Phase transitions of poly(ethylene terephthalate-*co*-*p*-hydroxybenzoic acid) liquid crystal by dynamic mechanical analysis

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Linear viscoelastic dynamic mechanical analyses are found to be useful methods for phase transition investigations for a dual domain thermotropic liquid crystal polymer, like PET/60 PHB. The values of shear storage, shear loss moduli, complete viscosity, etc., read as a function of temperature show changes at various phase transitions. By simultaneously analysing the results obtained from polarizing microscopy and dynamic mechanical measurements, the crystal–nematic disordering and nematic–isotropic transition in the PHB-rich domain and the crystal melting and the metastable isotropic–nematic transition in the PET-rich domain have been specified.

(Keywords: phase transitions; liquid crystal; dynamic mechanical analysis)

INTRODUCTION

Liquid crystals are characterized by displaying both fluidity and molecular ordering. They may be classified as either lyotropic or thermotropic, depending on the method by which the fluidity and the molecular ordering can be developed. The liquid crystalline polymers are of great importance in the preparation of polymeric materials exhibiting ultra-high modulus and strength. Although lyotropic liquid crystalline polymers, for example, DuPont's 'Kevlar' fibres, have already found significant commercial uses, more research activity has now been directed to thermotropic liquid crystalline polymers (LCPs).

The first known thermotropic LCPs were a series of modified linear poly(ethylene terephthalate)s incorporating X more per cent of p-hydroxybenzoic acid residue as a chain unit (designated as PET/XPHB)[1]. One of these copolyesters, PET/60PHB, has mechanical properties which are superior to the corresponding glass-fibre reinforced PET. To develop processability–structure–property relationship of LCPs, an understanding of phase transition is critical. Indeed, the phase transitions of these copolyesters have been the subject of many investigators[1–6]. The published results are mainly obtained from differential scanning calorimetry (d.s.c.) measurements. However, they are contradictory and in some cases ambiguous.

As shown in earlier work, PET/60PHB exhibits a dual glass transition[2] and presents dual domain morphologies[5,7] in both the solid and liquid states[8,9]. To specify the phase transition in each domain of this copolyester, a single d.s.c. method is insufficient. An additional characterization method may offer clearer evidence on phase transitions. In this view, the rheology of a thermotropic LCP should show a change at phase transitions. Therefore, it is expected that the phase transitions can be sensitively resolved by viscoelastic measurements. To mechanically evaluate the static morphologies, a test, dynamic mechanical analysis (d.m.a.) was considered over steady flow measurements. Little activity appears to have been expended on this aspect[10]. The present work is thus aimed at the phase transitions of PET/60PHB by dynamic mechanical tests.

EXPERIMENTAL

Materials

All three of the copolyester compositions (PET/28 PHB, PET/60 PHB and PET/80 PHB) were supplied by the Tennessee Eastmann Company, Kingsport, TN. PET/28 PHB and PET/60 PHB had intrinsic viscosities of 0.55 and 0.68 dl g^{-1}, respectively. The PET/80 PHB was characterized by the melt flow (27 g/10 min at 325°C).

Dynamic mechanical measurement

Viscoelastic properties were measured on a Rheometrics Dynamic Spectrometer (RDS), using parallel plates. Before measurements, the copolymer chips were dried in a vacuum oven at 110°C for 48 h. Then they were moulded under vacuum at 260°C to make discs with a diameter of 25 mm and a thickness of 1.2 mm. During the measurement, nitrogen flow was used to reduce sample oxidation.

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RESULTS AND DISCUSSION

The effect of oscillatory shear strain amplitude on dynamic mechanical moduli for PET/60 PHB is shown in *Figure 1*. In the experimental temperature range, the copolyester shows linear viscoelasticity at small strain amplitudes ($\gamma_0 \leqslant 0.05$). The large amplitude oscillatory shear probably induced structural changes, as shown by the large decay of dynamic mechanical moduli[10]. The strain amplitude adopted in the present study was limited to the linear viscoelastic region.

Results of frequency sweep at various constant temperatures are shown in *Figure 2*. The log plot of both shear storage, G', and shear loss moduli, G'', *versus* frequency results in a rather linear correlation in the experimental frequency range. This means that the phase transition temperatures, as indicated by the changes of linear viscoelastic properties, does not shift significantly with frequency. A frequency of 10 rad s^{-1} was used in the subsequent work.

Dynamic moduli, G' and G'', of PET/60 PHB, as a function of temperature are shown in *Figure 3*. From these plots, four distinct temperature regions can be seen:

(1) Region I—from 190 to 230°C, the moduli drop by two orders of magnitude;

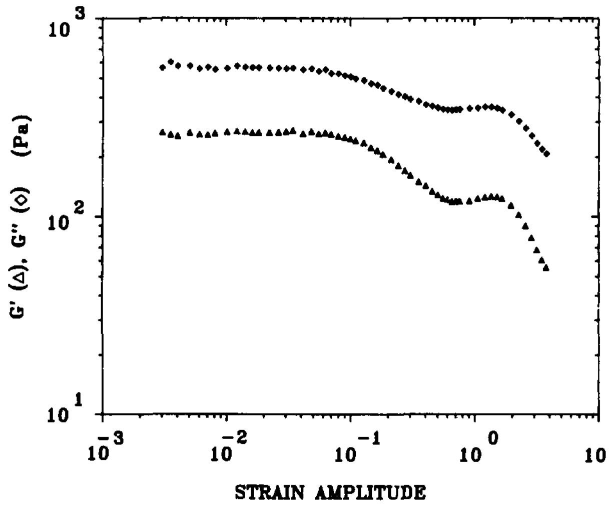

Figure 1 Strain sweep at 260°C and 10 rad s^{-1} for PET/60 PHB

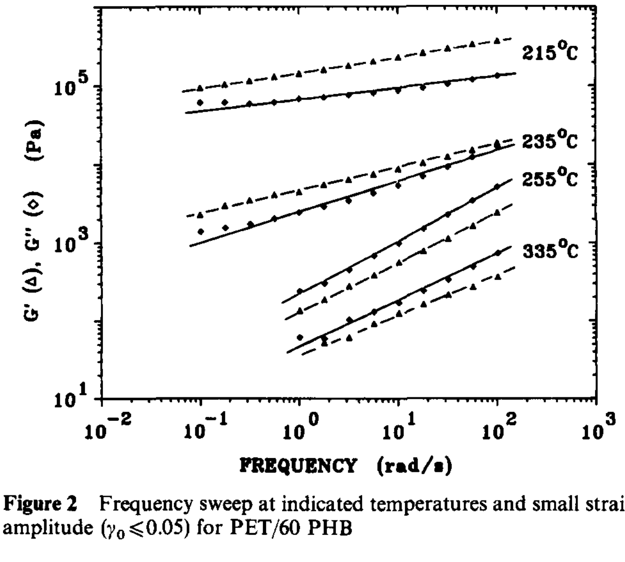

Figure 2 Frequency sweep at indicated temperatures and small strain amplitude ($\gamma_0 \leqslant 0.05$) for PET/60 PHB

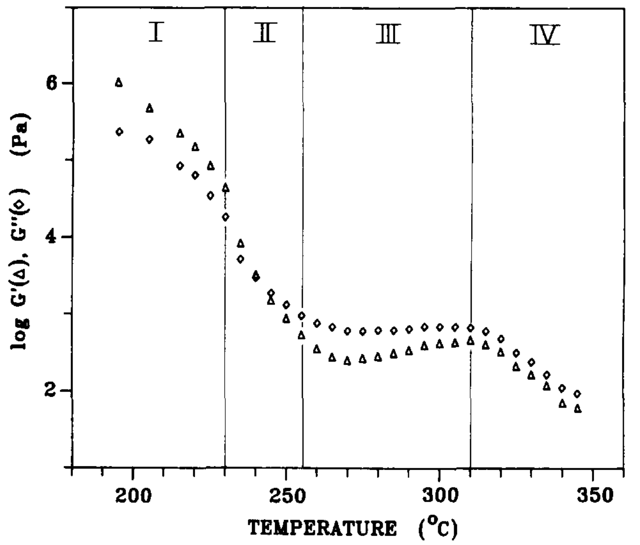

Figure 3 Temperature sweep at 10 rad s^{-1} and small strain amplitude ($\gamma_0 \leqslant 0.05$) for PET/60 PHB

(2) Region II—from 230 to 255°C, the moduli drop even more drastically;

(3) Region III—from 255 to 310°C, the curves level off to form, more or less, a plateau;

(4) Region IV—from 310 to 340°C (our maximum temperature), the moduli apparently drop again.

It has been shown previously, by polarized microscopy, that PET/60 PHB exhibits dual domains, both in the solid and liquid states, in which the PHB-rich domain is a continuous one and the PET-rich domain is discontinuous[8]. As seen from the following discussion, dynamic mechanical measurements strongly support these previous conclusions and detail the phase transitions in each domain.

Region I. A remarkable drop in both G' and G'', above 190–200°C, has been observed (*Figure 3*). Both G' and G'' were not measurable at 190°C, due to the high modulus of the sample, i.e. the torque response exceeds the instrument capability. By estimation, G' should be $>10^7$ Pa <190°C, consistent with a reported glass transition temperature T_{g1} for a PHB-rich phase, which is 167–182°C, depending on d.s.c. measurement conditions[2]. An emergence of flow lines in the continuous PHB-rich domain has been observed between crossed polarizers at a temperature ~ 200°C (ref. 8). Therefore, the remarkable drop in G' and G'' starting at 190–200°C may be attributable to the onset of mobility due to liquid crystal formation in the PHB-rich domain.

Region II. In the range from 230 to 255°C a more drastic decline in G' and G'' is observed. Beyond the liquid crystal formation in the PHB-rich domain, mentioned above, there must exist another feature, which intensifies this tendency. From polarized microphotographs, the amount of PET-like crystallites in the discontinuous domain melt gradually with temperature and vanish completely between 250°C and 270°C (compare *Figures 4a* and *b*)[8]. This is probably due to the non-random sequence distribution in the macromolecular chains of PET/60 PHB (refs. 2 and 11) and a composition distribution in the PET-rich domains. This composition distribution results in a melting range for PET-like crystallites[8]. The composition of PET/60 PHB consists of

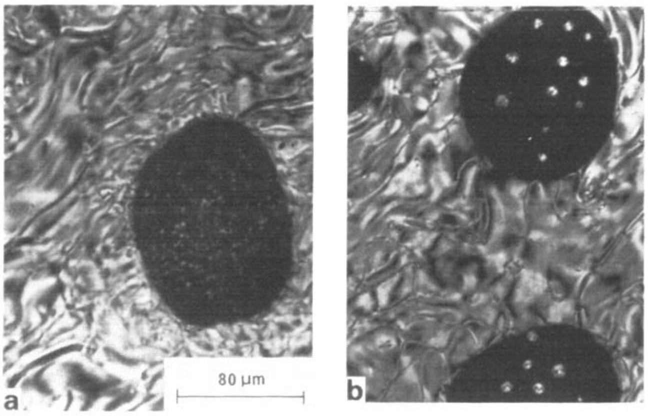

Figure 4 Photomicrographs between crossed polarizers of PET/60 PHB[8] at (a) 250°C, and (b) 270°C. Scale bar = 80 μm

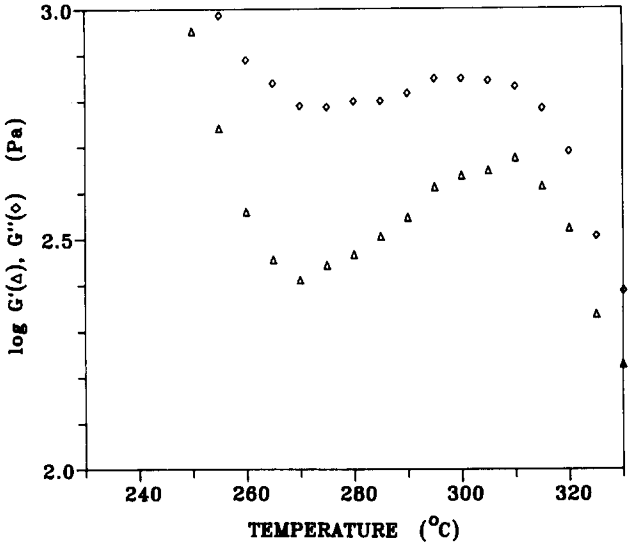

Figure 5 Temperature sweep at 10 rad s^{-1} and small strain amplitude ($\gamma_0 \leq 0.05$) for PET/60 PHB

discontinuous PET-rich domains and continuous PHB-rich domains in both the solid and liquid states[9]. A fraction of the copolymer chains can cross the interface between the two domains, giving rise to an additional interaction. Therefore, it can be expected that phase transitions, due to one domain, will influence the overall viscoelastic properties. In addition to the 'liquefaction' of the PHB-rich domain, the rather wide melting range of PET-rich crystallites contributes to a further gradual decay of G' and G'' in this region. The change from an elasticity dominant state ($G' > G''$ at $T < 240$°C) to a viscosity dominant state ($G'' > G'$ at $T > 240$°C) is due to the combined effects of the liquid crystal formation in PHB-rich domains and the melting in PET-rich domains.

Region III. In the range from 255 to 310°C the log G'–T and log G''–T plots nearly level off. This implies that both the liquid crystal formation in the PHB-rich domain and the melting transition of PET-like crystallites are basically completed. However, if we examine this region carefully, it can be subdivided into two parts: from 255 to 270°C d$\log G'/\mathrm{d}T$ is negative, while from 270 to 310°C it exhibits a small positive value. This unusual feature can be seen more clearly from an enlargement of this region as shown in *Figure 5*.

From *Figure 4b* a new anisotropic phase can be seen in the PET-rich domain as the original PET-like crystallites vanished completely. The anisotropic phase found at $\geq$270°C is assumed to be minute aggregates of PHB-rich segments, phase-coseparated with PET-rich segments in to the PET-rich domains. Below 260°C, the small amount of PHB-rich segments is dispersed among PET-rich segments in a metastable state. The PET-like crystallites prevent their aggregation. Only above the melting point of PET-like crystallites these PHB-rich segments can undergo a segmental motion. A peak found in $t_g\ \delta$–T plots at 265°C (see *Figure 6*) can be interpreted as an evidence of such segmental motion. These newly formed PHB-rich small liquid crystals located in PET-rich domains act as physical crosslinks and cause a slight but real increase in G' from 270 to 300°C. In short, the 'abnormal' positive thermal coefficient of G' in PET/60 PHB is due to the presence of separated PHB-rich segments dispersed in the PET-rich domains. If this explanation is valid, a log G' vs. T plot, when measured with cooling down mode, should not exhibit a minimum in this region. The cooling down

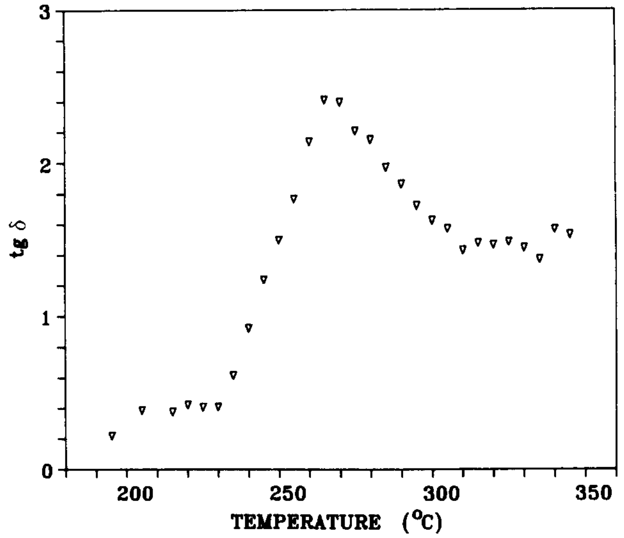

Figure 6 Evolution of $t_g\ \delta$ in the temperature sweep at 10 rad s^{-1} and small strain amplitude for PET/60 PHB

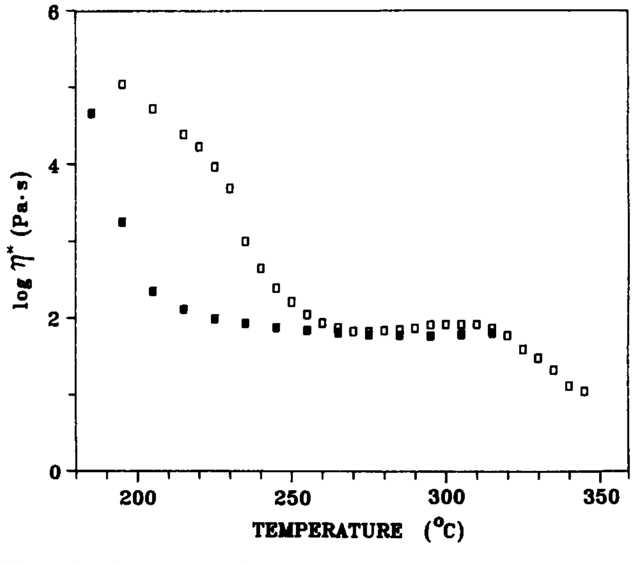

Figure 7 Comparison of storage modulus of PET/60 PHB while heating at a rate of 1 K min^{-1} (□) and cooling at a rate of -1 K min^{-1} (■)

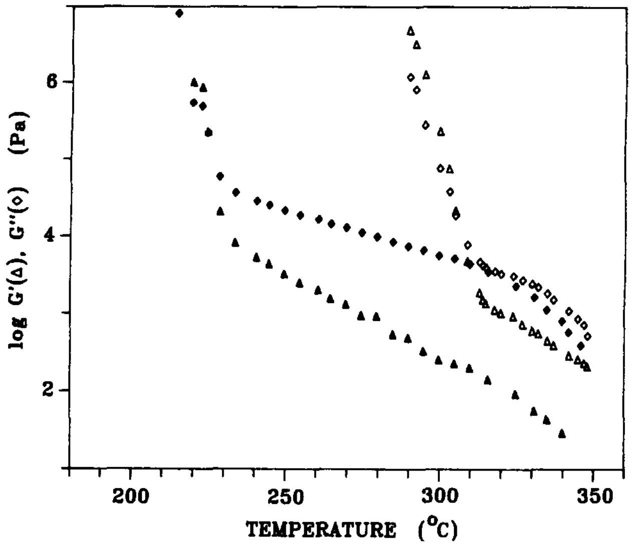

Figure 8 Temperature sweep at 10 rad s^{-1} for PET/28 PHB (filled symbols) and PET/80 PHB (open symbols)

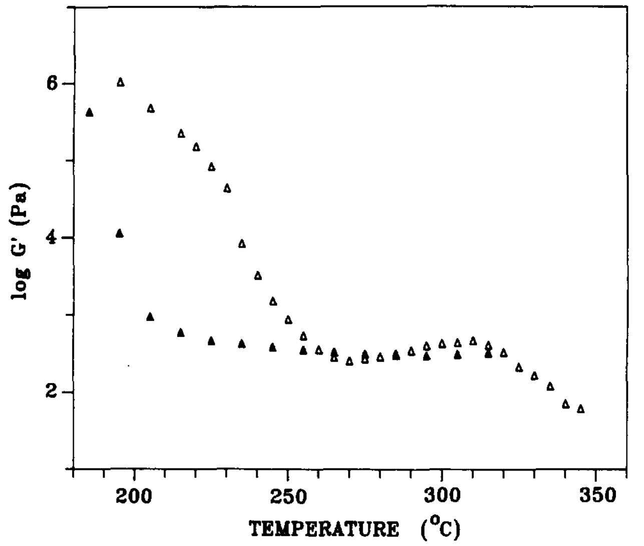

Figure 9 Evolution of complex viscosity of PET/60 PHB at 10 rad s^{-1} while heating (△) and cooling (▲). The heating/cooling rate was 1 K min^{-1}

curve does show a plateau in the temperature range of 255–310°C (see *Figure 7*). Further, PET/28 PHB and PET/80 PHB are reference compositions. PET/28 PHB presents no liquid crystalline state and indeed no 'abnormal' thermal coefficient of G' is found (see *Figure 8a*). In the case of PET/80 PHB, the temperature range, in which its mesophase can exist is higher than the melting point of PET-like crystallites (*Figure 8b*). Therefore, the PHB-rich segments can never be hindered.

Region IV. An apparent drop in G' and G'' at 310°C implies an additional transition. This temperature is far above the melting point of PET-like crystallites, thus the phase transition must be associated with PHB-rich domains. Viney and Windle[4] have reported a smectic–nematic phase transition at 320°C. The G' of a smectic phase for low molecular weight liquid crystal is reported in the range of 10^5–10^6 Pa (ref. 12). From these facts, along with the relatively low level of G' and G'' values ($\sim 10^2$ Pa) we found in this temperature range, it is likely that the phase transition at 310°C is a nematic–isotropic transition occurring in the PHB-rich domain.

It is generally expected that the viscosity of an isotropic melt is higher than that of the corresponding nematic phase. But in the nematic–isotropic transition (T = 310–340°C) the complex viscosity, η^*, decreases with increasing temperature as shown in *Figure 9*. The isotropization point of this copolyester has been reported as 420–430°C (refs. 4 and 8). Our Rheometrics Dynamic Spectrometer measurements were limited to 340°C, below this temperature. There are two contradictory factors governing the viscosity–temperature relationship of a nematic–isotropic melt system: (1) with the increasing of temperature the increased amount of isotropic melt may lead to an increase of viscosity; (2) with the increasing of temperature the viscosity of the melt itself will decrease. The net effect of temperature on viscosity of this system must depend upon which one of these two factors is dominant.

CONCLUSIONS

The phase transitions reported in the literature for PET/60 PHB are in conflict. This seems due mainly to the structural inhomogeneity of this copolyester. This inhomogeneity makes the transition temperature assignment more difficult and complicated in a d.s.c. analysis, due to the possible overlap of various thermal effects evolved from the dual domains. Polarized microscopy morphology studies as a function of temperature offer valuable qualitative phase behaviour information for each domain. To investigate the phase transitions of a polydomain thermotropic LCP, like PET/60 PHB, a study of its steady flow behaviour can lead to misunderstanding, due to the ultra structure change during the measurement.

Linear viscoelastic dynamic mechanical analyses are found to be a useful method for phase transition investigation of the inhomogeneous thermotropic LCP. The values of G', G'', η^*, etc., read as a function of temperature can also give an estimation of the type of phase present at a given temperature and hence aid the transition assignment. For PET/60 PHB, a large number of polymer chains probably cross the interfaces of the two domains, giving rise to important physical interactions. Phase transitions taking place in either domain influence the total viscoelasticity. This is why the crystal–nematic disordering, nematic–isotropic transition, crystal melting and even a small amount of metastable isotropic–nematic transition in the domain can be found sensitively by the methods outlined in the present work. By simultaneous analysing the results obtained from polarized microscopy and dynamic mechanical measurement, the phase transitions in each domain have been identified.

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