (-C=C).

The T–T/MWNTs nanocomposites were synthesized by the following steps: the MWNTs were added into the solution of triethylene glycol and terephthaloyl-di-poxybenzoyl chloride in diphenylether, followed by supersonic treatment for 2 h. The subsequent procedure was the same as the T–T preparation. In order to investigate the effect of different MWNTs content on the properties of T–T/MWNTs nanocomposites, we prepared a series of nanocomposites with the CNT content ranging from 0.1 to 5.0 wt%. For simplicity, the composites were referred to as 0.1, 0.3, 1.0, 5.0 wt% and so on.

2.3. Characterization

The Fourier transform infrared spectrum (FT-IR) of TLCP was recorded from 400 to 4000 cm⁻¹ to identify the structure of synthesized 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-K α radiation. The scanning was



Scheme 1. Preparation steps and structure of T-T.

 8° /min over a range of $2\theta = 2-70^{\circ}$. The morphology of the samples was investigated using a JSM-6701 Scanning Electron Microscopy (JEOL, Japan). The thermal and thermogravimetric analyses of TLCP/MWNTs were carried out under N₂ atmosphere on Netzsch STA 449C equipment. The samples were heated at 10 °C/min. A polarized optical microscope (XS-402P) equipped with a hot stage was used to examine the liquid crystalline behavior, at a heating rate of 10 °C /min The characterization of interactions between CNTs and LCPs was performed on a Perkin Elmer Lamda 35 UV-VIS Spectroscopy and a Hitachi F-4500 Fluorescence Spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction

Figure 1 shows the representative WAXD patterns of pure T-T and the T-T/MWNTs nanocomposites in the region of $2\theta = 2-70^\circ$. The sharp diffraction peak is indicative of the presence of crystallites in the copolyester. From the WAXD plots, it can be seen that there is a sharp diffraction peak around $2\theta = 20^\circ$, while a little more diffuse diffraction peak appears around $2\theta = 23.5^{\circ}$ for the neat TLCP, demonstrating that T-T is a semicrystalline TLCP. This can be further evidenced from the DSC thermograms. With the increase of MWNT concentration from 0.1 wt% to 5.0 wt%, the strong reflections observed for pure T–T were also seen for T-T/MWNTs nanocomposites. Compared to neat T-T, the T-T/MWNTs nanocomposites showed virtually featureless XRD patterns. This observation seems to suggest the presence of strong attractive interactions between T-T matrix and MWNTs, as well as the highly dispersion of MWNTs in the nanocomposites.³⁴ However, the crystalline peaks become weaker with the increase of MWNT contents, demonstrating that the introduction of MWNT caused a reduction in crystallinity of TLCP



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

host. Fortunately, the mesophase structure of T-T in the nanocomposite might seems not significantly affected.

3.2. Morphological Characterization

SEM micrographs in Figure 2 clearly show that the MWNT loading can significantly affect the morphology of the nanocomposites.²⁹ It is evident that nanotubes are aligned along the LC director at a low concentration and fiberlike nanostructures are formed in the T–T/MWNTs composites (Fig. 2(a)), demonstrating that liquid crystals could induce the CNT alignment. However, with the increase of MWNT content, the pull-apart shape of MWNTs appears (Fig. 2(b)). Figure 2(c) shows that at high MWNTs content,³⁵ the degree of polymer structural organization lost and disruption of the orientation and aggregation of the MWNTs appeared.

3.3. Thermal Behaviors

The TGA curves for neat T-T and the prepared T-T/MWNTs nanocomposites are presented in Figure 3. The two phases in the thermal decomposition curves are attributed to the fact that the main chain of the polymer is composed of flexible diol segments and thermally stable rigid aromatic units.³⁶ The diol segments decomposed first, followed by the heat resistant aromatic chain. The weight loss due to the decomposition of TLCP and its hybrids (0.1-5.0 wt% MWNTs) was nearly the same until the temperature reached about 390 °C. After this point, the initial degradation temperature was influenced by MWNT loading in hybrids. When the content of MWNTs increased from 0 wt% to 1 wt%, the initial degradation temperature increased from 399 °C to 403 °C, correspondingly. From Figure 3, it seems that the degradation rate of pure T-T was faster than its nanocomoisites (0.1–1.0 wt% MWNTs).

In this work, an extreme case (with 5.0 wt% MWNTs) was also created to investigate the negative effects of excessive content of MWNTs. Though the incorporation of MWNTs into TLCP increased the thermal stability and the residual weight for T-T/MWNTs nanocomposites, the initial degradation temperature of 5.0 wt% MWNTs/T-T decreased sharply. This may be due to the poor MWNT dispersion in the TLCP matrix and the CNTs segregation and reagglomeration when the composite was melted, which could have caused more deterioration on the crystallinity of the TLCP. In the meantime, the induced LC defects actually decreased the thermal stability. Another possible mechanism was that the presence of MWNTs reduced crosslinking of the matrix chain.³⁷ The results demonstrate that the presence of MWNTs could help stabilize the T-T matrix at low concentrations, thereby enhancing the thermal stability of TLCP nanocomposites. The introduced CNT could induce protective barriers against thermal decomposition and retard the thermal decomposition of T-T nanocomposites, as a result of the



Fig. 2. SEM images of (a) 0.3 wt.% MWNTs/T-T, (b) 1.0 wt.% MWNTs/T-T and (c) 5.0 wt.% MWNTs/T-T.

effective function of CNTs as physical barriers to hinder the transport of volatile decomposed products out of TLCP nanocomposites during thermal decomposition.^{38, 39}

The DSC traces of T-T and T-T/MWNTs nanocomposites are shown in Figure 4 and some parameters are summarized in Table I. Neat T-T is a semicrystalline TLCP having a melting temperature (T_m) of ca. 173.1 °C and a clearing (isotropization) temperature (T_i) of ca. 385.3 °C. It could be seen that incorporation of MWNTs into T-T matrix had little effect on T_m , while T_i of the nanocomposites was obviously increased with MWNT concentration. This is probably because rigid aromatic units of T-T could interact strongly with the CNTs, mainly through $\pi - \pi$ conjugation, restricting the movement of rigid mesogenic units.⁴⁰ Thus T_i of T–T/MWNTs is logically enhanced. However, there is no π -stacking between CNTs and the flexible diol spacers, and hydrogen bond interaction is the most possible one.²⁶ Due to the very few carboxylic acid groups or hydroxyl groups on the nanotube surface, the interactions across the liquid crystal-carbon nanotube interface are too weak to limit the diol segment motion. Finally, no significant change in the melting point of the T-T phase was detected in the hybrids. The melting and isotropization associated enthalpy changes $(\Delta H_m, \Delta H_i)$ were also given (Table I), which decreased as MWNT content increased.



Fig. 3. TGA thermograms of the pure TLCP and TLCP/MWNTs nanocomposites.

3.4. Liquid Crystalline Properties

Figure 5 shows the representative POM micrographs of T-T and T-T/MWNTs nanocomposites during heating from the solid state. Polarized optical microscopy studies revealed the presence of a nematic mesophase, typical birefringence of T-T (Fig. 5(a)). When the content of MWNTs was 0.3 wt%, we could not see the CNT agglomeration, demonstrating that MWNTs were dispersed very well in the hybrid (Fig. 5(b)). From Figures 5(b and c), it could be seen that MWNTs were aligned along the vector of liquid crystal phase. However, the agglomeration of MWNTs began to appear for the 1.0 wt% sample (Fig. 5(c)). Some disorientation of the nematic domains was also observed, due to the many LC defects induced by the nanotube aggregates.³⁵ The liquid crystallinity of the nanocomposites was not obvious when the MWNT content was up to 5.0 wt%. Here we only chose a local glimpse for 5.0 wt% sample to illuminate the interfacial interactions of the nanocomposites. It was observed that at the temperature of the phase transition the birefringence texture was still stable in the proximity of large bundles of nanotubes (Fig. 5(d)), indicating the persistence of the nematic phase in these regions. In other areas, the phase turned black and thus became isotropic. However, when the temperature was decreased, the first signs of birefringence appeared



Fig. 4. DSC thermograms of the pure TLCP and TLCP/MWNTs nanocomposites.

35.1

25.6

nanocomposites.				
Sample (wt%)	$T_m(^{\circ}\mathrm{C})$	T_i (°C)	ΔH_m (J/g)	ΔH_i (J/g)
0.0	173.1	385.3	23.6	117.2
0.1	174.6	410.9	22.9	63.3
0.3	175.1	412.3	21.7	57.2

428.0

430.6

21.2

19.3

175.3

177.2

Table I. DSC results of the pure TLCP and TLCP/MWNTs

again around the nanotube bundles. These observations confirmed that the T–T molecules interact strongly with the MWNTs surface, making the degree of order in the vicinity of large-scale aggregates of MWNTs increased. The CNT bundles could also be regarded as nucleation centres for liquid-crystalline organization.^{24, 41} The temperature ranges of all nematic phases we observed during heating were basically consistent with the DSC thermograms.

3.5. Optical Spectroscopies

1.0

5.0

The optical spectroscopies support a typical $\pi - \pi$ interaction between T–T and the nanotubes (Fig. 6). Pristine T–T shows a strong absorption band at around 208 nm, which is attributed to the $\pi - \pi^*$ transition. When doped with MWNTs (1.0 wt%), the $\pi - \pi^*$ characteristic peak of the T–T matrix in the nanocomposite are shifted to lower wavelength (203 nm) and a substantial decrease in absorbance occurs. This suggests that there are strong interactions between the aromatic rings of T–T and MWNTs. The other possibility responsible for the blue shift is that when the backbone conformation of polymer was modified due to its interaction with a nanotube,⁴² the extent of π -conjugation decreased and the band gap increased, similar to a blue shift. In 1.0 wt% MWNTs/T–T, no significant shift was seen in the energy absorption band



Fig. 5. POM images of (a) pure T–T at nematic phase, (b) 0.3 wt.% MWNTs/T–T at nematic phase, (c) 1.0 wt.% MWNTs/T–T, and (d) 5.0 wt% MWNTs/T–T at the transition from nematic to the isotropic phase. Large bundles were chosen in order to easily investigate the texture of T–T around them.



Fig. 6. Room-temperature solution-phase (C_2H_5OH) UV-visible spectra (25 μ g/mL) and solid state fluorescence spectra (inset) (excitation wavelength: 383 nm).

for T–T, indicating that the π -conjugation of T–T is largely unchanged.⁴³

The strong fluorescence of T–T is efficiently quenched in the nanocomposite (1.0 wt% MWNTs) by *in-situ* polymerization (inset). The quenching likely arises from efficient energy transfer between T–T and MWNTs, suggesting the disruption of π -conjugation caused by a conformational change was not a big issue. Energy transfer quenching between molecules and for molecules on graphitic carbon and metal surfaces was reported long before.⁴⁴ In this work, we prepared the reference sample (mixing 5.0 wt% MWNTs with pristine T–T by simple stirring) to remove the effect of MWNT itself and to make the *in-situ* polymerization easier.

On the basis of the UV-vis and fluorescence results, we come up with the following hypothesis: Owing to the favorable *in-situ* polymerization, the T–T chain gets more closer to the graphitized MWNT surface, which may promote more efficient $\pi - \pi^*$ interaction⁴⁵ and such parallel stacking and interaction are quite common in many cases.^{42, 46, 47}

4. CONCLUSIONS

A series of MWNTs/TLCP nanocomposites have been prepared via *in-situ* polymerization. The crystal structure of T–T matrix was not greatly perturbed by the incorporation of MWNTs. On the basis of POM and SEM studies, we found that MWNTs could be well dispersed and aligned along the vector of the liquid crystal phase at low content. At the same time, the MWNT aggregates probably acted as the nucleation centres for liquid-crystalline organization and could stabilize the liquid crystal phase. The enhanced thermal properties were also observed from TGA and DSC results. In the end, optical spectroscopies were used to

RESEARCH ARTICLE

characterize the interfacial interaction between T-T and the MWNTs.

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