# Physical properties of blends of a liquid crystalline copolyester with poly(butylene terephthalate)*

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Physical properties, including rheology, dimensional stability, dynamic viscoelasticity and differential scanning calorimetry (d.s.c.) of blends of thermotropic 60% *p*-hydroxybenzoic acid–40% poly(ethylene terephthalate) P(HBA–ETP) copolyester with poly(butylene terephthalate) PBT are studied. The viscosity of the blend is not decreased by the addition of a small quantity of P(HBA–ETP) which contradicts the general trend observed in the literature for blends of liquid crystalline polymers. In our case the viscosity decreases only for blends of $\geqslant 40\%$ P(HBA–ETP). Dimensional stability (shrinkage) measurements, however, reveal more sensitivity to the influence of small quantities of P(HBA–ETP), e.g. 5P(HBA–ETP)/95PBT blends show very good dimensional stability, similar to that of P(HBA–ETP) samples. The shrinkage results are related to d.s.c. measurements and we consider that PHBA crystallites act to lock the retraction in the case of blends. We suggest that the presence of PBT favours the formation of crystals in P(HBA–ETP), when both polymers are blended. The heterogeneous morphology of P(HBA–ETP) copolymer is manifested by the existence of various relaxations detected by dynamic viscoelastic measurements. Compatibility between PBT and the PET-rich phase of the liquid crystalline copolyester is deduced from dynamic viscoelastic results.

**(Keywords: thermotropics; rheology; shrinkage; calorimetry; dynamic viscoelasticity; compatibility; crystallites)**

## INTRODUCTION

Since the development of lyotropic aromatic polyamides in 1965, basic and applied research on polymeric liquid crystals has been continuously increasing. The interest in this type of material grew with the development of the first thermotropic polymer, a copolyester containing 60 mol% poly(*p*-hydroxybenzoic acid) (PHBA) and poly(ethylene terephthalate) (PET)[1], and intense patent activity started in the mid-seventies. The main advantage of thermotropics is that they can be processed as ordinary thermoplastics, whereas lyotropics can only be spun by using very complicated and expensive techniques.

At the same time as technical interest in thermotropic copolyesters has been increasing, research in polymer science has focused on the development of new materials based on blends of homopolymers. But, until now, few papers and patents have dealt with blends in which one of the components is a thermotropic polymer liquid crystal. A compilation of some of the published papers on blends composed of thermotropic liquid crystal copolyesters is presented in *Table 1*. Several of these papers concern blends of P(HBA–ETP), although this copolyester has some shortcomings which reduce its commercial interest. However, the fact that it is available in sufficient quantity and that its melting point makes experimentation easier than with other thermotropic copolyesters had led some researchers to study blends based on this copolymer. On the other hand, because of the heterogeneous nature of P(HBA–ETP) copolyester (with the presence of a PET rich phase and a PHBA rich phase), blending such a liquid crystalline polymer with classical thermoplastics represents an interesting procedure for basic studies of phase behaviour and properties and, eventually, industrial applications. In particular, blends of flexible poyesters like PET and PC with P(HBA–ETP) have been studied from the morphological and rheological point of view. Poly(butylene terephthalate) (PBT) has received less attention and, to our knowledge, only the work by Kimura and Porter[2] (where compatibility in the terephthalate-rich phase is observed) is dedicated to P(HBA–ETP)/PBT blends.

In this paper we present some results of the rheology of blends of PBT and 60 mol% poly(*p*-hydroxybenzoic acid)–poly(ethylene terephthalate), interpreted in the light of phase behaviour and compatibility analysed by differential scanning calorimetry (d.s.c.) and dynamic viscoelasticity.

## EXPERIMENTAL

### *Materials*

The liquid crystalline copolyester used in this work is a copolyester consisting of 60 mol% *p*-hydroxybenzoic acid and 40 mol% ethyleneterephthalate P(HBA–ETP) (X7G®), kindly provided by Tennessee Eastman. Its inherent viscosity = 0.68 dl g$^{-1}$, which, according to

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* This paper is dedicated to Professor Dr Gonzalo Martin Guzmán on the occasion of his nomination as Professor Emeritus at the University of the Basque Country

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**Table 1** Published papers on blends composed of thermotropic liquid crystal copolyester

| Components of the blends[a] | Studied properties | Reference |
|---|---|---|
| P(HBA–ETP)/PBT | Compatibility by d.s.c. | 2 |
| P(HBA–ETP)/PC | Morphology, rheology | 3 |
| P(HBA–ETP)/PC | Morphology, n.m.r., transreactions | 4 |
| P(HBA–ETP)/PC | Rheology, d.s.c., dielectric, mechanical | 5 |
| P(HBA–ETP)/PC | Rheology, shrinkage, morphology | 6 |
| P(HBA–ETP)/PET | D.s.c., morphology, mechanical | 7 |
| P(HBA–ETP)/PET | Drawing, dynamic viscoelasticity, d.s.c. | 8 |
| P(HBA–ETP)/PET | D.s.c., mechanical properties | 4 |
| P(HBA–ETP)/PET | Rheology, d.s.c., dielectric, mechanical | 5 |
| P(HBA–ETP)/PET | Phase separation | 9 |
| P(HBA–ETP)/nylon | Morphology, rheology | 3 |
| PHBA–PET/CPVC | Rheology, spiral mould flow | 10 |
| PHBA–PET/PS | Rheology, d.s.c., dielectric, mechanical | 5 |
| P(HBA/ETP)/PHMT | Interaction between components | 11 |
| P(HNA–HBA)/PA | Rheology, morphology, mechanical | 12 |
| P(HNA–HBA)/PC | D.s.c., spinning, shrinkage, dynamic viscoelasticity | 13 |
| P(HNA–HBA)/PC | Rheology, mechanical | 14 |
| P(HNA–HBA)/PC | Morphology | 15 |
| P(HNA–HBA)/PC | Morphology, mechanical, rheology | 16 |
| P(HNA–HBA)/PET | Morphology, mechanical | 17 |
| Naphthalene based LCC/PES; PAr; PEEK PC; PBT; Nylon | Morphology, processing, mechanical | 18 |
| Hoechst Celanese Polyesteramide/nylon | Processability, mechanical | 19 |
| TBBA/PS | D.s.c., shrinkage | 20 |
| EBBA/PVC | Permeability, d.s.c., morphology | 21 |
| PB8/PBT | D.s.c. | 22 |
| Polyesteramide/PBT | D.s.c. | 22 |

[a] P(HBA–ETP), 60% *p*-hydroxybenzoic acid–40% poly(ethylene terephthalate); PBT, poly(butylene terephthalate); PC, polycarbonate; CPVC, chlorinated poly(vinyl chloride); PHMT, poly(hexamethylene terephthalate); PA, polyamide; P(HNA–HBA), poly(2-hydroxy-6-naphthoic acid)–poly(*p*-hydroxybenzoic acid); LCC, liquid crystalline copolyester; PES, poy(ether sulphone); PAr, Polyarylate; PEEK, poly(ether ether ketone); TBBA, terephtal bis-4-n-butylaniline; EBBA, *N*-(4-ethoxybenzylidene)-4′-butylaniline; PB8, poly(bisphenyl-4,4′-ylene sebacate)

Jackson and Kuhfuss[1], corresponds to a number average molecular weight $M_n \approx 20000$.

The poly(butylene terephthalate) (PBT) is a commercial BASF product (Ultradur® B4500) with a molecular weight $M_n = 30200$ as determined by intrinsic viscosity measurements at 25°C in 60/40 phenol/tetrachloroethane solvent[23].

Before mixing, X7G and PBT were vacuum dried at 90°C for 48 h and 14 h, respectively. The blends were made at a temperature of 250°C, using a Kenicks static mixer adapted to a Sieglaff–McKelvey extrusion capillary rheometer. The basic polymers, X7G and PBT, were also extruded through the static mixer, to submit all the materials (homopolymers and blends) to the same thermomechanical history.

### *Rheological measurements*

Shear viscosity was measured in a Sieglaff–McKelvey extrusion capillary rheometer at temperatures and shear rates detailed below. The dimensions of the capillary die were $L/D = 25.4$ and $R_c = 0.05$ cm and the entrance angle was 180°. In all cases, at a constant force (constant shear stress) corresponded to a constant piston velocity (constant shear rate in the capillary wall), which indicated that there was no degradation.

### *Shrinkage*

Filaments of both basic polymers and their blends, with average values of $L_0 = 10$ cm and $R_0 = 0.05$ cm, were prepared by extrusion in the capillary rheometer at a temperature of 250°C and shear stress $\sigma_{21} = 1.5 \times 10^4$ Pa. The filaments were placed in a poly(dimethyl siloxane) (PDMS) oil bath at a temperature of 235°C and allowed to shrink: the length of the filament, $L(t)$, was measured optically at various times up to 3600 s. All the results presented are the average of 5–10 experiments.

### *Dynamic viscoelasticity*

Shear and bending dynamic viscoelastic properties were measured in a Polymer Laboratories DMTA apparatus. Scans of temperature at frequencies 0.03, 0.1, 0.3, 1, 3, 5, 10, 20, 30 and 50 Hz were carried out in bending mode, with samples of dimensions $2 \times 15 \times 1$ mm$^3$. The dynamic or complex viscosity, $\eta^*$, was determined in shear mode, at 210°C and 240°C at the same range of frequencies. In this case the samples were cylindrical with a diameter of 12 mm and a thickness of 1 mm; the amplitude of the strain was $<2\%$. The rectangular and cylindrical samples were die-cast from a plate 1 mm thick, obtained by compression moulding at 250°C.

### *Differential scanning calorimetry*

Calorimetric measurements were performed in a Perkin–Elmer DSC-4 calorimeter at a heating rate of $10^{\circ}$ min$^{-1}$. All the measurements were made with samples (10–15 mg) taken from extrudates obtained at 250°C.

## RESULTS AND DISCUSSION

### *Rheological characterization of PHBA–PET copolyester*

*Figure 1* shows viscosity results obtained by extrusion capillary rheometry at temperatures ranging from 220 to 260°C. We have superimposed these data to obtain a master curve, at reference temperature $T_R = 220$°C, which is shown in *Figure 2*.

*Figure 3* shows the dependence of the dynamic viscosity, $\eta^*$, on frequency, and steady-state viscosity data, at 210 and 240°C.

To compare our results with literature data, in *Figure 4* we present viscosity–shear rate curves at different temperatures. Clearly, the results of different authors do not coincide, which is attributed to the fact that in some cases 60 mol% PHBA–40 mol% PET of different molecular weights was used. On the other hand, the influence of thermal history is very important in viscosity results, as has been pointed out by Wissbrun[24].

The most remarkable aspect of the superimposed data presented in *Figure 2* is the presence of a concave upward

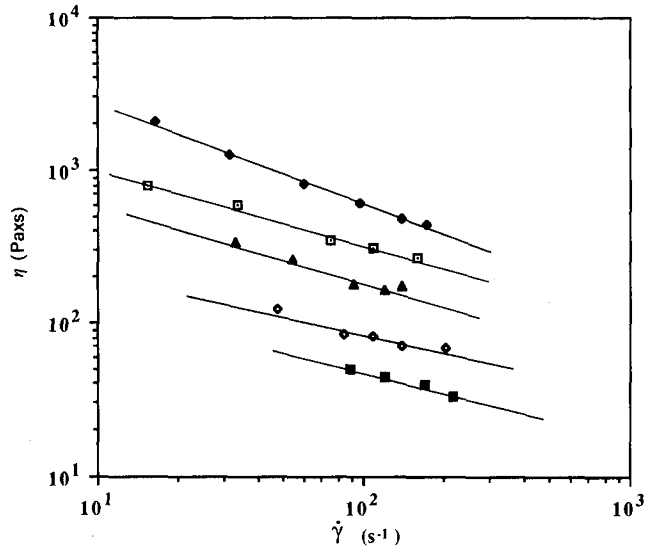

**Figure 1** Viscosity curves of X7G: ◆, 220°C; □, 230°C; ▲, 240°C; ◇, 250°C; ■, 260°C

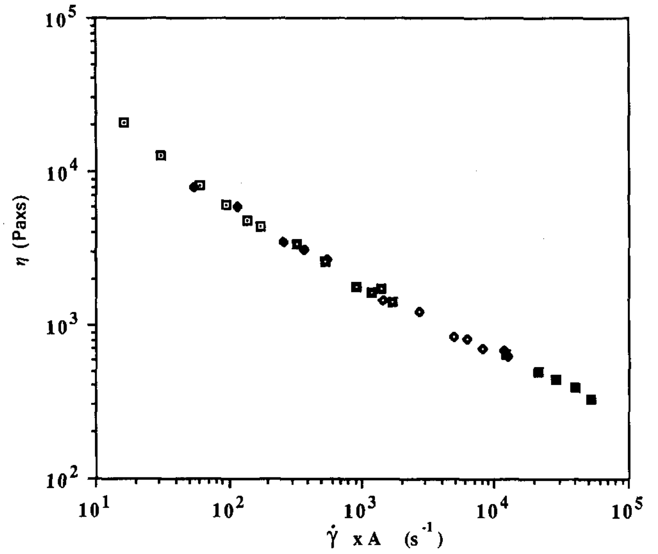

**Figure 2** Master curve of data presented in *Figure 1*. $T_R = 220°C$

shear thinning region of flow behaviour, at low shear rates. It is observed that the slope of the curve tends to $-1$, which corresponds to the so-called plastic behaviour observed in some lyotropic and thermotropic systems[25–29] and also in the case of P(HBA–ETP) thermotropic copolyester at low temperatures (210–230°C)[24]. This plastic, solid-like, behaviour is confirmed by the results of dynamic viscosity presented in *Figure 3* (where a slope of $-1$ is observed for $\log \eta^* - \log \nu$ plots at a temperature of 210°C) and in Reference 10. However, at a temperature of 240°C the slope is $-0.75$, which corresponds to a more classical non-Newtonian flow behaviour (a very similar result is also presented in Figure 1 of Reference 30).

On the other hand, in *Figure 3*, comparison of dynamic and steady-state viscosity results shows that, as has been pointed out in the literature[10–24], the steady-state values, $\eta$, were lower than those obtained by dynamic experiments, $\eta^*$. This result is a consequence of the different thermo-mechanical history of the samples in each experiment (extrusion or oscillation) and must be interpreted in the light of theories which relate the effect of texture to rheology, e.g. the phenomenological models based on domains whose size is a function of stress[31,32].

In an attempt to determine the apparent yield stress value corresponding to the plastic behaviour, we have used the model of Casson[33]:

$$(\sigma_{21})^{1/3} = (\sigma_0)^{1/3} + (\eta_\infty)^{1/3}\dot{\gamma} \qquad (1)$$

where $\sigma_0$ is the apparent yield stress and $\eta_\infty$ the so-called plastic viscosity. As can be seen from *Figure 5*, the experimental values do not fit satisfactorily to equation (1), but a value of $\sigma_0 = 750$ Pa can be inferred to evaluate the plastic behaviour.

As pointed out in the excellent review by Wissbrun[34], the yield stress in liquid crystals can be attributed to plastic flow of piled domains but also to phase separation.

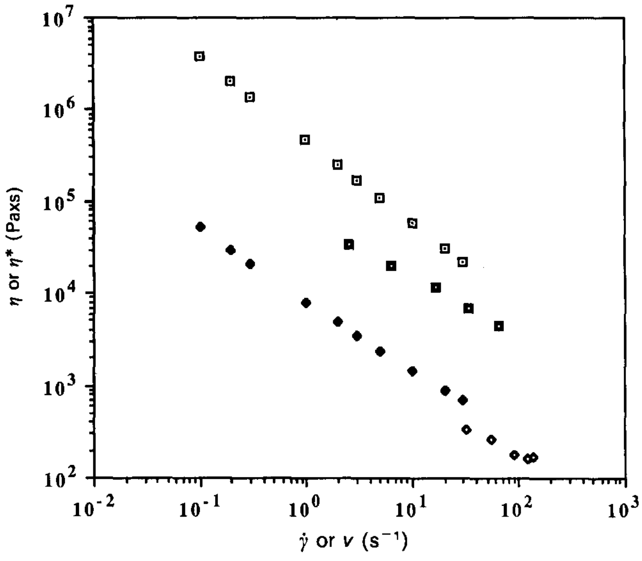

**Figure 3** Dynamic viscosity compared with steady-state viscosity: ⊡, steady-state, 290°C; ▣, dynamic, 210°C; ◆, steady-state, 340°C; ◇, dynamic, 210°C

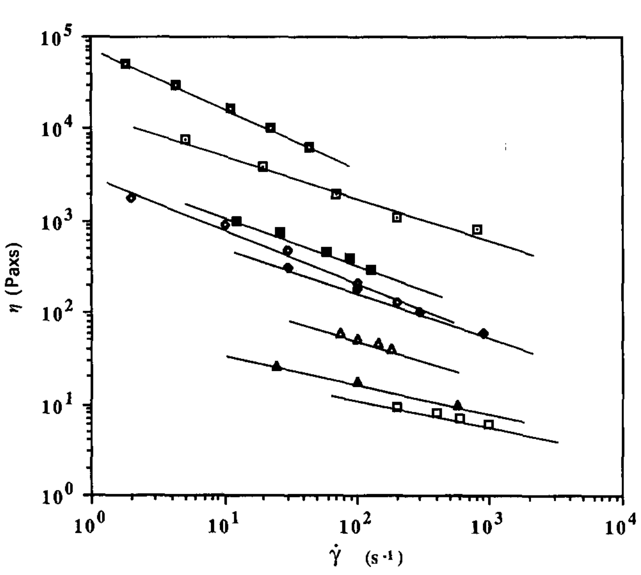

**Figure 4** Viscosity curves reported in the literature for P(HBA–ETP) (X7G): □, Reference 24, 210°C; ◆, Reference 10, 210°C; ▣, our work, 210°C; ◇, Reference 5, 230°C; ■, our work, 230°C; □, Reference 24, 260°C; ▲, Reference 6, 260°C; △, our work, 260°C

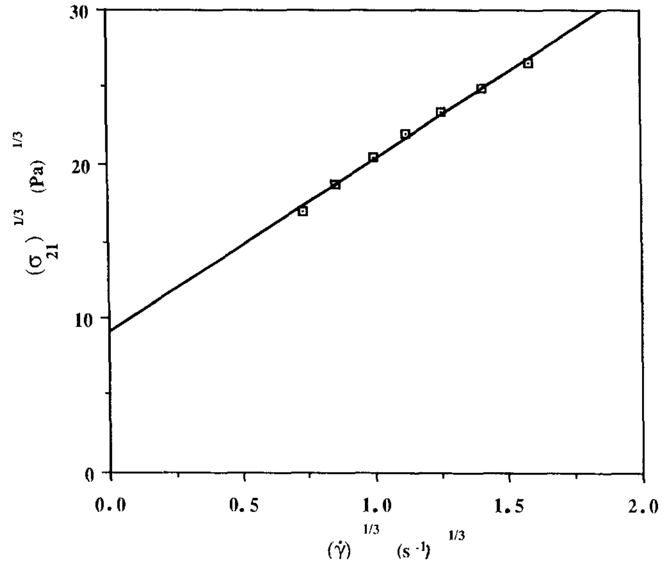

**Figure 5** Experimental data for $\sigma_{21}$ (Pa) against (s$^{-1}$) fitted to equation (1)

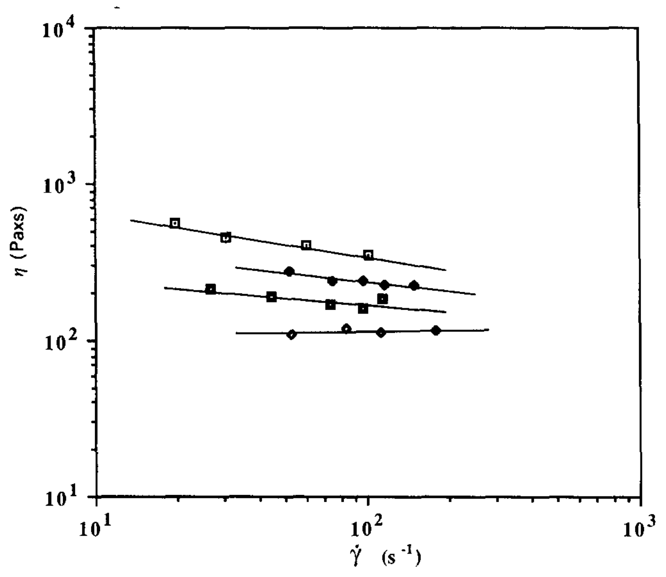

**Figure 6** Viscosity curves of PBT: ▣, 240°C; ◆, 250°C; ■, 260°C; ◇, 270°C

The structural inhomogeneity of the copolyester we are considering in this work might support the latter hypothesis.

The literature contains some data concerning values of apparent yield stress of small molecule liquid crystals, but for thermotropics we can only quote the case of a phenyl ring based polyester with flexible spacers in the main chain, for which Wissbrun and Griffin[35] report a value of $\sigma_0 = 638$ dyn cm$^{-2}$ (63.8 Pa).

The activation energy of flow, obtained from adjustment of data of *Figure 1* to an Arrhenius type equation in the range 220–260°C, is $E_a = 37$ kcal mol$^{-1}$, which is in agreement with the results presented by Cuculo and Chen[36] in the range 225–250°C. However, the results of Wissbrun[24] differ: 30 kcal mol$^{-1}$ at 280°C and 80 kcal mol$^{-1}$ in the range 210–245°C.

### *Rheology of blends*

The viscosity curves of the second component of the blend, PBT, are shown in *Figure 6*. An almost Newtonian flow behaviour, which is one of the characteristics of current polyesters like polycarbonate and polyethylene terephthalate, is observed. The activation energy of flow, calculated from data of *Figure 6*, is $E_a = 22.5$ kcal mol$^{-1}$, considerably smaller than that obtained for X7G copolyester.

The viscosity curves of the blends at 220°C are presented in *Figure 7*. As a general trend the curves can be grouped into two zones: one corresponding to PBT-like behaviour (Newtonian), which includes PBT and 80 PBT/20 X7G, the other to liquid crystalline-like behaviour. The change in viscosity at compositions above 20% of X7G is clearly seen in *Figure 8*, where the viscosity is plotted against composition at a constant shear stress, $\sigma_{21} = 10^4$ Pa. The viscosity is reduced to 30% of its value, when the content of liquid crystal copolyester is 40%.

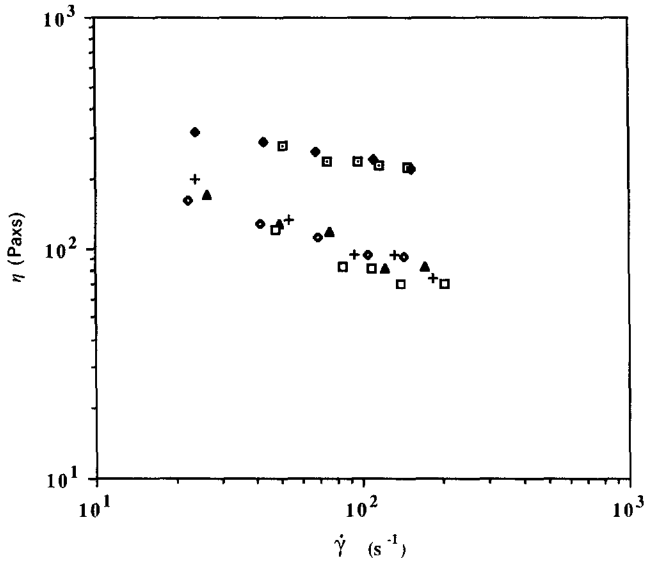

**Figure 7** Viscosity curves of the blends at 220°C: ▣, PBT; ◆, 20X7G/80PBT; ◇, 40W7G/60PBT; ▲, 60X7G/40PBT; +, 80X7G/20PBT; □, X7G

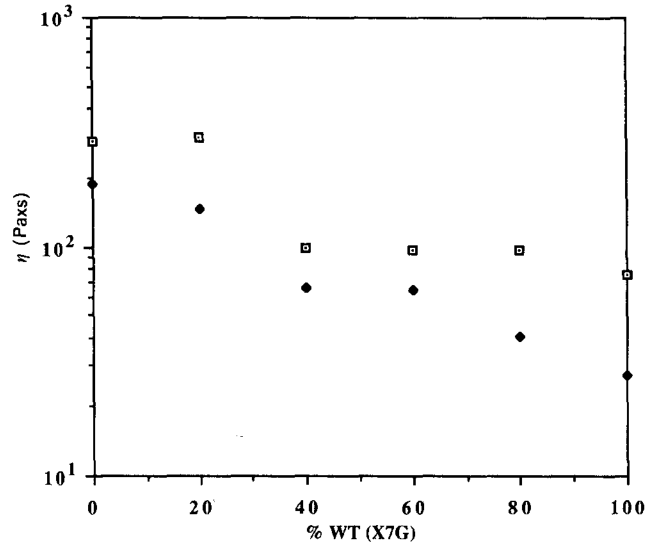

**Figure 8** Viscosity, taken at $\sigma_{21} = 10^5$ dyn cm$^{-2}$ ($10^4$ Pa), as a function of composition. ▣, 250°C; ◆, 260°C

**Table 2** Compilation of viscosity data (Pa s) for liquid crystalline copolyesters[a] and their blends with various thermoplastics

| $\eta$(LCC) | $\eta$(thermotropic) | $\eta$(80 thermotropic/20 LCC) | Conditions | Reference |
|---|---|---|---|---|
| $5.1 \times 10^1$ | $6.8 \times 10^2$ (CPVC) | $1.8 \times 10^2$ | 220°C, 427 $s^{-1}$ | 10 |
| $1.6 \times 10^1$ | $3.2 \times 10^2$ (PET) | $1.2 \times 10^2$ | 270°C, $2.5 \times 10^3$ Pa | 5 |
| $2.1 \times 10^3$ | $1.8 \times 10^3$ (PS) | $8 \times 10^2$ | 230°C, $2.3 \times 10^3$ Pa | 5 |
| $1.6 \times 10^1$ | $1.6 \times 10^3$ (PC) | $4.8 \times 10^2$ | 270°C, $2.3 \times 10^3$ Pa | 5 |
| $2.4 \times 10^2$ | $5 \times 10^3$ (PA) | $1.9 \times 10^2$ | 260°C, 2700 $s^{-1}$ | 12 |
| $7 \times 10^3$ | $7 \times 10^3$ (PA) | $8 \times 10^2$ | 260°C, 541 $s^{-1}$ | 12 |
| 7 | $10^3$ (PC) | $10^2$ | 260°C, 1000 $s^{-1}$ | 3 |
| $6 \times 10^1$ | $10^3$ (PC) | $5 \times 10^2$ | 240°C, 700 $s^{-1}$ | 6 |
| $6 \times 10^3$ | $6 \times 10^3$ (PC) | $6 \times 10^3$ | 240°C, 0.3 $s^{-1}$ | 6 |
| $1.4 \times 10^2$ | $3.5 \times 10^2$ (PBT) | $3.6 \times 10^2$ | 250°C, $5 \times 10^3$ Pa | This work |
| $9 \times 10^1$ | $3 \times 10^2$ (PBT) | $3.1 \times 10^2$ | 250°C, $10^4$ Pa | This work |

[a] LCC refers to P(HBA–ETP), except for the data of Reference 12, in which P(HNA–HBA) was used

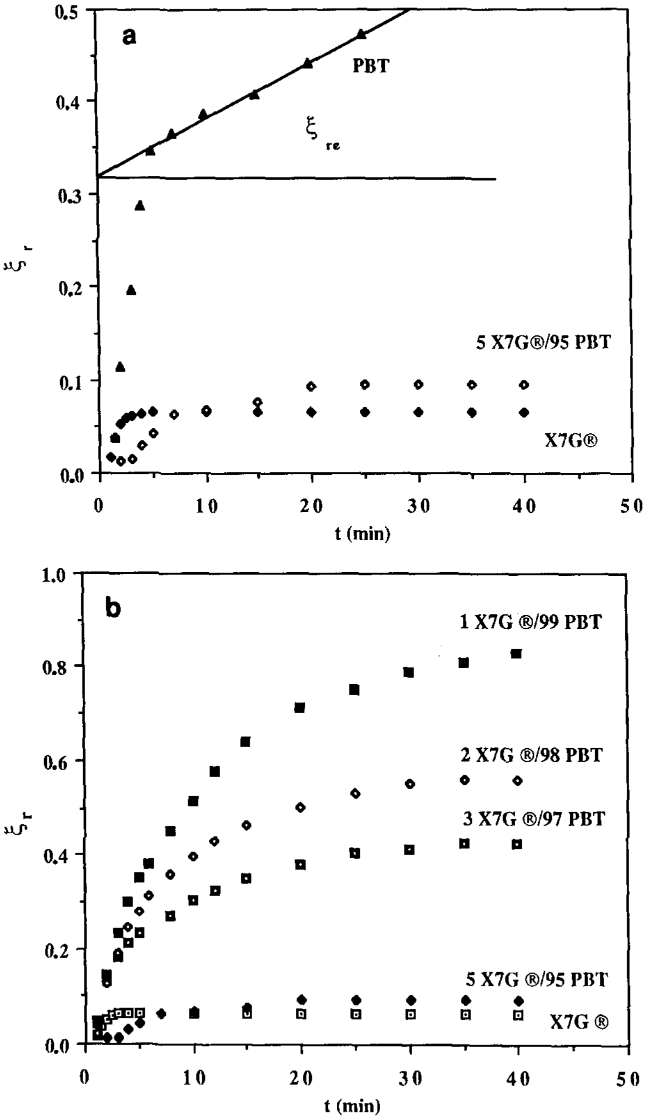

**Figure 9** Shrinkage of various blends as a function of time ($T = 235$°C). $\zeta_{re}$ is obtained from the extrapolation of the linear part to $t = 0$

Our results are not in agreement with the general trend observed in literature. In fact, for blends based on chlorinated PVC[10], polycarbonate[3,5], polystyrene[5] and PET[5], the addition of even a very small quantity of P(HBA–ETP) lowers the viscosity of the blend considerably. The same behaviour has been observed for blends of polyamides with P(HNA–HBA) liquid crystal copolyesters[12]. *Table 2* gives compilation of literature data concerning the effect of liquid crystal copolyesters (LCC); in some cases a reduction of the viscosity to one tenth of the value of the original polymer can be observed. The effect of shear rate in this reduction is remarkable in the data of Reference 6. Changes in morphology have been proposed[3] to explain this influence: elongational flows (more remarkable at high shear rates) at the entrance of the capillary deform dispersed particles into fibrils which can be aligned in the flow direction, acting in fact as lubricants. This phenomenon is not exclusive to blends based on polymer liquid crystals, being rather common to dispersed systems. The clearest case of the influence of fibrillar morphology in viscosity results (a very deep minimum in viscosity at high shear rates but a maximum at low shear rates) has been presented by Ablazova *et al.*[37] for molten mixtures of polyoxymethylene and a copolyamide.

On the other hand, it is worth pointing out that compatibility between original polymers does not seem to affect the rheological behaviour. Blends of PET/ P(HBA–ETP), PC/P(HBA–ETP) and PBT/ P(HBA–ETP) are compatible (at least in the flexible low $T_g$ phase of copolymer[38]), whereas blends with PS, chlorinated PVC and polyamide are incompatible. This difference is not reflected in the results of *Table 2.*

### *Shrinkage behaviour*

The shrinkage of extruded filaments has been presented in terms of the Hencky measure of strain:

$$\xi_r = \ln[L_0/L(t)] \qquad (1)$$

where $L_0$ is the original length of the filament and $L(t)$ is the length at time $t$. *Figure 9* shows the measured strain recovery, $\xi_r$, for PBT and some blends with small X7G content.

The most striking result is the tremendous effect of the presence of only 5% X7G on PBT shrinkage behaviour. There is a major difference between the PBT curve and X7G and 95PBT/5X7G blend curves: whereas for the liquid crystal copolyester and the blend the values of $\xi_r$ level off, for PBT $\xi_r$ continues to increase with time. In fact, shrinkage values of PBT at times >25 min are very difficult to determine because the sample loses its shape and finally breaks.

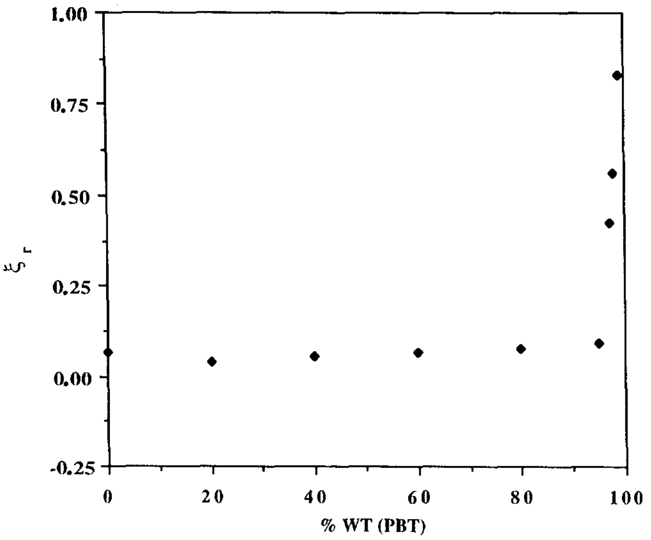

**Figure 10** Shrinkage (at long times) against composition at $T = 235°C$

After Laun and Munstedt[39], two effects must be considered in the retraction of a filament introduced into an oil bath at high temperature: the relaxation of internal orientation (due, for instance, to elongational flow in the entrance of the capillary) frozen during filament preparation, called 'elastic strain recovery', $\xi_r$; and the influence of the interfacial tension, $\sigma_\alpha$, between the sample and the surrounding silicon oil, which gives rise to a $\xi_\alpha$ strain. The experimentally determined shrinkage $\xi_r$ (equation (1)) is, therefore, the sum of the two effects:

$$\xi_r = \xi_{re} + \xi_\alpha \qquad (2)$$

Since it is assumed that the elastic response takes place rapidly, the linear part of *Figure 9* must correspond to the interfacial tension, $\sigma_\alpha$, and consequently, $\xi_\alpha = \dot{\xi}_\alpha t$, where $\dot{\xi}_\alpha$ is the strain rate.

The true elastic response, $\xi_{re}$ of the sample to orientation produced during its preparation is, therefore, determined by subtracting the linear part from the experimentally obtained $\xi_r$. This is shown in *Figure 9a* for the PBT sample. However, for blends of even very low X7G content (*Figure 9b*) there is no effect of interfacial tension (levelling off means $\xi_\alpha = 0$) and all the measured recovery corresponds to elastic strain recovery.

The value of strain rate due to interfacial tension, $\dot{\xi}_\alpha$, estimated from *Figure 9a*, is $\dot{\xi}_\alpha = 10^{-4}\,s^{-1}$ for PBT. According to Laun and Munstedt[39] the elongational viscosity can be evaluated from equation

$$\eta_E = \sigma_\alpha / \dot{\xi}_\alpha R \qquad (3)$$

where $\sigma_\alpha$ is the interfacial tension between filament and silicone oil and $R$ the radius of the sample at the beginning of the linear behaviour of shrinkage. For PBT in silicone oil, after Wu[40], we have evaluated[41] $\sigma_\alpha = 0.82$ Pa, which gives for $R = 0.035$ cm an elongational viscosity $\eta_E = 1.94 \times 10^5$ Pa s.

Expressing equation (3) in the form $\dot{\xi}_\alpha = \sigma_\alpha/\eta_E R$, one can deduce that the particular shrinkage behaviour observed for blends is due either to the high elongational viscosity or to the low interfacial tension $\sigma_\alpha$ of the blends. However, as the parameters used in determining $\sigma_\alpha$ (see Reference 40) are not likely to be affected by such a small presence of the second component of the blend, we consider the possibility of elongational viscosity as the variable affecting shrinkage.

The very much higher elongational viscosity of the blends with respect to PBT, which would explain the shrinkage results, may be due to the formation of piled polydomains[42] (as a consequence of the presence of the liquid crystalline component). These polydomains make the flow difficult, at low shear rates, as is the case in shrinkage experiments. At high shear rates, however, a monodomain continuous phase structure is attained and the viscosity is considerably lowered.

The excellent dimensional stability of the blends, including those with a small proportion of P(HBA–ETP) (X7G), is reflected in *Figure 10*. Shrinkage measurements on blends of liquid crystalline polymers have been made by Nicolais *et al.*[6,20], observing that for compatible (PS/TBBA) (see *Table 1* for meaning of symbols) and partially compatible blends (PC/P(HBA–ETP)) no improvement in dimensional stability was achieved. However, adding a low percentage of non-compatible liquid crystalline polymer to PS gave rise to a significant improvement in the dimensional stability.

In our case, improvement of stability is observed in a partially compatible blend, as discussed in the next section.

### *DMTA and d.s.c. results*

*Figure 11* shows loss tangent, tan $\delta$, relaxation spectra obtained at a frequency of 1 Hz of PBT, P(HBA–ETP) (X7G) and 90PBT/10X7G and 80PBT/20X7G blends. The heterogeneous morphology of P(HBA–ETP) copolyester is manifested by the existence of various relaxations, which reflect segmental motion in PET-rich and PHBA-rich phases. Considering literature results on dynamical viscoelasticity[43], we interpret our peaks at 62.5 and 79.5°C as corresponding, respectively, to PET segments found in the PET-rich phase which have interactions with PHBA units and to the glass transition process of PET components.

On the other hand, the spectrum of PBT reveals a glass transition at 50°C, with a low value of the tan $\delta$ maximum ($(\tan\delta)_M = 0.12$), characteristic of semi-crystalline polymers. The 20% P(HBA–ETP) content in the PBT based blends produces two changes; the maximum in tan $\delta$ is shifted to 60.5°C and the value of this maximum

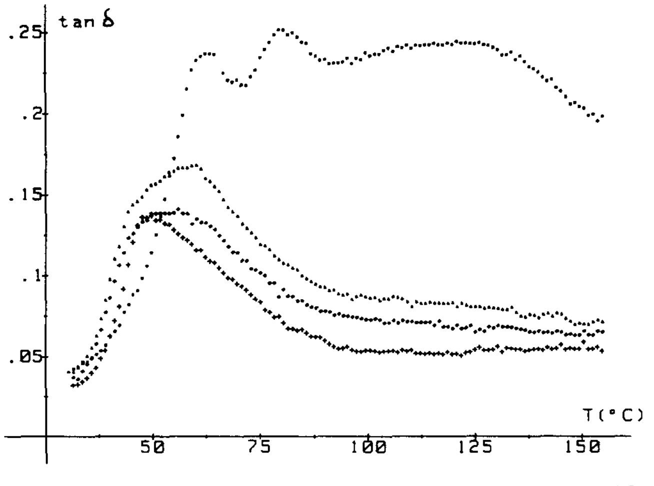

**Figure 11** Loss tangent relaxation spectra. From top to bottom: X7G; 80 PBT/20 X7G; 90PBT/10 X7G; PBT

**Table 3** Transitions and relaxations observed by d.s.c. for P(HBA–ETP) copolyesters

| Reference | $T_{g1}$ (°C) | $T_{g2}$ (°C) | $T_{m1}$ (°C) | $T_{m2}$ (°C) | Remarks |
|---|---|---|---|---|---|
| 24 | – | – | – | 235 | Depends on thermal history |
| 36 | 75 | 190 | – | 236–260 | $T_{m2}$ depends on extrusion temperature |
| 44 | 61 (59) | 149 (161) | – | 257 (255) | Values in parentheses correspond to quenched samples $\Delta H_f = 0.33$ (0.21) J $g^{-1}$ |
| 45 | 80 (86) | – | 194 (191) | – | Values in parentheses correspond to quenched samples |
| 46 | 80 | – | 188 (189) | – | Samples moulded at 235°C (moulded at 260°C) |
| 47 | – | – | – | 248 | Annealing above 235°C increases melting temperature |
| 2 | 53 | 187 | – | – | The higher $T_g$ refers to PHBA-rich phase |
| 6 | 72 | 172 | – | 245 | Peak at 245°C is associated with melting of small crystallites |
| 5 | 64 | – | 195 | – | $\Delta H_f = 1.65$ J $g^{-1}$ |
| 48 | 72 | 171.9 | – | 244.8 | An endotherm at 453.8°C is associated with isotropization |
| 49 | 63 | – | 196 | 245 | $T_{m2}$ is eliminated in second heating |
| 7 | 76 | – | 188 | – | Initial heating experiments with extruded samples |
| This work | 55 | 170 | – | 244 | $T_{m2}$ is eliminated in second heating |

increases to $(\tan \delta)_M = 0.16$. For 90PBT/10X7G blends the glass transition presents an intermediate value, as there is a maximum at 56.5°C.

The existence of a unique glass transition for blends seems to confirm the compatibility between PBT and the PET rich phase of P(HBA–ETP) copolyester, pointed out by Kimura and Porter[2]. In preliminary investigations of the blends of P(HBA–ETP) with PET and PBT no specific interactions between the components has been shown: the absence of transesterification was confirmed in Reference 2 by nuclear magnetic resonance (n.m.r.) measurements on the blends made before and after moulding. However, recently[11] reactions in the melt have been considered as the cause of the apparent miscibility of poly(hexamethylene terephthalate) with P(HBA–ETP).

Several authors have focused their attention on transitions and relaxations in this particular liquid crystalline copolyester. In *Table 3* we present some differential scanning calorimetry (d.s.c.) results from the literature, as well as our own data. The variation in the data obtained by different authors may well be explained by differences of thermal treatment to differences in the sequence distribution (ordering or randomization) of the comonomer units in the polyesters. The existence of a glass transition temperature $T_{g1}$, associated with PET-rich phase, is remarked on by most authors. However, transitions at intermediate temperatures (in the range 149–196°C), defined as $T_{g2}$ or $T_{m1}$, are the subject of controversy: e.g. some authors[2,48] associate this transition with the glass transition of PHBA-rich phase, whereas others[5,7,36,44,45,47] report a melting endotherm at approximately the same temperature. Concerning the high endotherm, referred to in *Table 3* as $T_{m2}$, the authors agree that this corresponds to the melting of PHBA crystallites. It is interesting to note the papers of Cuculo and Chen[36] and Muramatsu and Krigbaum[47], remarking on the influence of extrusion temperature on $T_{m2}$ peaks: with increasing extrusion (heating) temperature, $T_{m2}$ moves to higher temperatures and endothermic peaks become smaller and less obvious (see Figure 16 of Reference 36). These results confirm the X-ray measurement data reported by Wissbrun[24]: at room temperature the fibres spun at 230°C contained crystalline X-ray reflections, whereas no such reflections were observed in fibres spun at 280°C.

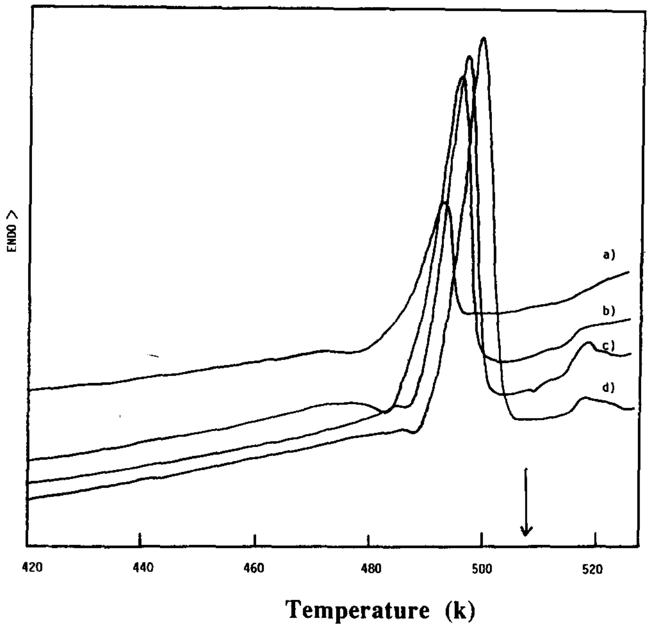

**Figure 12** D.s.c. thermograms for various blends: (a) 80X7G/20PBT; (b) 40X7G/60PBT; (c) 20X7G/80PBT; (d) 10X7G/90PBT. The arrow indicates the temperature at which shrinkage measurements are carried out

The endothermic peak observed in our case (reported in *Table 3*) is in fact very small and it becomes difficult to measure such a low enthalpy of fusion. This is perhaps due to the fact that our d.s.c. measurements are made on extrudates obtained at a relatively high temperature ($T = 250$°C). But the most remarkable aspect of our d.s.c. results concerns measurements made on blends. These are presented in *Figure 12*. For all the blends the melting of PBT is clearly observed, giving a melting temperature and enthalpy of 225°C and 40 J $g^{-1}$ respectively. On the other hand, an endothermic peak with a maximum at

244°C is observed for blends of low X7G content, whereas for 80X7G/20PBT composition the peak is not so obvious. The endotherm is very clear for 10 and 20% X7G content and an enthalpy of 13.5 J g$^{-1}$ (grams of X7G as discussed in the next paragraph) is estimated. We note that this second endotherm of *Figure 12* is eliminated on second heating.

Taking into account the previously reported data and discussion, we think that the endothermic peak at 244°C corresponds to the melting of crystallites of X7G. This assertion seems to contradict the fact that the more X7G we have in the blend, the smaller the endotherm. In fact, the endothermic peaks observed in the literature for pure P(HBA–ETP) (X7G) samples are very much smaller than those of *Figure 12* (except for the 80X7G/20PBT blend).

However, as it is clear that the second endotherms observed in *Figure 12* do not correspond to PBT, the only possibility we see is to confirm the assertion that assigns the endothermic peak at 244°C to the melting of P(HBA–ETP) (X7G). Further studies involving other techniques will be necessary. We currently think that PBT, as the most abundant component of the blend, leads to the formation of more perfect crystals of PHBA. The case could be similar to that of polymers which crystallize due to the incorporation of solvent, e.g. atactic PS crystallizes due to carbon disulphide[50].

D.s.c. results, in particular thermograms presented in *Figure 12*, can help to explain the shrinkage behaviour of the blends. In fact, shrinkage measurements are made at 235°C, i.e. above the melting temperature of PBT, but below the melting temperature of crystallites of X7G. Accepting the hypothesis that crystallites lock the molecular network in the extended conformation, avoiding shrinkage[51,52], then the results presented in *Figures 9* and *10* (where practically no shrinkage is observed for blends of very low content of X7G) can be related to the presence of the second endothermic peak in *Figure 12*. We have not carried out shrinkage measurements at temperatures higher than 244°C (melting temperature of X7G crystallites), which would have given shrinkage values similar to those of PBT, but the results presented by Nobile *et al.* (Figure 21 of Reference 6) demonstrate the anchoring effect of crystallites in P(HBA–ETP) copolyester: no shrinkage is observed between 150 and 245°C but above this temperature shrinkage can be evaluated.

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## REFERENCES

1 Jackson, W. J. and Kuhfuss, H. F. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 2043

2 Kimura, M. and Porter, R. S. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 1697

3 Blizard, K. G. and Baird, D. G. *Polym. Eng. Sci.* 1987, **27**, 653

4 Friedrich, K., Hess, M. and Kosfeld, R. *Makromol. Chem. Macromol. Symp.* 1988, **16**, 251

5 Zhuang, P., Kyu, T. and White, J. L. *Polym. Eng. Sci.* 1988, **28**, 1095

6 Nobile, M. R., Amendola, E., Nicolais, L., Acierno, D. and Carfagna, C. *Polym. Eng. Sci.* 1989, **29**, 244

7 Joseph, E. G., Wilkes, G. L. and Baird, D. G. in 'Polymeric Liquid Crystals' (Ed. A. Blumstein), Plenum Press, 1985

8 Ameno, M. and Nakagawa, K. *Polymer* 1987, **28**, 263

9 Nakai, A., Shiwaku, T., Hasegawa, H. and Hashimoto, T. *Macromolecules* 1986, **19**, 3010

10 Lee, B. L. *Polym. Eng. Sci.* 1988, **28**, 1107

11 Laivins, G. V. *Macromolecules* 1989, **22**, 3974

12 Siegmann, A., Dagan, A. and Kenig, S. *Polymer* 1985, **26**, 1325

13 Isayev, A. I. and Modic, M. *Polym. Comp.* 1987, **8**, 158

14 Malik, T. Q., Carreau, P. J. and Chapleau, N. *Polym. Eng. Sci.* 1989, **29**, 600

15 Beery, D., Siegmann, A. and Kenig, S. *J. Mater. Sci. Lett.* 1988, **7**, 1071

16 Kohli, A., Chung, N. and Weiss, R. A. *Polym. Eng. Sci.* 1989, **29**, 573

17 Ko, C. U. and Wilkes, G. L. *J. Appl. Polym. Sci.* 1989, **37**, 3063

18 Kiss, G. *Polym. Eng. Sci.* 1987, **27**, 410

19 La Mantia, F. P., Valenza, A., Paci, M. and Magagnini, P. L. *J. Appl. Polym. Sci.* 1989, **38**, 583

20 Apicella, A., Iannelli, P., Nicodemo, L., Nicolais, L., Roviello, A. and Sirigu, A. *Polym. Eng. Sci.* 1986, **26**, 600

21 Kajyama, T., Washizu, S. and Takayanagi, M. *J. Appl. Polym. Sci.* 1984, **29**, 3955

22 Paci, M., Liu, M., Magagnini, P. L., La Mantia, F. P. and Valenza, A. *Termochim. Acta* 1988, **137**, 105

23 Arruabarrena, L., Muñoz, M. E., Peña, J. J. and Santamaria, A. *Polym. Comm.* 1986, **27**, 92

24 Wissbrun, K. F. *Br. Polym. J.* December 1980, 163

25 Jerman, R. E. and Baird, D. G. *J. Rheol.* 1981, **25**, 272

26 Suto, S. *J. Appl. Polym. Sci.* 1987, **34**, 1773

27 Papkov, S. P., Kulichikhin, V. G., Kalmykova, V. D. and Ya Malkin, A. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 1753

28 Aoki, H., Coffin, D. R., Hancock, T. A., Harwood, D., Lenk, R. S., Fellers, J. D. and White, J. L. *J. Polym. Sci., Polym. Symp.* 1978, **65**, 29

29 Gonzalez, J. M. Muñoz, M. E., Cortazar, M., Peña, J. J. and Santamaría, A. *J. Polym. Sci., Polym. Phys. Edn.* 1990, **28**, 1533

30 Done, D. and Baird, D. G. *Polym. Eng. Sci.* 1987, **27**, 816

31 Marruci, G. 'Proc. IX Int. Congress on Rheology', Vol. 1, 1984, p. 441

32 Wissbrun, K. F. *Faraday Discuss. Chem. Soc.* 1985, **79**, 161

33 Casson, N. 'Rheology of Disperse Systems' (Ed. C. C. Mill), Pergamon, London, 1959, p. 84

34 Wissbrun, K. F. *J. Rheol.* 1981, **25**, 619

35 Wissbrun, K. F. and Griffin, A. C. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 1835

36 Cuculo, J. A. and Chen, G. Y. *J. Polym. Sci. B, Polym. Phys.* 1988, **26**, 179

37 Ablazova, T. I., Tsebrenko, M. B., Yudin, A. B. V., Vinogradov, G. V. and Yarlykov, B. V. *J. Appl. Polym. Sci.* 1975, **19**, 1718

38 Porter, R. S., Jonza, J. M., Kimura, M., Desper, C. R. and George, E. R. *Polym. Eng. Sci.* 1989, **29**, 55

39 Laun, H. M. and Munstedt, H. *Rheol. Acta* 1975, **17**, 415

40 Wu, S. in 'Polymer Blends' (Eds D. R. Paul and S. Newman), Academic Press, New York, 1978

41 Zaldua, A. Tesina de Licenciatura degree, University of Pais Vasco/Euskal Herriko University, San Sebastian

42 Onogi, S. and Asada, T. 'Proc. 8th Int. Congress on Rheology', Vol. 1, 1980, p. 127

43 Benson, R. S. and Lewis, D. N. *Polym. Commun.* 1987, **28**, 289

44 Gedde, U. W., Buerger, D. and Boyd, R. H. *Macromolecules* 1987, **20**, 988

45 Meesiri, W., Menczel, J., Gaur, U. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 719

46 Joseph, E., Wilkes, G. L. and Baird, D. G. *Polymer* 1985, **6**, 689

47 Muramatsu, H. and Krigbaum, W. R. *J. Polym. Sci. B, Polym. Phys.* 1987, **25**, 2303

48 Amendola, E., Carfagna, C., Nicodemo, C. and Nobile, M. R. *Makromol. Chem. Macromol. Symp.* 1989, **23**, 253

49 Shih, H. H., Hornberger, L. E., Siemens, R. L. and Zachariades, A. E. *J. Appl. Polym. Sci.* 1986, **32**, 4897

50 Francois, J., Gan, J. Y. S. and Guenet, J. M. *Macromolecules* 1986, **19**, 2755

51 Keskkula, H. and Schmitt, J. A. *J. Appl. Polym. Sci.* 1965, **9**, 2681

52 Tunnicliffe, J., Blundell, D. J. and Windle, A. H. *Polymer* 1980, **21**, 1259