ELECTRICAL AND MECHANICAL PROPERTIES OF CARBON NANOFIBER/ThERMOTROPIC LIQUID CRYSTALLINE POLYMERS COMPOSITES

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Abstract

Carbon nanofibers (CNF) are two orders of magnitude smaller in diameter than regular carbon fibers (~0.1 μm vs ~10 μm), and have potential applications in nanocomposites used for micro-molding or films (where product thickness can be as small as 25 μm). CNFs were dispersed in a thermotropic liquid crystalline polymer (TLCP, A950) at 0.7 and 3.6 vol% content using twin-screw extrusion. The injection molded plaques, used for flexural tests, revealed no significant difference in flexural modulus and strength of pure TLCP and nanocomposites. A significant increase of electrical conductivity was observed at 3.6 vol% CNF content (~ 4 × 10\textsuperscript{7} cm-ohm). In addition, a reduction in the severe anisotropy, which results from molecular orientation of TLCP, was observed in the presence of CNFs.

Introduction

Thermotropic liquid crystalline polymers (TLCPs) form highly oriented fibrils in the flow direction during processing due to the semi-rigid nature of the TLCP molecules, coupled with weak intermolecular interactions [1]. This structural feature results in excellent mechanical properties. In addition, TLCPs have been attractive due to their thermal stability, chemical and flame resistance, low oxygen/water vapor permeability, a good processibility [2]. These unique properties allow TLCPs to have potential applications in high temperature components, apparatus for chemical processes, medical equipment, and aerospace industry.

A technical challenge one faces in using TLCPs is their low electrical conductivity, which is inadequate for applications that need electrostatic dissipative (ESD) or electromagnetic interference (EMI) shielding materials. To improve ESD properties and EMI shielding effectiveness, carbon black [3], carbon fiber [4], and carbon nanofiber [5] have been incorporated into TLCPs. Further, carbon nanofibers (CNFs) have been incorporated into thermoplastic polymers [6-7] and thermosetting polymers [7-8] as reinforcement because they have good thermal and electrical conductivity. In the present study, TLCPs containing carbon nanofibers were processed by injection molding to investigate mechanical and electrical properties. To assess the effect of CNF on the microstructure of TLCP, wide angle X-ray diffraction studies were conducted.

Experimental

Materials and Processing

The TLCP used in this study was Vectra® A950 (Ticona, the technical polymers business of Celanese A. G.) [2]. Carbon nanofibers need throughout this study. PR-24-PS were obtained from a commercial source (Applied Science, Inc., Cedarville OH) [9]. A lab scale twin screw extruder with 10 mm diameter and 24:1 L/D ratio (Model MP2015, APV Chemical Machinery Inc., USA) was used for mixing of TLCP and CNFs at 0.7 and 3.6 vol% levels. Prior to mixing, all materials were vacuum dried at 120°C for 24 h. The temperature of four heating zones was 260, 280, 290, and 260°C, respectively. The screw rotation speed was 15 rpm. Physically blended TLCP and CNFs were fed into the hopper and the extrudate was palletized into 3mm diameter pellets (Haake PP1 pelletizer, USA). This twin screw extrusion process was repeated three times for ensuring adequate dispersion of CNFs.

The resulting pellets were vacuum dried at 120°C for 24 h before injection molding (ARBURG model Allrounder 221-55-250, Germany). Heating temperatures were 290, 295, 295, and 295°C from feeding zone to nozzle. The injection pressure (5 MPa), holding pressure (7 MPa), and screw speed (200 rpm) were held constant to produce ASTM D638 Type I specimens.
**Characterization**

The electrical resistivity was measured by a digital ohmmeter (Megohmmeter ACL 800) at ~25°C with compression molded sample of pure TLCP and composite pellets using Carver laboratory hot press at 210°C. The electrical measurements were conducted at a voltage of 10 V and corrected for specimen geometry. Measurements were conducted at ten different locations on three replicates.

To measure the flexural properties, three-point bending test was performed using an ATS Universal Tensile Tester 900. The displacement rate was 0.05 in/min for all specimens. The flexural properties of each sample were an average of data from five specimens.

The orientation in pure TLCP and its composites was observed from the azimuthal intensity distribution of wide angle X-ray diffraction (WAXD). Wide angle X-ray scattering patterns were obtained from a Rigaku 2-D diffractometer using CuKα radiation. The WAXD image was analyzed using POLAR software.

**Results and discussion**

Volume resistivity of pure TLCP and its composites displays in Figure 1. For pure to 0.7 vol% nanocomposite, the volume resistivity does not change significantly as compared to that of the pure TLCP. However, it was found that at 3.6 vol% CNF content, a volume resistivity drop was 3 orders of magnitudes (down to ~4×10⁷ ohm-cm), indicating that CNF in this composite could form percolation network.

Three-point bending test was performed for measuring flexural properties for injection molded sample of pure and its composites. According to ASTM D790, flexural stress (σ) and strain (ε) can be calculated using following the two equations:

\[ \sigma = \frac{3PL}{2bd^2}, \text{ and } \varepsilon = \frac{6Dd}{L^2} \]

where \( P \) is the load, \( L \) the span length, \( b \) the width, \( d \) the thickness of the specimens, and \( D \) the deflection of the specimens. From the flexural stress-strain curves, the flexural strength and flexural modulus were calculated. The average flexural moduli were found to increase slightly from 7.3 GPa for the pure TLCP to 7.8 and 7.5 GPa for nanocomposites containing 0.7 and 3.6 vol%. Although the changes were not significant at 95% confidence interval, the general trend is consistent with that observed for any discontinuous reinforcement composite. On the other hand, strength can often decrease for discontinuous reinforcement. Here, we observe that flexural strength is retained fairly constant at 210 MPa in spite of the addition of the dispersed CNFs.

Wide angle X-ray diffraction (WAXD) was conducted to investigate the microstructure of nanocomposites. For integrated azimuthal intensity profiles (2θ scans) for pure TLCP and 0.7 vol% nanocomposite (Figure 2), two peaks were observed at ~19° and ~27° associated with (110) and (211) planes of the liquid crystalline polymer. This verifies pseudo-hexagonal packing of oriented TLCP polymer chains [10]. For 3.6 vol% nanocomposite, a small peak at ~25.7° appeared in addition the peak at ~19° and a shoulder at ~27°. This peak is due to (002) planes from carbon nanofibers. To evaluate axial orientation, Herman’s orientational order parameter was calculated: \( f = 0.5(3<\cos^2\varphi>-1) \). The (110) peak of the TLCP was used to measure the orientation distribution using POLAR software based on pseudo-hexagonal packing of TLCP chains. The average orientation parameter was measured to be 0.69 for the injection-molded pure TLCP dog-bones. For 0.7 and 3.6 vol% nanocomposites, the orientation parameter deceased slightly to 0.66 and 0.65, respectively. We believe that CNFs can disrupt the highly orientated polymer chains in the molded samples and can lead to a reduction of anisotropy of TLCP. This is consistent with our earlier observation on extruded TLCPs, which also displayed a reduction of \( f \) value with an addition of CNFs [11].
Figure 1. Volume resistivity of pure TLCP and its nanocomposites.

Figure 2. Integrated azimuthal (2θ) intensity profiles of pure TLCP and its nanocomposites using wide angle X-ray diffraction.
Conclusions

CNFs were incorporated into a thermotropic liquid crystalline polymer (TLCP, A950) at 0.7 and 3.6 vol% content using twin-screw extrusion. For compression molded sheets, a significant increase of electrical conductivity was observed at 3.6 vol% CNF content (~ $4 \times 10^{7}$ cm-ohm). Injection molded plaques were prepared for flexural tests and wide angle X-ray diffraction. The flexural modulus increased slightly with an addition of CNFs, but there was no significant difference in the flexural strength of pure TLCP and nanocomposites. However, the $f$ values indicate a small decrease of polymer chain orientation with the addition of CNFs, suggesting a reduction of TLCP molecular anisotropy in the presence of nanofibers.

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