

Dynamic mechanical analysis of thermotropic copolyester-short glass fiber composites

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1. Abstract

The influence of short glass fibers (SGF) on the dynamic mechanical properties and microstructure of thermotropic copolyesters based on 1,4-hydroxybenzoic acid and 2,6-hydroxynaphthoic acid (denoted B-N) has been investigated. The mechanical relaxations of the reinforced B-N/SGF composites were studied under torsion mode and the results were correlated with the degree of molecular alignment and degree of crystallinity as revealed by wide-angle X-ray scattering (WAXS). Addition of SGFs to B-N liquid crystalline polymer (LCP) produced an increase in the solid-to-nematic transition temperature as well as an increase in the decomposition temperatures. Dynamic mechanical analysis showed that the local motions associated to the β -transition ($\sim 61^\circ\text{C}$) are enhanced as the frequency of oscillation increases. Thus, the cooperative molecular motions involving segments of the molecular chains associated with the α transition were compromised by the presence of SGFs resulting in an increase of the storage modulus, melting and degradation temperatures. X-ray scattering showed that the SGFs disrupted the degree of molecular alignment (as quantified by the order parameter \overline{P}_2). The degree of crystallinity in the composites decreased as the concentration of SGFs increased.

2. Introduction

The best known example of high performance thermotropic LCP is based on 1,4-hydroxybenzoic acid (**B**) and 2,6-hydroxynaphthoic acid (**N**) and composition 73:27 mol %, respectively, it is marketed as the Vectra[®] resin for injection molding applications (Ticona, Celanese Co.). The disruption of crystallinity of this LCP reduces the melting transition making the materials melt processable [1]. Ward and coworkers have investigated the influence of type of monomers and hence the influence of molecular configuration [2] as well as the effect of temperature treatment on the molecular relaxations. This research focuses on the influence of short glass fibers on the dynamic mechanical properties, molecular relaxations and microstructure of the LCP based on 1,4-hydroxybenzoic acid and 2,6-hydroxynaphthoic [3].

3. Experimental conditions

3.1 Samples

The liquid crystalline polymer B-N (molecular weight 30,000 g/mol, figure 1) and B-N/short glass fiber composites were prepared by melt extrusion and injection molded into bars by the Hoechst Celanese Research Corporate (Summit, NJ, USA). Table 1 lists the samples.

Table 1 Glass fiber reinforced thermotropic copolyester composites

Sample	<i>c</i> (wt%)	T_g (°C)	$T_{s \rightarrow n}$ (°C)	$T_{n \rightarrow s}$ (°C)	T_{dec} (°C)	$E_{a,dec}$ (KJ/mol)	$E_{a,\alpha}$ (KJ/mol)
B-N	0	112.3	287	241	503	217	1510
B-N 15	15	111.6	289	239	504	225	1390
B-N 30	30	115.0	293	238	516	296	1370

3.2 Dynamic mechanical analysis

Dynamic frequency/temperature scans were carried out in torsion mode from 25 to 240°C by using an ARES rheometer manufactured by Rheometric Scientific. A strain sweep was applied from 0.001 to 1 % strain at 1 Hz. The shear storage and loss moduli of the samples were measured at 0.01 % and at the frequencies of 0.5, 1, 2, 5, 10 and 15 Hz. Sample dimensions were typically 29 mm-long, 13 mm-wide, and 1 mm-thick.

3.3 Differential scanning calorimetry and Thermogravimetric analysis

The thermal scans were carried out at 20 °C/min under nitrogen atmosphere by using the Q1000™ DSC (TA Instruments, DE, USA). The decomposition temperatures, T_{dec} , were determined by TGA analysis, at 20 °C/min, using the TGA2950 analyzer.

3.4 Wide angle X-ray diffraction

Two-dimensional X-ray diffraction patterns were obtained using the High Star area detector manufactured by Bruker AXS (Wisconsin, USA). The X-ray source consisted of a rotating anode generator with Cu target. The patterns were background corrected and analyzed using GADDS® analysis software (Bruker AXS).

4. Results and discussion

4.1 Thermal properties. Figure 1a show that the solid-to-nematic phase transition temperature, $T_{s \rightarrow n}$, increased as the concentration of glass fiber increased. The Vectra/SGF composites exhibited supercooling, with a shifting of the recrystallization temperature $T_{n \rightarrow s}$ to lower temperatures than the melting temperatures ($T_{n \rightarrow s} < T_{s \rightarrow n}$). TGA analysis showed that the maximum rate of degradation occurred at 533°C and the activation energy for thermal degradation was determined using the Broido equation [3] by plotting $\ln[-\ln(1-\alpha)]$ vs. $1/T$ (figure 1b). Finally, SGF fillers also produced an increase of the activation energy for degradation in the composites (see Table 1).

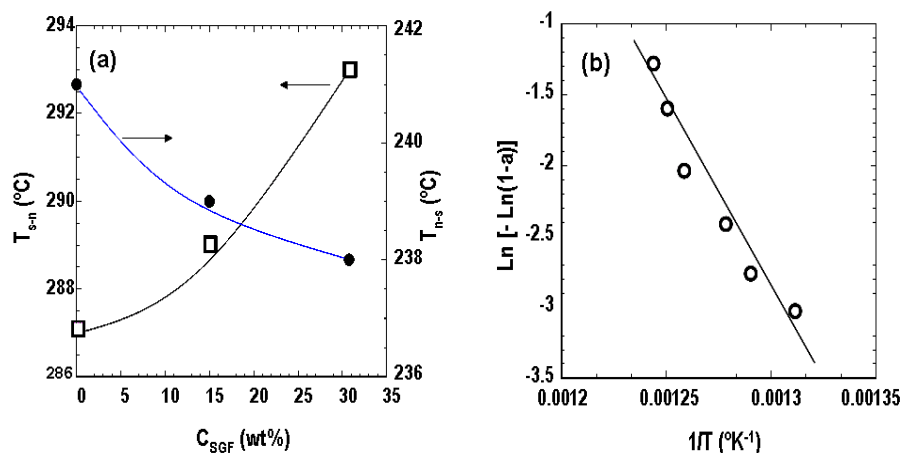


Figure 1. (a) Solid-to-nematic $T_{s \rightarrow n}$ and nematic-to-solid $T_{n \rightarrow s}$ transition temperatures (b) Thermal degradation kinetics of B-N copolyester using Broido equation

4.2 Dynamic mechanical analysis. Figure 2 shows the results for B-N, two relaxations can be seen within this temperature range. It was found that the overall magnitude of the mechanical damping decreased as the amount of SGF increased. The diminution of the mechanical damping with the increase of SGF concentration was correlated with an increase of storage modulus. Comparison among the temperature-frequency sweeps for the three samples, at a given frequency, showed that the strength of the α -transition decreased as the concentration of SGF increased. The activation energies (E_a) corresponding to the α and β transitions were determined for each sample. As discussed above, it is significant that the addition of SGF to the B-N LCP decreased the

activation energy values making in fact less temperature sensitive the α -transition. This finding is important in terms of applications and performance of these materials.

4.3 Wide angle X-ray scattering. Figure 3 shows the normalized azimuthal intensity traces obtained from the WAXS-patterns (not shown here) and the order parameter \bar{P}_2 was quantified. It can be seen from azimuthal broadening that the degree of molecular alignment decreased as the concentration of SGF increased evidencing the detrimental influence of SGF in the molecular orientation induced by the injection molding process. The size of the crystallites was estimated from line broadening and a crystal size of 61 Å was obtained for B-N as well as the composites.

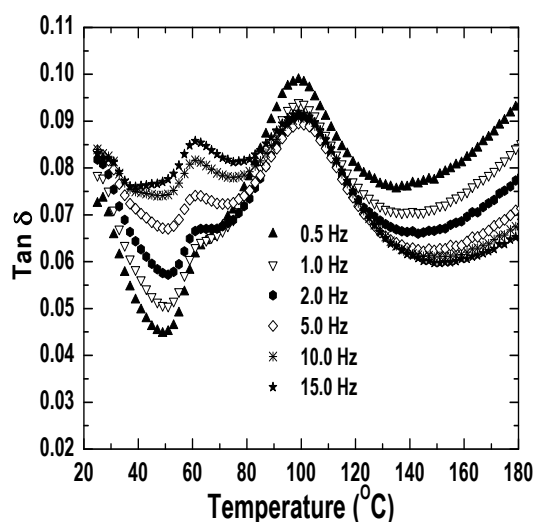


Figure 2. Dynamic mechanical damping $\tan \delta$ spectra in a torsion mode as a function of frequency of oscillation and temperature for B-N sample.

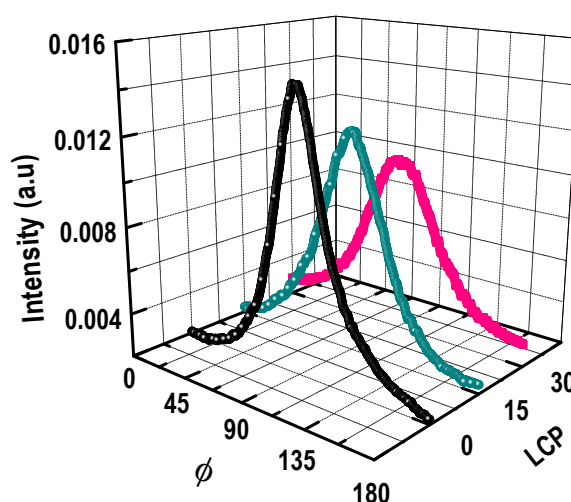


Figure 3. Azimuthal intensity scans for B-N/SGF composites. B-N (0 wt% SGF), B-N15 (15wt% SGF) and B-N30 (30wt% SGF).

5. Conclusions

Addition of SGFs to B-N copolyester increased the solid-to-nematic transition temperature as well as the decomposition temperatures. X-ray scattering showed that the degree of molecular alignment induced by the injection flow processing was decreased by the addition of SGFs. On the other hand, DMA showed that SGFs induced higher G' and weaker α and β relaxations.

6. References

1. Donald AM, Windle AH. *Liquid Crystalline Polymers*, 1992. Cambridge University Press: Cambridge.

2. Troughton MJ, Unwin AP, Davies GR, Ward IM., *Polymer*. 1988; **29**: 1389-1396.
3. Romo-Uribe A, Alvarado-Tenorio B, Romero-Guzman ME, Rejon L, Saldivar-Guerrero R, *Polym. Adv. Techn.* 2008, in the press.