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Preparation and characterization of carbon nanotubes/monotropic liquid crystal composites

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ABSTRACT

In this work, we fabricated the composites containing multi-walled carbon nanotubes (MWNTs) and 4-methoxyphenyl-4′-propylbenzoate (MPPB), a monotropic nematic liquid crystal (LC), via ultrasonication. The nematic phase and thermal stability of the resultant MWNTs/MPPB nanocomposites were investigated by polarized optical microscopy (POM) and thermogravimetric analyzer (TGA) respectively, aiming at examining the effect of the dispersion of MWNTs on the MPPB director field and thermal properties. Because of the weak ability to impose anisotropic order on carbon nanotubes (CNTs) in its matrix, the nematic domains became disoriented with MWNT loads. From the TGA results, we found that the MWNTs nearly had no effective barrier effect on the decomposition of the composites. The dispersion of MWNTs and interfacial interactions between the LC molecules and the CNTs were investigated through scanning electron microscopy (SEM) and Raman spectroscopy. The experimental results showed that the electrical conductivity of the nanocomposite was enhanced with the increment of the concentration of MWNTs. The surface resistance of the composite could fall from 10^{11} to 10^{4} Ω (by 7 orders of magnitude), which was favorable for many practical uses, especially in one-way electronic devices.

1. Introduction

Due to their unique electronic, mechanical, and physical properties, carbon nanotubes (CNTs) have been envisioned as promising materials for potential applications in many fields [1,2]. Many non-conductive materials were expected to improve thermal or electrical properties by combining conductive CNTs with their insulating matrices of different nature [3,4]. The improved properties were thought to be related to the formation of the percolation chains of CNTs inside an insulating matrix, and sometimes the percolation threshold was observed at extremely low concentrations of CNTs [5,6]. Intense research has focused on CNTs composite materials with enhanced mechanical [7,8], electrical [5,9] and thermal properties [3,10]. Many promising applications of these composites as functional conductive materials, electrical switch devices, glues, and sensors of gas, PH and pressure, have been explored [1].

Despite the extraordinary promise of CNTs, their realistic application as one-dimensional conductors or semiconductors has been restricted because of difficulties in aligning them in the desired direction. Well-arrayed CNTs are highly desirable for the preparation of a variety of nanodevices, particularly where one-dimensional charge migration is important. Much effort has been invested in recent years to achieve significant control over the orientation of the carbon nanotubes in the matrix. Among the methods that have been proposed can be mentioned magnetic [11] and electric [12] field alignment, shear flow [13] or other mechanical techniques (i.e. molecular combing [14]), as well as aligned growth [15,16]. However, all of these are either dependent on ‘external force’ or restricted to a narrow range of size scales.

Liquid crystals (LCs) 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 [17]. LC alignment should be possible with the CNTs, offering a general route for controlled assembly of organized nanomaterials and devices. There are probably three relevant parameters for a highly ordered liquid crystal phase: the degree of orientational order of the host phase, the nanotubes well incorporated in the phase, and the interactions across the liquid crystal–carbon nanotube interface. An efficient transfer of order from the LC to the nanotubes would happen if there were strong interactions between the guest and the host molecules having strongly aligning effects [18]. The self-organizing properties of anisotropic, calamitic nematic liquid crystals have been exploited to align a minute number of CNTs [19–23]. Aligned CNTs in the

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supramolecular order of discotic LCs was reported by Kumar and Bisoyi [24]. Using lyotropic LCs to align the nanotube has also been proposed [25]. What is more, the formation of lyotropic liquid-crystalline phases by acid-functionalized CNTs in water [26], DNA-stabilized CNTs in water [27], and functionalized CNTs in acids [28] has been reported. The integration of SWNTs in a hexagonal lyotropic liquid-crystalline phase of the well-known surfactant Triton X 100 has recently been described by Weiss et al. [29], and the preparation of nematic nanotube gels was reported by Islam et al. [30]. Herein, we use a monotropic nematic LC (MPPB) matrix as a source of the alignment of the multi-walled carbon nanotube (MWNTs) for the first time and investigate the interactions between MWNTs and host matrix. The resulted MWNTs/MPPB nanocomposites are also carefully studied for various properties in our present work.

2. Experimental

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, 1 g of raw MWNTs 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 323 K for 12 h to remove mineral and catalyst additives, as well as increase –COOH or –OH groups on the surface. After filtration, the remaining black power was washed with deionized water until the pH value reached neutral.

The 4-methoxyphenyl-4′-propylbenzoate (MPPB) provided by HeBei LuQuan New Type Electronic Materials Ltd. Co (China) was used as received. The MPPB has a monotropic liquid crystal phase as the mesophase is only observed on cooling at probably 313 K. The phase sequence is K–I on heating, and I–N–K on cooling (K = crystal phase, N = nematic phase, I = isotropic melt phase). It displays an isotropic phase above 331.9 K.

The MWNTs/LC composites were obtained by addition of the appropriate weights of MWNTs (0.05–8%) to the LC solvent in the isotropic state ($T = 343$ K) with subsequent 2–3 h ultrasonication of the mixture.

Polarized optical microscopy was performed using an ECLIPSE 80i microscope fitted with a Mettler FP-82 hot stage, at a cooling rate of 10 K/min. The TG analysis was carried out on a Dupont-1090 TG analyzer in flowing N_2 at a heating rate of 10 K/min. The electrical conductivity of the final products was measured by depositing silver microelectrode contact pads on the surface of composite films and using a Keithley 2004 multimeter, which was operated by LabView software. Each measurement was repeated five times to calculate the mean value of the experimental data. Microscope measurements were taken on a JSM-6701F electron microscope to investigate the morphology of the composites. The Raman scattering spectrum was measured at room temperature using an excitation wavelength of 532 nm (JY-HR800) under the backscattering geometry.

3. Results and discussion

Fig. 1 shows the representative POM micrographs of MPPB and MWNTs/MPPB nanocomposites during cooling from the melt. Polarized optical microscopy studies revealed the presence of a nematic mesophase, typical of MPPB, and MWNT aggregates, probably due to CNTs segregation and reagglomeration when melting the composite, or to poor MWNT dispersion in the monomer. The transition from isotropic to the nematic phase was also explored herein. We could see the nematic director, *n* clearly in Fig. 1a. The nematic phase lose its director in Fig. 1b, though it exhibits the characteristic texture, as well as birefringence. The MWNT aggregate was much too large to allow LC alignment of the contained nanotubes, same to the discussion in previous report [31]. In that case, the CNTs influenced the director, rather than the other way around, stabilizing the starting configuration and counteracting the effect of the electric field. The disorientation of the nematic domains was also explained as a large number of LC defects induced by the nanotube aggregates [32]. Besides the aggregation, the nature of the LC matrix also plays an important role. Due to the nematic phase occurring only during the cooling process and fading away very soon, the MPPB matrix is expected to have little ability to align the MWNTs with very large surface areas and strong Van der Waals forces tying them together.

Comparing Fig. 1a with Fig. 1b, one also could find that Fig. 1a is brighter than Fig. 1b. The MWNTs/MPPB nanocomposite had low birefringence. The reason was that the sample was too black to enable sufficient light transmission through it. It was also probably related to the polarizability of the LC molecule influenced by MWNTs, which brought about the different refractive index from the LC medium [33].

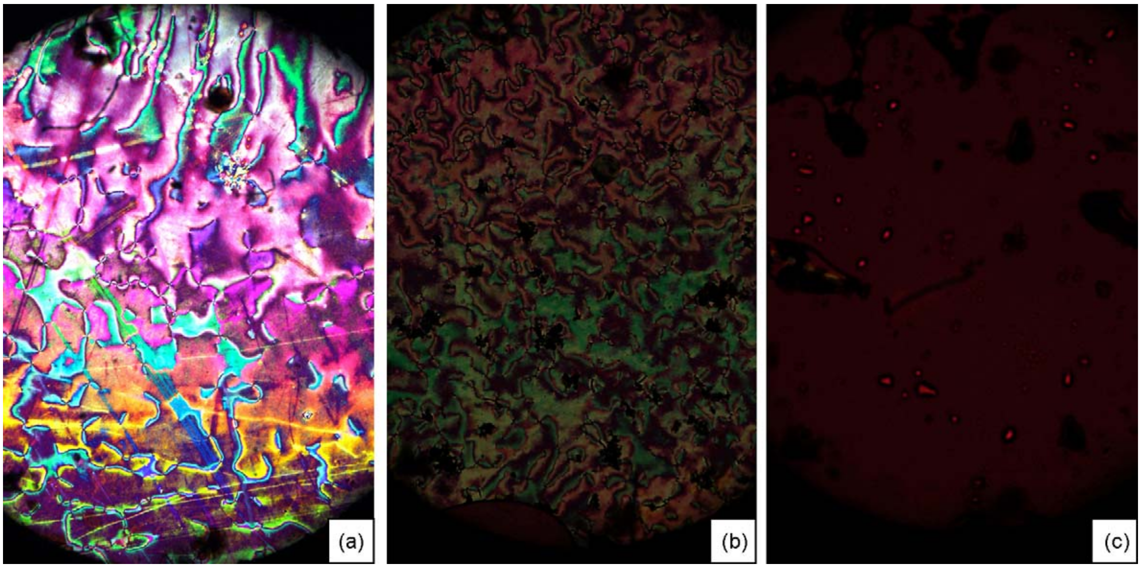

Fig. 1. POM images taken during cooling of (a) pure MPPB at nematic phase, (b) 3 wt.% MWNTs/MPPB at nematic phase, and (c) 3 wt.% MWNTs/MPPB at the transition from isotropic to the nematic phase.