

Matrix mediated alignment of single wall carbon nanotubes in polymer composite films

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Abstract

Alignment of single wall carbon nanotubes (SWNT) in liquid crystalline (LC) polymer matrix imparting orientation to the nanotubes along the nematic director was studied by atomic force microscopy, measurements of electrical conductivity and Raman spectroscopy of the composite in the directions parallel and perpendicular to the nematic director. The composites were prepared through dispersion of SWNT with LC monomer in a common solvent, their alignment in nematic monomer and consequent UV polymerization of the monomer. The anisotropy of electrical and optical properties of the system depends strongly on the concentration of the nanotubes in the range of 1–10% SWNT being especially strong for smaller concentrations and negligible at higher loads. A simple semi-quantitative model is suggested to account for the orientational behavior of nanotubes in nematic matrices. It successfully describes the observed anisotropy of physical properties at microscale (up to 200 μm) in terms of anchoring of the polymer chains to the nanotubes surface and adjustment of the nanotubes orientation to the nematic direction due to such coupling. The increasing disorientation of the nematic domains at higher nanotubes loads is explained as a development of larger number of LC defects induced by the nanotubes in the nematic matrix due to their intrinsic nature of aggregation. The anisotropy of physical properties at macro scale (several millimeters) is much smaller and less dependable on SWNT concentration because differently oriented LC domains effectively wash out the anisotropy.

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1. Introduction

Carbon nanotubes are considered as highly prospective filler materials for future polymer composites due to the large surface to volume ratio, high mechanical strength and extraordinary electrical properties [1–3]. For a long time intrinsic conducting polymers (ICP) like polyaniline (PANI) and their composites have been considered as the only choice in the field of flexible electronics [4]. However, due to their poor processability, low stability and prohibitive cost alternate materials are imperative. Polymer composites with tunable electric properties are an important alternative to meet the demands of flexible electronics. Single wall carbon nanotubes, which exhibit metallic and semi-conducting properties

depending on their chirality are a natural choice for developing new polymer composites. However, due to the size of carbon nanotubes and significant intertube van der Waals interactions, the synthesis of polymer/nanotube composites with desired distribution and tailored properties (isotropic or anisotropic) has been a significant challenge. Dispersion of carbon nanotubes has been previously achieved by choosing the right solvent [5] for nanotubes and polymer, applying high shear forces and functionalizing carbon nanotubes in order to improve the compatibility with the matrix. Carbon nanotubes have also been dispersed in the polymer matrix by polymerization of the monomer in the presence of a filler [6].

In order to tune the electronic properties (i.e. conductivity) of the composite it is desirable to achieve significant control over the orientation of the carbon nanotubes in the matrix. The orientation of carbon nanotubes has been controlled by a variety of methods including alignment in the presence of strong electric and magnetic fields, mechanical stretching, shear forces, and fluid flow [7–11]. Recently, the alignment of carbon nanotubes in layer-by-layer assembled polyelectrolyte

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films was achieved by blowing air at the air–water interface and inducing the evaporation of the solvents [12]. In all the methods demonstrated so far an ‘external force’ producing the orientation of the nanotubes has been a common factor.

Anisotropic distribution of SWNT in the polymer matrices results in conductivity increased by several orders of magnitude compared to the isotropic distribution and causes a significant alteration of percolation thresholds [13,14]. Polymer composites of polyvinyl alcohol with less than 1% of multi-walled carbon nanotubes (MWNT) have an increased Young’s modulus by a factor of two [15]. This was attributed to the formation of a well-ordered polymer coating, which served as the interface layer between the nanotubes and the matrix.

Liquid crystals (LCs) are expected to have the ability to impose anisotropic order on carbon nanotubes dispersed in a LC matrix. Dierking et al. [7] have recently demonstrated that CNT aggregated into anisotropic fibrils could be aligned resulting in significant anisotropy of the electrical conductivity. However, the anisotropy was higher in the case of MWNT than in the case of SWNT.

In this communication, we describe a novel alignment method using a liquid crystalline polymer matrix as a source of the alignment of the SWNT, obviating any need for strong external forces.

We study the anisotropy of nanotubes’ alignment at different concentrations of carbon nanotubes in the matrix and quantify the anisotropy of electrical conductivity in terms of a simple model.

2. Experimental details

The structure of LC monomers used in preparation of oriented LC films is shown in Scheme 1. The LC mixture contained 28% of molecules A (bifunctional cross-linking mesogens), 70% of molecules B (monofunctional mesogenic units), and 2% of benzophenone (the initiator of polymerization). This composition was previously optimized to achieve relatively low melting temperature and satisfactory range of the mesogenic (nematic) phase [16].

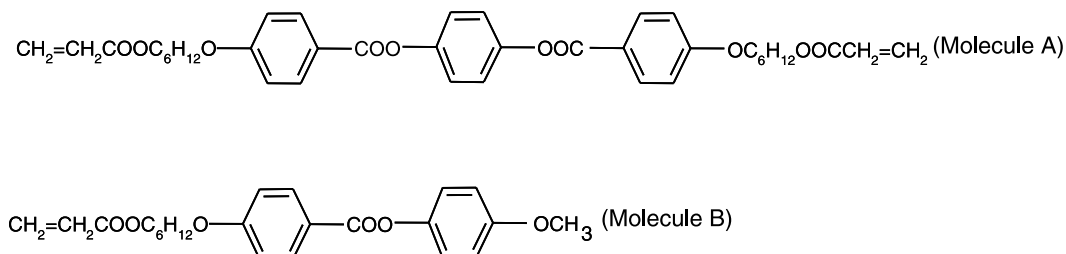
The nematic phase of the mixture exists in the temperature interval between 55 and 95 °C. The commercial mixture of LC monomers, RMM34 provided by Merck was also used to prepare some films. Physical properties such as electrical conductivity and optical anisotropy of films prepared from both mixtures were very similar. SWNT prepared by the arc discharge process with nickel and yttrium as the catalyst,

were donated by Carbolex Inc. and were used without further purification. AFM studied showed that nanotubes are characterized by average diameter of 1.4 nm and are bound into bundles of typically seven nanotubes as reported elsewhere [5].

Carbon nanotubes were mixed with monomers, stirred in a mixture, and heated above the melting temperature. Organic solvent (toluene, Aldrich) was added to the mixture of nanotubes and monomers in order to decrease a viscosity of the mixture. The solution was cast on glass substrates with the deposited aligning polyimide layers and solvent was slowly evaporated. Thin film of the polymer with embedded nanotubes was then heated, melted and covered with a top glass. The composite placed between two glass plates was oriented by rubbed polyimide coatings providing unidirectional orientation of the LC. Nanotubes had a tendency to aggregate during evaporation, but this tendency was overcome by sliding glass plates one with respect to the other. The distance between the glass plates was controlled by glass beads placed between the plates. The typical thickness of the samples was ~40 μm. The thickness of 40 μm was chosen because of consideration of several factors. The films with a smaller thickness were prone for spontaneous wrapping and folding after their detachment from the substrate, which made them very inconvenient for further manipulation. On the other hand in thicker films the orienting influence of the glass substrate is not transmitted through the whole film. The thickness of ~40 μm was therefore found to be the optimal as the films exhibited mechanical stability and satisfactory alignment of the nematic phase.

Polymerization of LCs was induced by UV lamp irradiation at 365 nm. Up to 20% of monomer may remain unpolymerized in highly cross-linked systems under UV polymerization conditions applied in this study. However, no traces of the monomer were found in DSC experiments. Moreover, the presence of the monomer should not influence the alignment of nanotubes since orientation of the latter occurs when the monomers are melted. The orientation achieved in the melted state is then almost instantly frozen in polymerization.

After polymerization, the upper glass was removed and polymer films with a low concentration of nanotubes were examined under the microscope in polarized light. The areas with the highest optical anisotropy were used for conductivity measurements and AFM imaging. The polymer films with a nanotube concentration higher than 4% were found to be completely opaque. The electrical conductivity of the composite films was measured by depositing silver microelectrode contact pads on the surface of composite films and using a



Scheme 1. Monomers used for LC polymer synthesis.

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