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Effect of carbon nanofibers on the anisotropy of an aromatic thermotropic liquid crystalline polymer

Sungho Lee[a], Myung-Soo Kim[b], Amit K. Naskar[a], Amod A. Ogale[a,*]

[a]*Department of Chemical Engineering and Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, SC 29634-0909, USA*
[b]*Department of Chemical Engineering, Myongji University, Yongin, Kyunggido 449-728, South Korea*

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Abstract

The microstructure of a thermotropic liquid crystalline polymer (TLCP, Vectran V400 P) was investigated in the presence of vapor-grown carbon nanofibers. Percolation threshold was observed at ∼5 wt% carbon nanofibers. During processing, strong flows resulted in severe anisotropy of the semirigid rod-like TLCP molecules. For a given type of flow, however, the nanofibers were found to reduce the overall anisotropy of the TLCP nematic phase in the nanocomposite. We believe that nanofibers provide surface anchoring for the nematic phase that helps disrupt the high degree of molecular order in the TLCP matrix and reduces its anisotropy in the nanocomposite.

Keywords: Thermotropic liquid crystalline polymers; Carbon nanofibers; X-ray diffraction

1. Introduction

Thermotropic liquid crystalline polymers (TLCPs) provide unique properties such as high strength and low oxygen/water vapor permeability, which make them promising candidates for high performance molding and extrusion applications [1]. Wide angle X-ray diffraction (WAXD) [2–5] studies on copolyester TLCPs indicate that the degree of orientation can be very high along the flow/processing direction. WAXD analysis of copolyester TLCPs fibers has revealed pseudohexagonal and orthorhombic structures depending upon the annealing conditions [4].

The degree of uniaxial orientation is typically very high, and this preferred orientation of the nematic phase imparts excellent tensile strength to TLCPs [6]. In recent studies on amorphous copolyester TLCP (Vectran V400P) that has potential applications in advanced packaging, we found that films obtained by blown film extrusion displayed a longitudinal tensile strength of ∼405 MPa [7]. We have observed the alignment of nematic domains even in moderately weak flows (shear rates ∼1 s^{-1}) [8]. Such molecular orientation leads to excellent tensile properties in the longitudinal (flow) direction. However, we found the transverse tensile strength to be only one-tenth of the longitudinal tensile strength, highlighting the anisotropy of TLCP films [7]. This anisotropy is caused by the semi-rigid nature of the TLCP molecules, coupled with weak intermolecular interactions in the transverse direction [6]. This severe anisotropy of TLCP poses significant challenges for film applications since the high degree of orientation in the longitudinal direction causes an imbalance of in-plane properties (e.g. low tear resistance).

Another challenge one faces in using TLCPs is their low electrical conductivity, which is inadequate for sensitive electronics packaging applications that need electrostatic dissipative materials. To improve electrostatic dissipative (ESD) properties, conducting fillers such as carbon black [9] or graphite [10] have been incorporated. Carbon nanofibers have also been incorporated into thermoplastic polymers [10–12] and thermosetting polymers [12–14] since they have good thermal and electrical conductivity. In the present study, the role of nanofibers was investigated for the purpose of controlling the microstructure of the TLCP. The primary focus of this study was enhancing electrical conductivity while reducing anisotropy in the TLCP matrix.

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* Corresponding author. Tel.: +1 864 656 5483; fax: +1 864 656 0784.
E-mail address: ogale@clemson.edu (A.A. Ogale).

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2. Experimental

The TLCP used throughout this study (Vectran V400P, Ticona, the technical polymers business of Celanese A. G.) was an aromatic copolyester composed of 1,4-hydroxybenzoic acid (HBA), 2,6-hydroxynaphthoic acid (HNA), and other comonomers that provide selected meta-linkages [15]. The polymer has a glass transition temperature of 110 °C, but displays no melting peak by differential scanning calorimetry. Carbon nanofibers were prepared from the chemical decomposition of ethylene gas over nickel–copper catalyst; details may be found in an earlier study [16]. The diameters of nanofibers ranged from 50 to 200 nm.

TLCP pellets were vacuum dried for 24 h at 110 °C before mixing. A Rheomix 600 mixer was used for intensive mixing of TLCP and 0.1–15 wt% of nanofibers for 20 min at 210 °C. Pure TLCP pellets without any nanofibers were also processed under the same condition; these samples served as the control material.

The compounded materials, both pure TLCP and nanocomposites, were extruded into rods using a circular die of 2.7 mm diameter at a low wall shear rate of 2 s^{-1} at 230 °C. The diameter of the extruded rods was close to 2.7 mm since no draw-down was imposed. A compression press (Carver model 30-12-2T) was used for processing of the polymeric rods into molded samples using a rectangular mold cavity (150 mm × 14 mm × 0.3 mm). A compression temperature of 210 °C, pressure of ~4 MPa, and a holding time of ~4 min was used for all of the molded samples. These conditions mimic those encountered in thermoforming type of processes that are used to produce packaging products. Further, we note that Vectran V400P polymer can be processed at temperatures as low as 210–250 °C [8,15], in contrast to the injection molding grade TLCP copolyesters (such as Vectra A950) that need to be processed at temperatures exceeding 300 °C.

To prepare extrudates, the pure TLCP and the nanocomposites were extruded under identical conditions in a capillary rheometer (Instron, Instruments) at 250 °C using a circular die of 500 μm diameter. The nominal wall shear-rate was 55 s^{-1} for all extrudates. The extrusion temperature was slightly higher than that used in the molding process because it was not possible to extrude the nanocomposite containing 5 wt% nanofibers at the lower temperatures of 210–230 °C. A draw-down ratio of ~3 was used for all materials resulting in samples with a diameter of ~275 μm.

The static decay time was measured at 25 °C using a static decay meter (Model 406D, Electro-Tech Systems, Inc.) to characterize the ability of molded samples to dissipate an induced surface charge. The test method was based on the Federal Test Method 101C, Method 4046, and Military Specification Mil-B-81705B that require 99% of the induced charge to be dissipated in less than 2 s. The electrical resistivity was measured by a digital ohmmeter (Megohmmeter ACL 800) at 25 °C. The electrical measurements were conducted at two different voltages (10 and 100 V) to account for low and high resistances and corrected for the specimen geometry. Ten replicate specimens were used for all electrical measurements.

The orientation in pure TLCP and composites was observed from the azimuthal intensity distribution of wide angle X-ray diffraction (WAXD) patterns obtained from an Osmic Micromax Cu K_α X-ray source with a collimator pinhole size of 0.3 mm. The distance from the sample to the detector was 10 cm. Diffracted patterns were captured on 2D image plates, which were scanned using a Fuji BAS 1800 scanner. An exposure time of 30 min per image was utilized throughout the study. The Fraser-corrected WAXD diffractograms were analyzed using Polar® 2.6.5 software. Two replicate scans were performed on all samples.

3. Results and discussion

The composite with nanofiber content above 5 wt% displayed a static decay time of less than 2 s for both positive and negative charges, indicating that the material is static dissipative at 5 wt% content of the nanofibers. Further, Fig. 1 displays the dependence of volume resistivity on the nanofiber content. At 5 wt% nanofiber content, a significant volume resistivity drop (over 3 orders of magnitudes) occurred, which corresponds to the onset of percolation. Thus, static decay time test and volume resistivity showed consistent results in that 5 wt% nanofiber content represents percolation threshold. We also note that in going from pure TLCP to 5 wt% nanofiber composite, the tensile strength dropped from ~129 to ~48 MPa for molded samples and from ~344 to ~134 MPa for extruded samples. The addition of short fibers is known to reduce the tensile strength of composites when the fibers are randomly oriented [17,18].

The highest scattering intensity in the diffraction intensity (2θ) profile of pure TLCP and nanocomposite molded samples was observed around 2θ of 19.8° in all cases (Fig. 2). For Vectra A950 TLCP, this peak results from (110) planes associated with pseudo-hexagonal (PH) packing of TLCP polymer chains [4]; this structure is also referred to as orthorhombic form III, in which the lattice parameters are related as $a = \sqrt{3}b$. A distinct (200) peak was not observed in the vicinity of $2\theta \approx 20°$, but a shoulder appeared in the 2θ region of 26–28° due to (211) planes. For V400P composite containing 5 wt% carbon nanofibers, there was a distinguishable peak in the broad shoulder region that was associated with graphene (002) planes from carbon nanofibers. It is noted that the location of the (110) peak for the extruded samples of neat Vectran V400P TLCP and its nanofiber filled composites is similar to that observed for their molded counterparts. The (200) peak associated with orthorhombic form I in Vectra A950 TLCP was never observed in Vectran V400P TLCP for the extruded samples that experienced significant extensional flow during draw

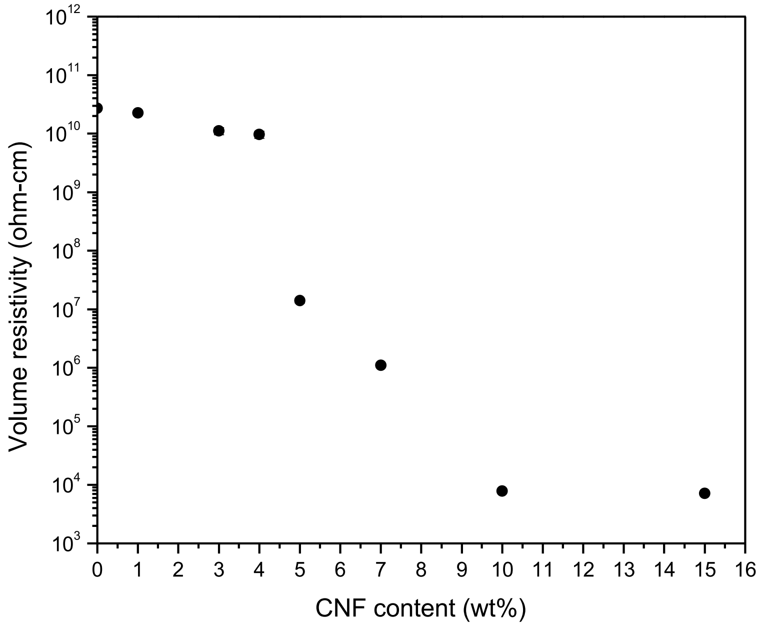

Fig. 1. Volume resistivity of pure and CNF-modified thermotropic liquid crystalline polymer (Vectran V400P TLCP).

down. The (200) peak did not develop in Vectran V400P samples even after annealing, in contrast to what has been observed for Vectra A950 type TLCPs [4,19].

In the diffraction patterns of the molded samples, the (110) plane formed an intense arc for pure TLCP. In contrast, for the same set of planes broader arcs were observed at 0.1 and 1 wt% nanofiber contents that finally evolved to a uniform ring at a nanofiber content of 5 wt%. It is noted that the shorter the arc length, the higher is the orientational order. Quantified azimuthal intensity profiles for (110) peak are displayed in Fig. 3, which show that intensity profiles of pure TLCP and 0.1 wt% nanofiber-modified TLCP were concentrated in the equatorial region. Higher contents of nanofibers led to broader profiles. Therefore, the orientation of TLCP chains becomes less severe with a gradual addition of nanofibers.

The equatorial (110) peak was used to evaluate axial orientation of the samples. The second order Legendre polynomial or Herman's orientation parameter in the longitudinal direction [$f = 0.5\,(3\langle\cos^2\phi\rangle - 1)$] was calculated

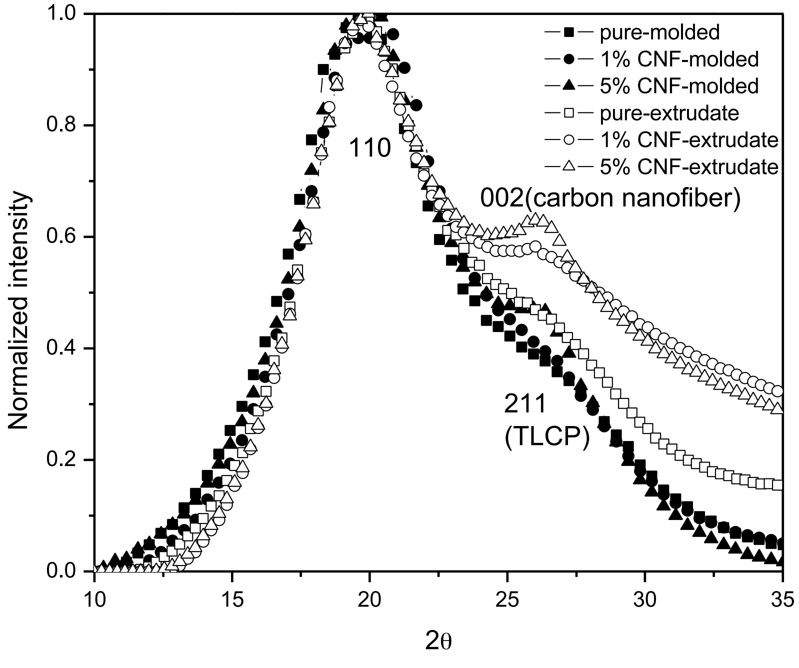

Fig. 2. Radial (2θ) intensity profiles of molded and extruded samples from pure, 1 and 5 wt% CNF-modified TLCP.

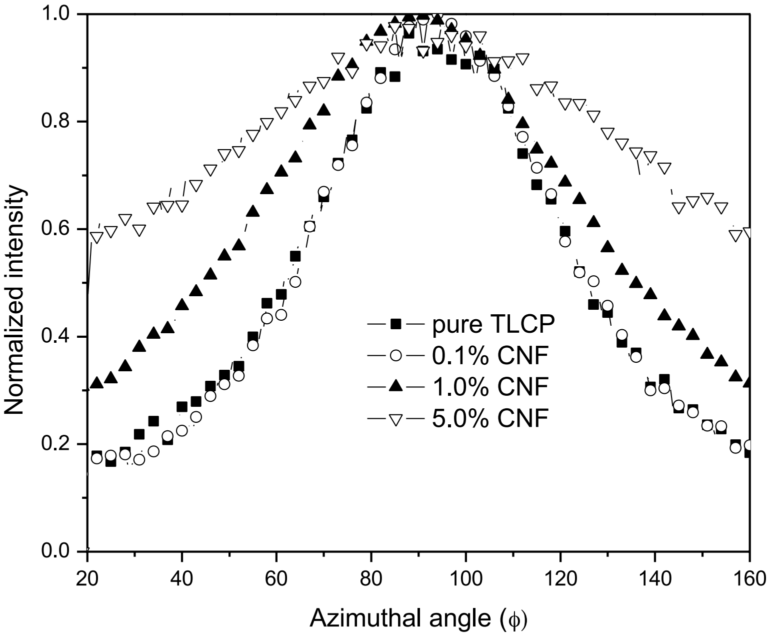

Fig. 3. Azimuthal intensity profiles at $2\theta = 19.8°$ of molded samples: pure TLCP, 0.1, 1 and 5 wt% CNF-modified TLCP.

for molded and extruded samples using POLAR software based on PH packing of TLCP chains. The f values, displayed in Table 1, ranged between 0.51 (pure TLCP) and 0.20 (5 wt% composites) for molded samples. At 1 wt% nanofiber content, a significant decrease of the orientational order was observed. The 1 and 5 wt% composites showed lower f values than those displayed by pure TLCP and dilute composites. For extrudates, the azimuthal profiles were significantly sharper than those for molded samples, and the orientation parameter ranged from 0.85 (for pure TLCP) to 0.71 (for 5 wt% nanofiber filled composite). The higher orientational order observed for extrudates (than for molded samples) may be attributed to flow-induced orientation and is well documented for strong flows, i.e. high shear rates and/or extensional flow field [3,5]. However, for a given type of flow, we found that the addition of nanofibers results in a reduced orientation order.

Using Polar™ image analysis software, isotropic intensity distribution $I(\theta,\phi)$ could be resolved and the residual anisotropic intensity distribution obtained. Fig. 4(a) and (b) display normalized radial distribution plots of the extruded samples with resolved anisotropic scattering intensity for pure TLCP and TLCP containing 5 wt% nanofibers, respectively. For pure TLCP samples, there was no significant difference between total and anisotropic intensity profiles, indicating primarily anisotropic distribution of TLCP molecules. In contrast, after subtracting isotropic contributions for 5 wt% nanocomposite, the intensity of anisotropic (110) reflection ($2\theta \sim 19.8°$) due to TLCP molecules decreased. Therefore, it is evident that incorporation of nanofibers reduces anisotropy for the (110) planes. Further, it is noted that the carbon (002) peak almost disappeared from the resolved anisotropic profile. Thus, it can be inferred that the carbon nanofibers do not have a significant preferred orientation, and help in reducing the preferred orientation of neighboring TLCP molecules.

A decrease of molecular alignment in TLCP, in the presence of nanofibers, can also explain the drop in tensile strength that was observed earlier. Addition of nanofibers prevents the TLCP matrix from forming a highly ordered structure and reduces the anisotropy. A reduction of anisotropy of in-plane properties has also been reported in the literature for aromatic copolyesters (HBA/HNA and HBA/isophthalic acid (IA)/hydroquinone (HQ)) in the presence of glass fibers [20].

The reduction of TLCP orientation is likely a consequence of surface anchoring of the nematic phase on the nanofiber surface. It has been reported that the molecular orientation of TLCP in TLCP/fiber composites was anchored by the carbon and glass fiber surfaces [21,22]. Furthermore, this observation is consistent with that reported in our earlier study [23], where we have shown that the incorporation of carbon nanotubes in discotic liquid crystalline pitch precursor disrupted the severe radial

Table 1
Herman's orientation parameter for molecular alignment of pure TLCP and CNF-modified TLCP extrudates

CNF (wt%)	0	0.1	1	5
Molded sample	0.51	0.50	0.27	0.20
Extrudate	0.85	0.79	0.73	0.71

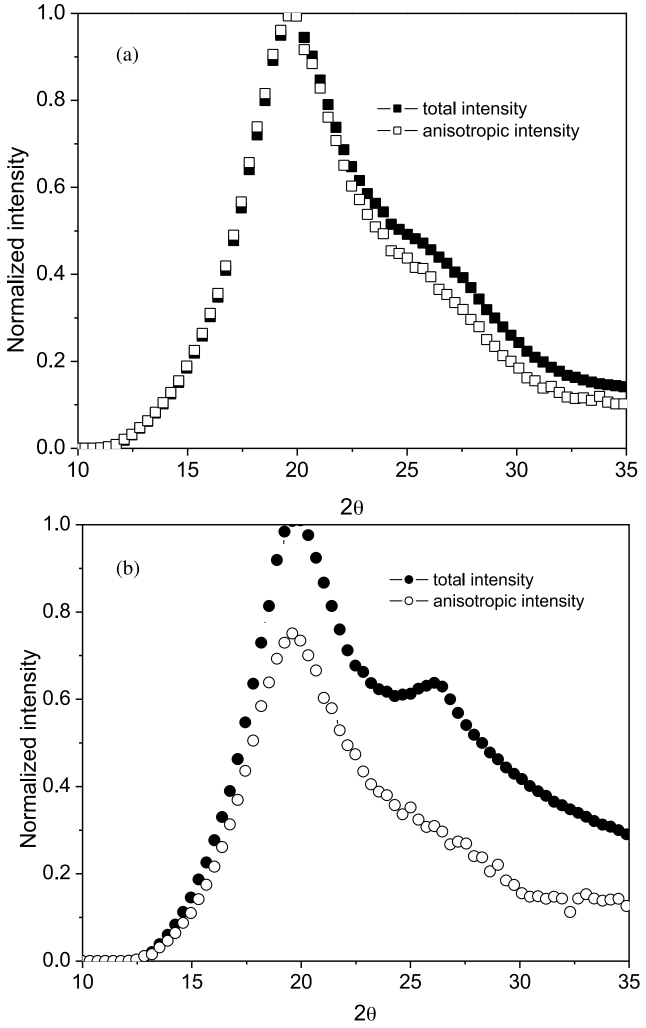

Fig. 4. Anisotropic and total radial (2*θ*) intensities of extrudates for: (a) pure TLCP and (b) 5 wt% CNF-modified TLCP.

orientation of the disc-like molecules and produced a more random orientation in the plane. Therefore, it is hypothesized that, for a given set of processing conditions, the microstructure of TLCP can be rendered less anisotropic due to the surface anchoring afforded by inclusions such as carbon nanofibers.

4. Conclusions

The incorporation of carbon nanofibers in a thermotropic liquid crystalline polymer (Vectran V400P) improved the electrical conductivity, as expected. The electrical percolation threshold was observed in the TLCP composite at approximately 5 wt% nanofiber. The preferred orientation of TLCP molecules was studied by WAXD and, as expected, was found to be higher for samples processed in strong flows. However, the TLCP molecular orientation distribution broadened with increasing nanofiber content. We believe that nanofibers provide surface anchoring for the nematic phase that helps disrupt the high degree of molecular order in the TLCP matrix and reduces its anisotropy in the nanocomposite.

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