Mechanical Properties and Fracture Behavior of Reinforced Thermotropic Liquid Crystalline Polymers

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1. Abstract

This research focuses on the mechanical properties and fracture behavior of injection molded reinforced thermotropic liquid crystalline polymers (LCPs). The LCPs are random copolyesters based on 1,4-hydroxybenzoic acid (B) and 2,6-hydroxynaphthoic acid (N). Tensile fracture toughness was investigated under uniaxial tension. The morphology and microstructure of as-received and fractured samples was investigated using optical microscopy. Glass fibers, carbon fibers and mineral fillers were used as microfillers. The influence of filler concentration was also investigated, varying the concentration from 15 to 30 wt %. The X-ray patterns of the injection molded bars showed anisotropic orientation, the molecular chains being oriented along the injection molding axis. Tensile tests revealed that the strain at failure of the neat LCP occurred within 3% deformation. Addition of glass fibers did not change the Young modulus and reduced the strain at failure. On the other hand, carbon fibers did increase the Young modulus, increased the yield stress and reduced significantly the strain at failure. X-ray scattering showed that the microfillers compromised the macromolecular alignment in the composites, and this appears to be the cause for the reduction in mechanical properties.

2. Introduction

Thermotropic LCPs for commercial applications are based on random copolymerization of two or more mesogenic units and without flexible (alkyl) spacers in the main-chain. The disruption of crystallinity by random copolymerization reduces the melting transition making the materials melt processable [1-3]. The best known example of a commercial thermotropic LCP is based on 1,4-hydroxybenzoic acid (B) and 2,6-hydroxynaphthoic acid (N) and it is marketed as the Vectra® resin for injection molding applications (Ticona, Celanese Co.), in fiber form it is marketed as Vectran® (Kuraray Co.). The thermal, optical textures, crystalline structure and rheological properties of B-N thermotropic LCPs have been extensively studied [1-4].

Important studies related to the molecular motions of thermotropic LCPs in the solid state have been carried out by dynamic mechanical analysis and dielectric relaxation studies [4]. This research focuses on the influence of glass and carbon fibers on the mechanical properties, microstructure and fracture behavior of commercial thermotropic copolyesters.

The mechanical properties of the reinforced LCP are studied under uniaxial tension mode and the results are correlated with the degree of molecular alignment as revealed by wide-angle X-ray scattering.

3. Experimental

3.1 Materials

The LCP is a random copolyester based on repeat units of 1,4-hydroxybenzoic acid (B) and 2,6-hydroxynaphthoic acid (N), and composition 73:27 mol %, respectively. The polymer has a weight average molecular weight of 30,000 g/mol (Hoechst-Celanese Corp.). The composites, prepared by melt extrusion and injection molding, were kindly provided by the Hoechst Celanese Research Corp. (Summit NJ, USA). The samples are listed in Table 1.

Table 1 Thermotropic copolyester composites

Sample	Microfiller	Concentration (wt%)	T_g (°C)
B-N	-	0	112.3
B-N GF15	Glass fiber	15	111.6
B-N GF30	Glass fiber	30	115.0
B-N GF50	Glass fiber	50	117.7
B-N CF30	Carbon fiber	30	116.4
B-N M15	Minerals	15	112.0

3.2 Mechanical properties

The samples were mechanically tested in accordance with the ASTM D638 standard [15]. Tension tests were carried out at room temperature on the universal testing machine Instron 4206 using a crosshead speed of 5 mm/min.

3.3 Microscopy

Optical micrographs of as-molded and fractured samples were obtained in reflection mode and under white light conditions. Photomicrographs were acquired using a Moticam 100 digital camera manufactured by Motic Inc. Image analyses were carried out using ImageTool software, v3.0 (UTHSCSA, Texas, USA).

3.4 Wide-angle X-ray scattering

X-ray diffraction patterns from the as-molded composites were obtained using the High Star area detector manufactured by Bruker AXS (Wisconsin, USA). A rotating anode

generator RU-200 with Cu target manufactured by Rigaku was utilized. The instrument was equipped with a graphite monochromator and the incident beam was collimated to 0.5 mm.

4. Results and discussion

The glass transition temperature T_g was determined by dynamic mechanical analysis (DMA), the results are listed in Table 1. There is increase of T_g, and increasing the amount of filler further increased the T_g. Previously it had been shown for B-N/glass fiber composites that glass fiber increased the solid-to-nematic phase transition as well as the degradation temperatures [5]. The microstructure of the composites was investigated by X-ray scattering, the results are shown in Figure 1. The background-corrected patterns show intensity concentration on the equatorial axis indicating that there is preferred macromolecular orientation along the extrusion direction. Note also that the crystalline reflections are superimposed on broad amorphous halos. The patterns also show that the microfillers greatly disrupt the macromolecular alignment, as evidenced from the azimuthal spread of intensity.

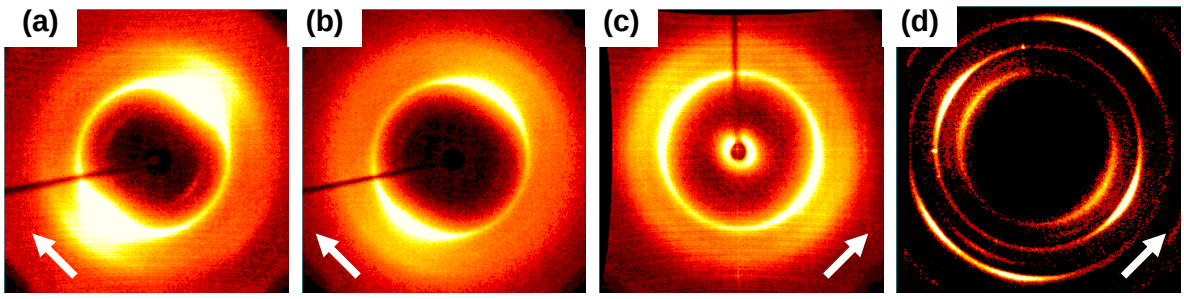

Figure 1. Wide-angle X-ray scattering pattern of B-N LCP. (a) neat B-N, and B-N reinforced with 30wt% (b) glass fibers, (c) carbon fibers and (d) minerals. Arrows indicate extrusion direction.

Figure 2 shows strain-stress curves for B-N and the 30wt% reinforced composites. The neat LCP and composites show limited strain deformation more akin to metals. It can be seen that fiber glass (trace ii) does not reinforce the LCP, contrary to filled thermoplastic behavior. It also reduced the strain at failure. On the other hand, carbon fibers (trace iii) increased the Young's modulus and significantly decreased the strain at failure. The optical micrographs of the fractured surfaces shown in Figure 2 show that there is little plastic deformation in the neat LCP (a). On the other hand, the fiber filled LCP mainly fails due to poor adhesion between the matrix and fibers (b and c). Finally, the mineral filled LCP (d) shows plastic deformation. These results show that the microfillers are effective to disrupt the LCPs

molecular alignment, and the poor adhesion with the matrix compromises the mechanical properties of the composite.

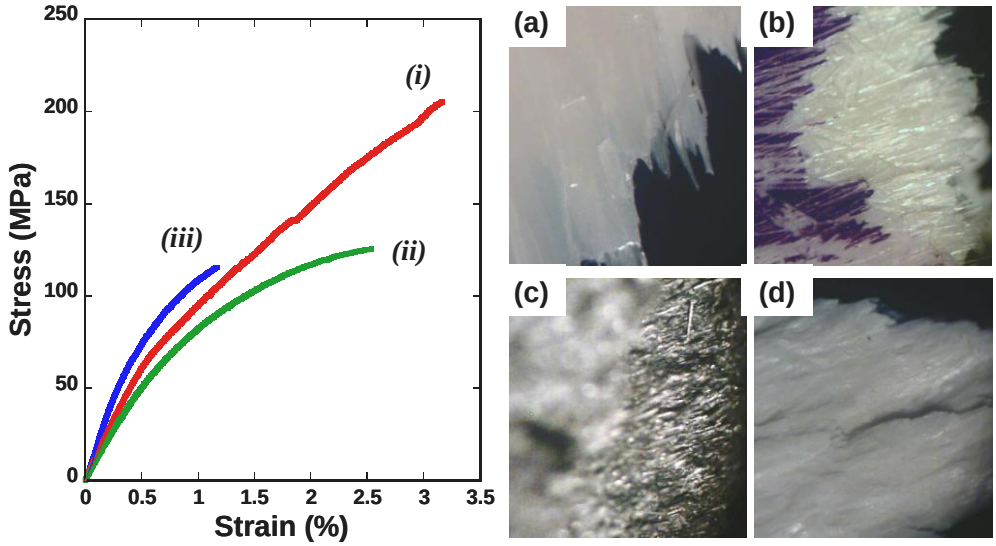

Figure 2. Stress-strain curves for B-N thermotropic composites (i) neat LCP, and composites with 30 wt% (ii) glass and (iii) carbon fibers. Optical micrographs of fractured regions: (a) neat LCP, composites with (b) 15wt% glass fibers, (c) 30wt% carbon fibers and (d) 15wt% minerals.

5. Conclusions

Addition of microfillers to B-N increased the glass transition temperature and decreased the strain at failure. The degree of macromolecular alignment induced by the injection flow processing was decreased by the addition of microfillers. The microfillers did not improve the mechanical properties, except for carbon fiber.

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6. References

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