

Electric Field Effect on the Rheology of MWCNT Dispersions in Liquid Crystalline Polymers

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ABSTRACT

To achieve the full potential of nanocomposites anisotropic particles have to be well dispersed and their orientation controlled. In this research, we combine the self-organizing properties of liquid crystal polymers (LCP) and the fact that the carbon nanotubes are electronically polarizable to develop novel oriented LCP nanocomposite materials. The electrorheological (ER) effect of multi-walled carbon nanotubes dispersions on LCP matrices was observed and quantified experimentally. A non-electric field responsive, hydroxypropylcellulose (HPC), was used as the polymeric matrix. A negative ER effect on the steady-state viscosity was observed. Simple mechanisms for homogeneous or heterogeneous ER fluids do not capture the observed behavior. Additionally, the electric field effect on quiescent samples has been analyzed by polarized optical microscopy to elucidate the mechanisms for the observed rheological response. Neither bundle aggregation nor migration to the electrodes was observed at the micro-scale.

Keywords: MWCNT, liquid crystalline polymer, nanocomposite, electrorheology

1 INTRODUCTION

Carbon nanotubes (CNTs) composites have attracted attention due to their exceptional mechanical, such as high tensile strength, and electronic properties. Proposed applications for light and high strength nanotube-reinforced composites span from biomedical to aeronautic industries. However, the control of the dispersion and orientation of CNTs in polymeric matrixes is an important issue to obtain better and efficient nanocomposites applications and to obtain multifunctionality.

Many techniques have been proposed to achieve their alignment such as the introduction of argon gas in a laser ablation reactor[1], application of an external electric or magnetic field [2-6], deposition of individual nanotubes using chemically functionalized nanolithography templates [7], electrophoresis [8], flow-induced alignment [9], and using the self-organizing properties of the liquid crystals (LC) [10-12]. Most of these methods are not suitable for the preparation of nanocomposites, since they cannot be transferred to continuous processing or are limited to

laboratory scale processes. For example, orientation with LC surfactants is not feasible because there is no efficient method to solidify the composite without adding stress to it, without losing the LC phase and the CNT disorientation [11, 13]. In spite of all the efforts to achieve a better orientation, no successful technique which allows a controlled and reproducible production of CNT nanostructures has been developed.

In this work, we take advantage of the self-organizing properties of a liquid crystalline polymer (LCP) matrix and its inherent processing flexibility to orient MWCNTs, and explore the use of the LCP's ability to orient with external flow and electric fields to orient the nanotubes. We present the electrorheological characterization of MWCNT dispersion on LCP matrices, and the electric field effect on quiescent samples using polarized optical microscopy. The chosen LCP matrix does not have a response with an electric field. These experiments provide additional understanding of the mechanisms of particle orientation on the LCP matrix.

2 EXPERIMENTAL METHODS

2.1 Materials

Hydroxypropylcellulose (HPC) ($M_w = 100$ kDa) and multiwalled carbon nanotubes (>95%, O.D. = 20-30 nm, L = 0.5-2 μm) were purchased from Sigma Aldrich, while *m*-cresol (97% purity) was purchased from Fisher Scientific. A completely liquid crystalline phase was observed for polymer concentrations above 35 wt% in a Micromaster II polarized optical microscope. The HPC/MWCNT/*m*-cresol solutions were prepared by mixing of HPC in MWCNT/*m*-cresol stock solutions up to a 45 wt% of polymer. Solutions were left to equilibrate for at least one week. Stock solutions and final mixtures were dispersed by ultrasonification in a Branson 450W sonicator. Previous work has shown that MWCNT particle loadings below one volume percent do not have an effect on the scaling of the linear viscoelastic moduli, which suggested no effect on the liquid crystalline structure of the solution [14, 15]. In the case of solutions for the optical study, sonication time was minimized to produce samples where MWCNT bundles could be identified on the micron scale.

2.2 Electrorheology

Electrorheological characterization was performed on a Rheologica StressTech HR (ATS RheoSystems) stress controlled rheometer using stainless steel 35 mm parallel plate fixture on an electrorheological (ER) cell equipped with a TReK high voltage power supply. After loading, the sample was allowed to relax for 10 to 15 min. Transient experiments at constant temperature of 25 °C were performed at a constant shear rate of 1 s⁻¹. The steady-state viscosity was obtained by averaging plateau measurements over an interval of at least 30-seconds. Error bars correspond to the standard deviation.

2.3 Polarized Optical Microscopy

The effect of an electric field on the phase behavior of quiescent samples was assessed by polarized optical microscopy on an Olympus BX51. A custom built glass slide set-up, shown in Figure 1, was used. In this configuration, a sample was placed between two square thin copper plates connected to a TReK 610E high voltage power supply. The applied electric field is perpendicular to the observation axis and its strength corresponds to the voltage divided by the plate separation. Texture plates were recorded as a function of the effect of field strength (up to 0.50 MV/m) and exposure time (up to 5 min) was evaluated. At higher electric fields attraction between the microscope objective and the copper electrodes prevented observations. The drawn current through the sample was directly measured on the power supply as a function of time.

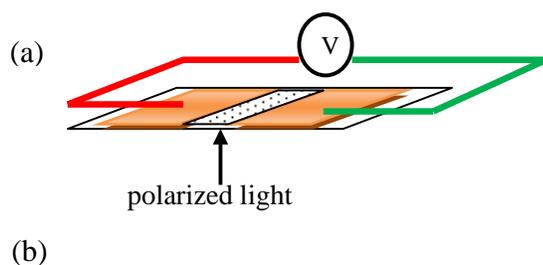


Figure 1: Custom-built POM slides – (a) schematic diagram and (b) actual set-up.

3 RESULTS & DISCUSSION

3.1 Electrorheology

The effect of an applied external DC electric field on the steady-state viscosity was elucidated and is shown in Figure 2 for an HPC solution without and with nanoparticles at a constant shear rate of 1 s⁻¹. The neat HPC solution was observed to be non-responsive to electric fields, since no significant change in the viscosity was measured. On the other hand, the particle loaded solutions showed a decrease in the viscosity, i.e. negative ER effect, with increasing field strength. Thus, electric field response is mainly attributed to the nanorod inclusions. At lower fields, the effect was more pronounced for the 0.48 vol% loading. The viscosity at a field of 2 MV/m has decreased by a factor of 14 from that at zero-field, for both cases. This effect was negligible at higher shear rates (i.e. 10 s⁻¹ - not shown). This indicates that the negative effect is not due to orientation along the flow direction. In homogeneous ER fluids, high shear forces dominate the orientation of the director. While in the case of heterogeneous ER fluids, shear forces dominate and prevent chain-formation perpendicular to flow.

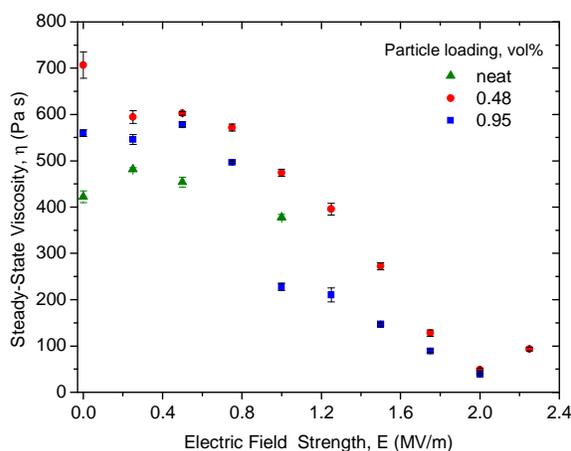


Figure 2: Effect of MWCNT loading on the steady-state viscosity of a liquid crystalline 45 wt% HPC in m-cresol solution under an applied external electric field.

A negative ER effect on the storage modulus of the carbon nanotube suspensions in silicone oil which disappears as electric field increases was reported by Lozano and coworkers [4]. The effect was attributed to the formation of layered nanostructures, which decrease the modulus, followed by migration of particles to the electrodes and formation of column-like structures along the electrodes, which in turn increases the storage modulus. Park and coworkers oriented single wall carbon nanotubes (SWNT) through the use of an AC electric field in a photopolymerizable matrix [6]. It was proposed that the

SWNT not only aligned with the field, but also migrated laterally to form thick columns between the electrodes.

In both reports, lower field strengths than those from our ER experiments were associated to the formation of the chain-like structures. Nevertheless, our results show a negative change in viscosity over the whole field range and there were no discernible chain-like structures or particle migration to the naked eye. The negative ER effect may be due to formation of small aggregates or bundles. Since the effective size of these bundles will be much higher than for single nanotubes, they may cause a distortion of the liquid crystal phase, displacing it into the biphasic regime. To test this hypothesis, we observed the effect of electric field on the liquid crystalline texture and MWCNT bundles.

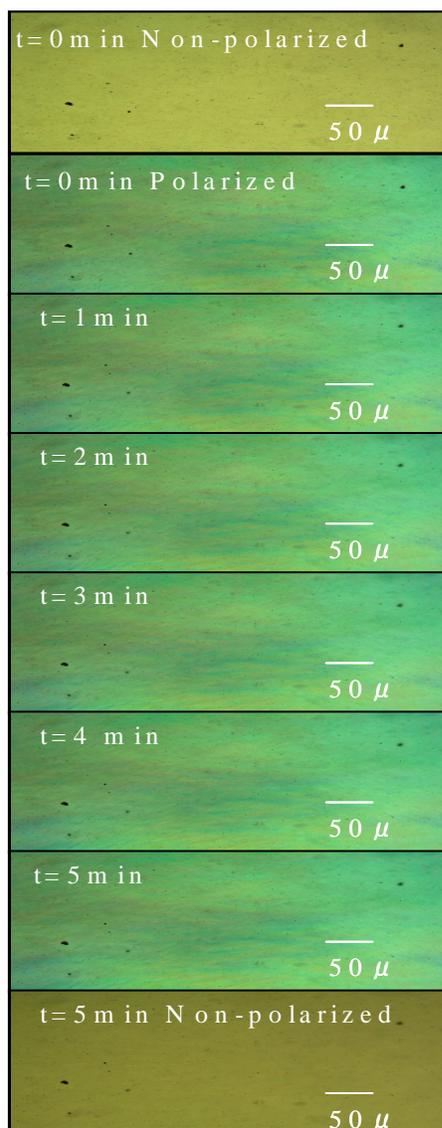


Figure 3: Liquid crystal textures of a 0.05 wt% MWCNT in a 45 wt% HPC in m-cresol solution at an applied electric field of 0.25 MV/m as a function of time.

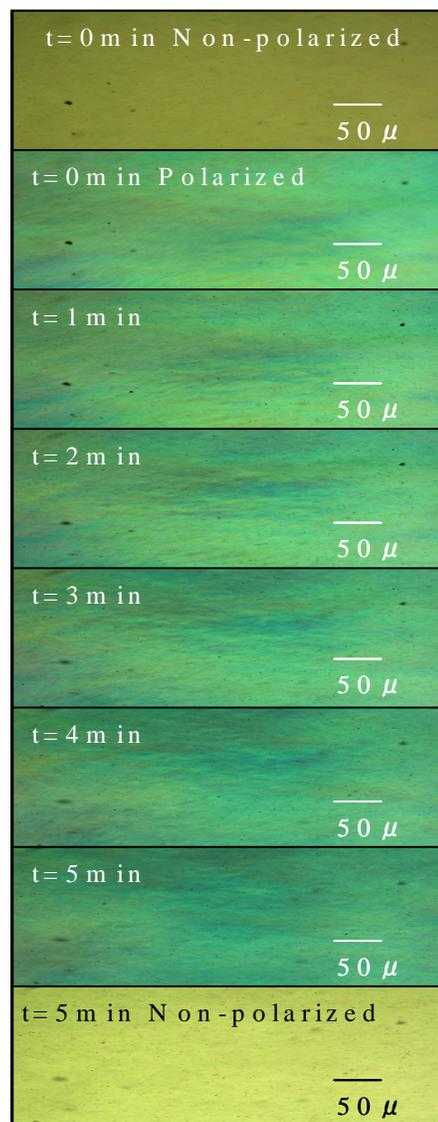


Figure 4: Liquid crystal textures of a 0.05 wt% MWCNT in a 45 wt% HPC in m-cresol solution at an applied electric field of 0.5 MV/m as a function of time.

3.2 Polarized Optical Microscopy

Figure 3 shows the liquid crystalline textures at electric field strength of 0.25 MV/m over a time interval of 5 min. No discernible changes on the liquid crystalline texture of 0.05 wt% MWCNT dispersions were observed for electric field strengths below 0.25 MV/m. Neither particle aggregation nor migration of the focused MWCNT bundles was observed. Figure 4 shows the liquid crystalline textures at an electric field strength of 0.5 MV/m over a time interval of 5 min. Slight changes on the textures were observed after four minutes. Yet, displacement of bundles was not recorded.

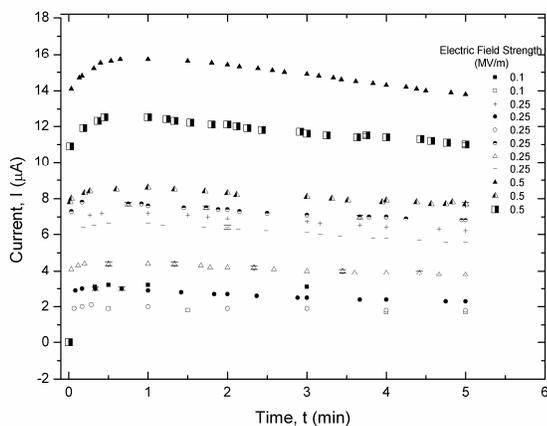


Figure 5: Change of drawn current over time for the MWCNT in HPC dispersions.

The drawn current is shown in Figure 5 for all the analyzed samples. The meager quantitative reproducibility was due to the intentional poor dispersion of the tested samples. Since current is inversely proportional to resistance, an increase in current correlates to a decrease in resistance and viceversa. No significant changes were observed for a 0.1 MV/m field. For 0.25 MV/m, a subtle increase in the current is observed in the first 30 seconds, but it decreases again until it reaches a steady-state. The initial increase of the current is more pronounced at 0.5 MV/m, where it reaches a maximum at 45 seconds after which it decreases. This initial increase in current may be associated with a decrease in resistance which in turn suggests orientation. The decrease may be associated with migration of particles with diminish the effective electron paths across the electrodes. This changes support the proposed mechanism of Lozano and coworkers [4]. Nevertheless, these changes may be happening at the nanoscale or in the bulk of the material since there were no changes in textures or displacement.

On the other hand, the optical studies were conducted at very low particle concentrations to allow for direct observation between the polarizers in transmitted mode. Higher concentration of nanotubes may cause significant changes in the LC phase, but limits direct observation in the transmitted polarized microscope. Reflected polarized light microscopy will be used in future work to expand our experimental concentration range.

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