

Hot Drawing of Partially Miscible Blends of Polycarbonate and Poly(butylene terephthalate)

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SYNOPSIS

Samples of PC-PBT blends over the entire composition range were drawn at 160°C to high extensions, 2.1–5.8, to study the mechanical reinforcement and the molecular structure development upon deformation. Elastic modulus E' increases with extension ratio for all compositions and temperatures. Blends with 25 and 40 wt % of PC show higher E' at low temperature than pure PBT blends do. Crystallinity increases with extension ratio and is relatively smaller with increasing PC content. The influence of the reversible α to β crystal form transformation was also studied. The second moment of the orientation function f for both crystal forms increases to high values > 0.9 at relatively low extensions. f decreases with PC content for α crystals but decreases for β crystals. The α fraction is high for PBT and decreases with PC content and extension ratio in the blends. Strain recovery experiments show that the α to β transformation is also elastic in nature at high extension ratios and that the reinforcing effect in high PBT content blends is not due to the α/β ratio.

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INTRODUCTION

Deformation and blending have long been an integral part of the tools to improve physical properties of polymers. Through deformation, higher orientation and crystallinity can be obtained, which enhance mechanical strength and shape retention under thermal and mechanical stress. Blending allows for the beneficial properties of two polymers to be combined in one material while shielding their mutual drawbacks. Deviations in the rule of mixing can lead to properties of the blend over and above those of its components. In this study, the influence of deformation of the blend of polycarbonate of Bisphenol A (PC) and poly(butylene terephthalate) (PBT) on mechanical properties and crystallinity is examined.

PC-PBT blends have been studied widely as an example of a partially miscible system of an amorphous polymer, PC, with a semicrystalline one, PBT. Recently a phase diagram with an upper critical solution temperature was proposed with less than 10% of each polymer dissolved in the other upon phase

separation.¹ Morphology ranges from a continuous PC phase, with PBT inclusions in high PC content blends, to a continuous PBT phase structure with PC inclusions at high PBT content. A bicontinuous structure is found at blend compositions with 50–60 wt % PC.²

The semicrystalline component in the blend studied here, PBT, exhibits a reversible crystal transformation between α and β forms between 4 and 12% strain in the elastic deformation region of the stress–strain diagram. Tensile and recovery measurements,^{3–5} wide-angle X-ray diffraction (WAXD),^{6–8} and IR spectroscopy^{4,5,7,9–11} have been widely used to study this transformation. The β form is the stressed form and is characterized by a more extended butylene segment. The fraction of β crystals remaining after deformation beyond the yield point depends largely on draw temperature and ratio.¹² Annealing at elevated temperatures transforms β form crystals back into α form crystals. Mechanical properties of semicrystalline polymers are generally related to crystallinity. As high crystallinity in commercial processing is achieved by hot drawing, this study focuses on the development of mechanical properties in hot-drawn samples. Structure development and ori-

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entation function for pure PBT has been studied at high strain, and a wide range of temperatures has been studied in this lab before.¹³ The aim here is to extend this knowledge to blends of PBT with PC. Mechanical properties are measured by dynamic mechanical thermal analysis. Crystallinity is studied by differential scanning calorimetry (DSC) and crystal structure development by WAXD techniques.

EXPERIMENTAL

Sample Preparation

The PC in this study is Teijin Panlite. The PBT used is a Duranex 2002 obtained from Polyplastics Co., Ltd. Blend sheets with PC-PBT compositions of 25–75, 40–60, 50–50, 60–40, and 75–25 wt %, and PC and PBT sheets were extruded using a twin-screw extruder with a coat-hanger die. The die temperature was 255°C for all samples. To prevent transesterification, 0.5 wt % of Irganox (generously supplied by Ciba Geigy) was added to the blends. The sheets were allowed to cool in air and take-up speed was 3 m/min. This resulted in films with thicknesses ranging from 90 μm at high PC contents to 300 μm at high PBT contents. Dumbbell shaped samples were cut from the films and uniaxially drawn at elevated temperatures in a UTM-III-10T tensile testing machine from Orientec Co. Ltd. Extension rate was 20 mm/min, which corresponded to an extension ratio of approximately 0.5/min.

Characterization

WAXD diffractograms were obtained using Ni-filtered Cu-K α radiation (40 kV, 40 mA) from a Geigerflex XGC-20 (Rigaku Denki Co., Ltd.). Intensity profiles were measured by a scintillation counter and pulse height analyzer. Azimuthal intensity distributions of meridional reflections were used to determine the second moment of the crystal orientation function.

Melting temperature and glass transition temperature were obtained from DSC traces measured from -10 to 250°C at a heating rate of $20^\circ\text{C}/\text{min}$ with a Perkin Elmer DSC-7. Temperature and heat of fusion calibration was performed with Indium as a standard. Percent crystallinity of PBT was calculated from the heat of fusion using the value of 140 J/g for perfect crystals.¹⁴

Elastic modulus E' was used as a measure of mechanical properties. Dynamic mechanical thermal

analysis experiments were done using a Rheovibron Mark II from Orientec Co. Ltd. at frequencies of 3.5, 11, 35, and 110 Hz at a heating rate of $2^\circ\text{C}/\text{min}$ between -150 and 220°C . Results reported are from 3.5 Hz experiments.

RESULTS AND DISCUSSION

Dynamic Mechanical Measurements

Figure 1 shows the extension to failure of blend samples with 25, 50, 75, and 100 wt % PC at temperatures from 130 to 160°C . Extension to break decreases significantly when the deformation temperature is below 150°C . As it was our aim to study the influence of high deformation on mechanical and molecular properties, 160°C was chosen as the deformation temperature unless otherwise indicated. It was observed that the DSC trace, around the T_g of PC, for samples drawn to failure exhibited a stress recovery peak slightly above the T_g of PC. This phenomenon interferes with accurate determination of T_g . For samples not drawn to break but instead cooled while clamped, this recovery peak was not observed. Therefore, a series of samples of all compositions were deformed to extension ratios $\rho = \lambda/\lambda_0$ between 2.1 and 5.8 at 160°C and held clamped while cooling to $< 40^\circ\text{C}$ by opening the oven door. λ_0 is the initial length of the sample while λ is the deformed length. Minimum extension ratios after yielding were 2.10, 2.35, 2.70, 2.90, 3.20, and 3.40 for

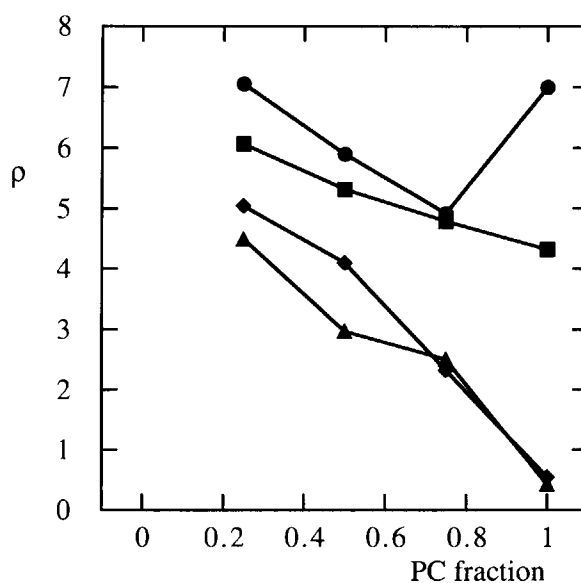


Figure 1 Extension to failure versus composition as a function of drawing temperature. (●) 160°C ; (■) 150°C ; (◆) 140°C ; (▲) 130°C .

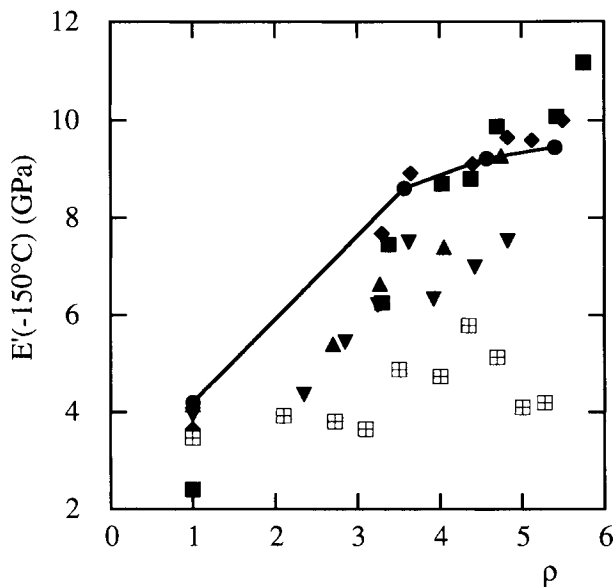


Figure 2 E' (3.5 Hz, GPa) at -150°C versus extension ratio ρ for different blend compositions. (●) PC-PBT 0-100; (■) PC-PBT 25-75; (◆) PC-PBT 40-60; (▲) PC-PBT 50-50; (▼) PC-PBT 60-40; (⊞) PC-PBT 75-25.

25, 40, 50, 60, 75, and 100% PBT samples respectively.

Figures 2-5 show the elastic modulus E' as measured by DMTA for temperatures of -150 , 20 , 110 , and 200°C , respectively. The $E'(-150^{\circ})$ is a measure of the average orientation of crystalline and amor-

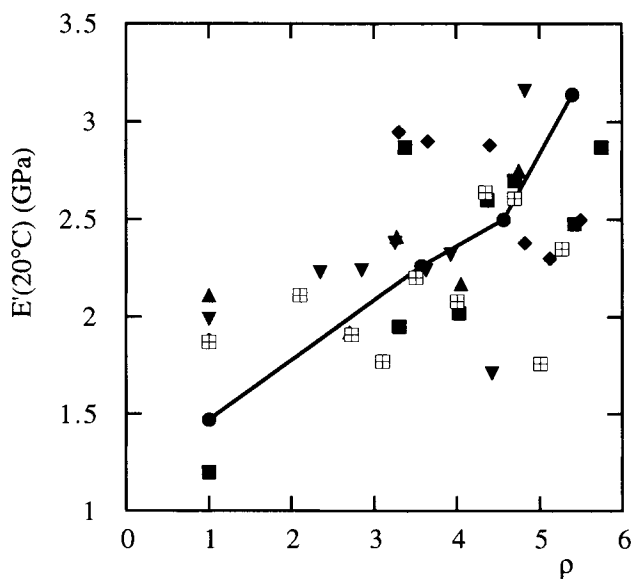


Figure 3 E' (3.5 Hz, GPa) at 20°C versus extension ratio ρ for different blend compositions. Symbols are the same as those in Figure 2.

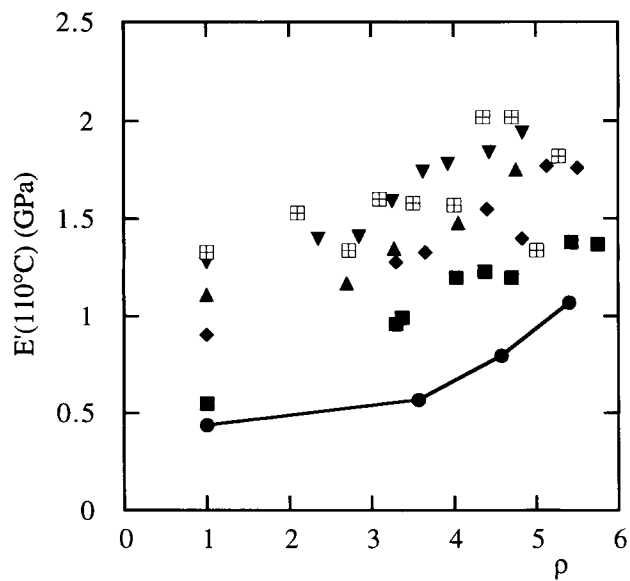


Figure 4 E' (3.5 Hz, GPa) at 110°C versus extension ratio ρ for different blend compositions. Symbols are the same as those in Figure 2.

phous parts of the material since -150°C is well below the β transition of both PC and PBT. A clear and significant increase is observed for all compositions, except PC-PBT 75-25, where the increase is marginal. For E' at 20°C an increase is again observed for all blend compositions, but the behavior is far less systematic. This temperature is above the β relaxation of PBT and PC but below the glass

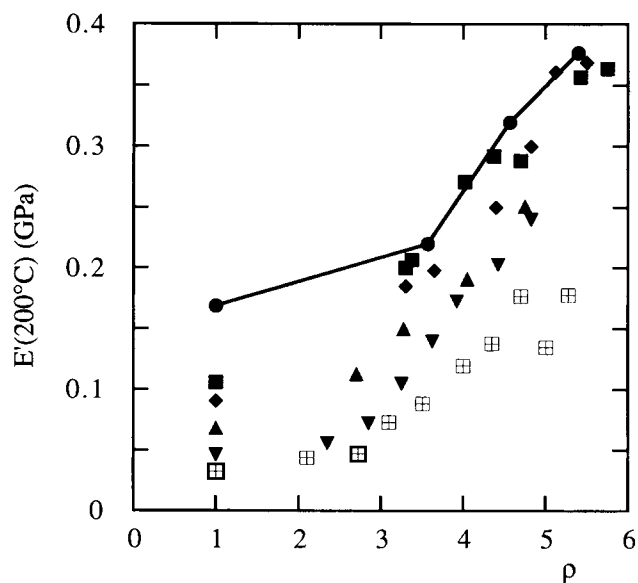


Figure 5 E' (3.5 Hz, GPa) at 200°C versus extension ratio ρ for different blend compositions. Symbols are the same as those in Figure 2.

transition temperatures of both PBT and PC. At 110°C, E' changes upon extension are more systematic with composition and ρ . Since this measurement is taken above the T_g of PBT and below the T_g of PC, it is not surprising to see that the samples with high PC content show higher E' values, but it needs to be noted that increases with ρ are modest. A strong systematic dependence of E' on ρ and composition is again observed at 200°C, above the T_g of both PC and PBT. To quantify the behavior of E' , as a function of ρ and composition, changes in E' with the change in ρ , $\Delta E'/\Delta\rho$, were calculated from the slope using a linear least square fits for -150, 110, and 200°C. $\Delta E'/\Delta\rho$ values are given in Table I with their respective correlation coefficients in brackets.

$\Delta E'/\Delta\rho$ is found to be higher than for the pure PBT samples in the samples with 40 (except at -150°C), 50, 60 and 75% PBT blends at all temperatures. The relatively small increases found in E' (110) indicate that the PC phase may be slightly oriented, but without significant influence on the mechanical properties. Together with the observation that $\Delta E'/\Delta\rho$ is significantly smaller for 25% PBT blends over the entire temperature range, this indicates that deformation or orientation of PC phase is not the reason for the larger increase of E' (-150) relative to pure PBT, but that blending with PC influences the properties of deformed PBT significantly. The reinforcing effect of PC on deformed PBT-PC blends is most prevalent in the 25 and 40% PC blends.

DSC Measurements

Figure 6 shows crystallinity versus extension ratio relative to the weight fraction of PBT for all samples. A clear, systematic increase in crystallinity is seen for all compositions. The relationship between the increase in crystallinity and ρ is practically linear. The crystallinity is lower at the same extension ratio

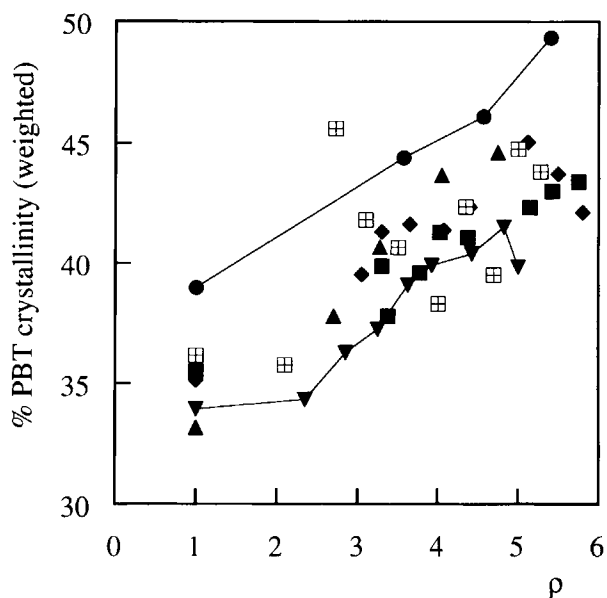


Figure 6 Wt % PBT crystallinity versus extension ratio ρ for different blend compositions. Weighted to PBT weight fraction in the blend. Symbols are the same as those in Figure 2.

for samples with higher PBT content. Figure 7 shows the melting peak for all compositions and ρ . The melting temperature at a certain ρ is lower for blends with higher PC content. This indicates smaller crystal sizes when the PC content is higher. The width of the melting peak decreases with extension, which indicates improving crystal perfection.

For each particular composition, a decrease in melting temperature is observed between the undeformed sample and the sample with the lowest extension ratio. With increasing ρ , the melting temperature increases. This phenomenon may originate from the reorientation of the spherulites during the yielding process, which lowers T_m , followed by stress-induced crystallization, which raises T_m . Another peculiar feature is seen in the thermograms of the series of 40 and 25% PBT samples. At no and low

Table I Increase of E' with Deformation, $\Delta E'/\Delta\rho$, as a Function of Blend Composition

PC-PBT Composition	$\Delta E'/\Delta\rho$ (-150°C)	$\Delta E'/\Delta\rho$ (110°C)	$\Delta E'/\Delta\rho$ (200°C)
0-100	1.25 (0.97) ^a	0.13 (0.91)	0.046 (0.93)
25-75	1.82 (0.98)	0.18 (0.98)	0.056 (0.98)
40-60	1.40 (0.97)	0.18 (0.94)	0.063 (0.96)
50-50	1.31 (0.97)	0.16 (0.92)	0.047 (0.97)
60-40	1.01 (0.91)	0.18 (0.96)	0.054 (0.93)
75-25	0.30 (0.56)	0.10 (0.56)	0.037 (0.94)

^a Value in parentheses is the correlation coefficient of the linear least square fit.

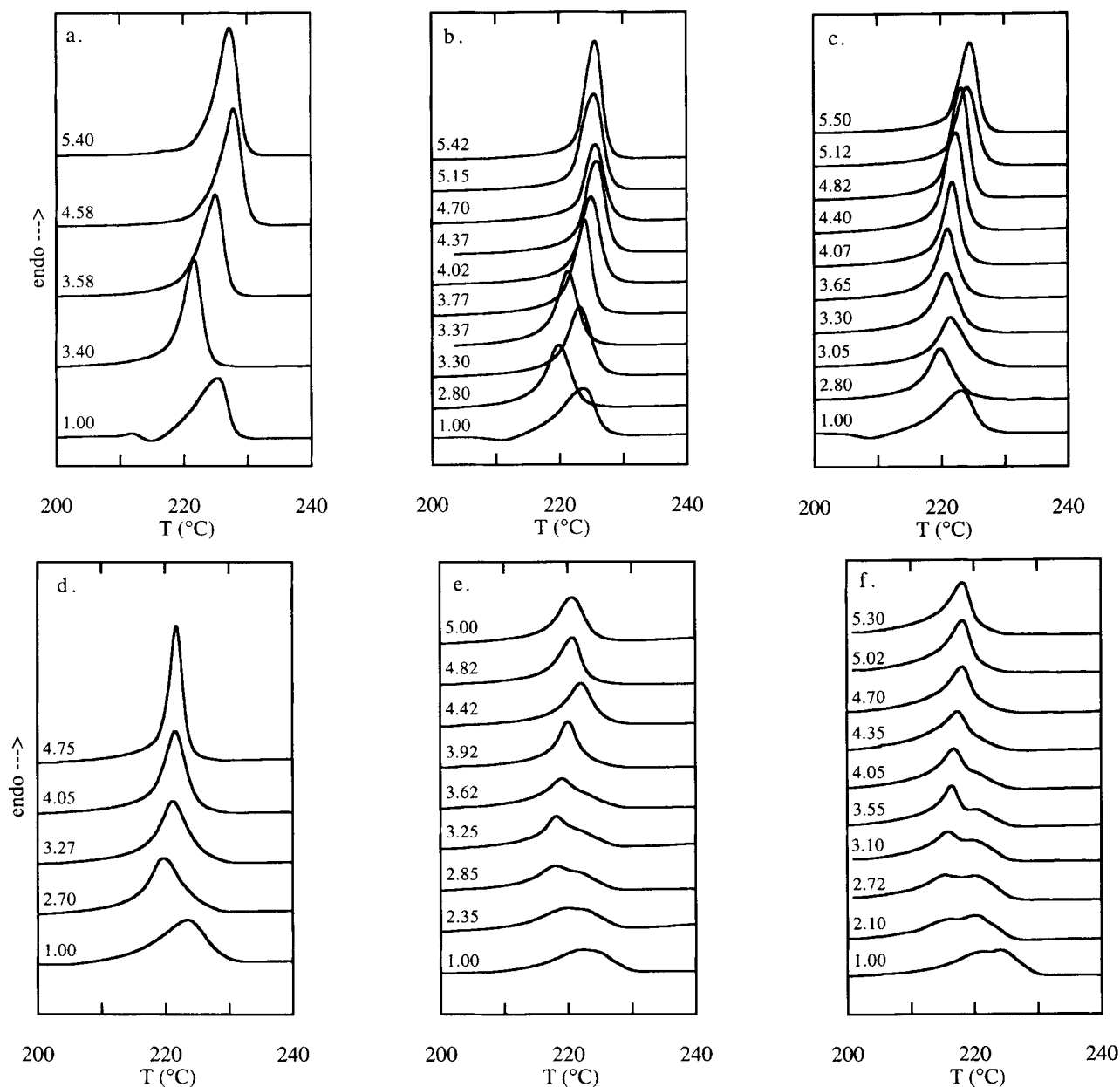


Figure 7 DSC traces between 200 and 240°C at heating rate 20°C/min for deformed and undeformed PBT and blends over the complete composition range. (a) PC-PBT 0-100; (b) PC-PBT 25-75; (c) PC-PBT 40-60; (d) PC-PBT 50-50; (e) PC-PBT 60-40; (f) PC-PBT 75-25. Extension ratio ρ for each trace indicated.

extensions, two overlapping melting peaks can be seen. Upon extension, the higher temperature peak disappears while the lower temperature peak becomes larger until it is eventually the only peak observed. The phenomenon is more prevalent in the 25% PBT sample series. Multiple melting peaks have been observed in PBT before.¹⁵ Elaborate studies have shown that, upon heating, smaller PBT crystallites start melting at fairly low temperatures,

followed immediately by their recrystallization into bigger ones. At lower temperatures, a peak is observed when the rate of melting of the small crystals exceeds the rate of recrystallization. A second peak is subsequently observed for the recrystallized crystals at higher temperature. The temperature difference between the two peaks is usually of the order of 0–15°C, depending on thermal history and heating rate in the experiment. Only one peak may be ob-

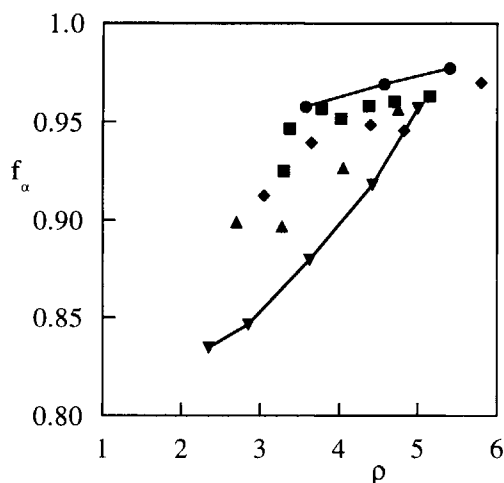


Figure 8 Second moment of the orientation function f_α of the α form crystals versus extension ratio ρ for different blend compositions. Symbols are the same as those in Figure 2.

served even though recrystallization is taking place. Observation of two melting peaks here indicates that recrystallization also occurs in these deformed blends.

The recrystallization phenomenon only becomes visible for the series with low PC content. It is possible that the phenomenon observed for these compositions stems from impeded recrystallization due to the smaller size of the crystallites and the higher orientation. Part of the small crystallites can recrystallize into relatively big crystallites, while others are impeded by orientation and cannot recrystallize. As deformation results in more orientation, and crystallites are smaller at higher PC contents, the results of recrystallization can only be observed in the low PBT content/low deformation blends.

WAXD Experiments

The second moment of the orientation function f was determined by evaluating the azimuthal intensity distribution for both the α and β crystal form of PBT by using the $2\theta = 39.8$ reflection of the $\bar{1}05$ plane of the α form, and the $2\theta = 42.9$ reflection of the $\bar{1}06$ plane of the β form. The second moment was calculated from the intensity profile, $I(\phi')$ while taking into account the correction by Gupta and Kumar for off-meridional reflections.¹⁶

$$\langle \cos^2 \phi' \rangle = \frac{\int_0^\pi I(\phi') \cos^2 \phi' \sin \phi' d\phi'}{\int_0^\pi I(\phi') \sin \phi' d\phi'} \quad (1)$$

$$\langle \cos^2 \phi \rangle = \frac{\langle \cos^2 \phi' \rangle}{\cos^2 \gamma} \quad (2)$$

$$f = \frac{3\langle \cos^2 \phi \rangle - 1}{2} \quad (3)$$

Figures 8 and 9 show the orientation function f_α and f_β as a function of the extension ratio for the α form and β form crystals, respectively.

For the α form of pure PBT, a plateau value of $f_\alpha = 0.97$ was found, while relatively high $f_\alpha > 0.92$ are found for lower ρ . For the deformed blend films, slightly yet significantly lower plateau values are found for f_α with the difference being bigger for blends containing more PC.

The f_β for pure PBT is significantly lower than f_α . A trend opposite to the α form result is found for blends in that f_β values increase with PC content.

Relative intensities of α and β form in stretched PBT have been reported before, as obtained from DSC measurements under tension⁵ and comparison of the meridional WAXD scan peak intensity of the 104 reflections of the α and β form crystals for samples of known crystallinity.¹² The first method is impractical for films. The second method is only a first approximation as it does not take into account that the actual peaks for the 101 reflections are not on the meridian but are found at an angle of 5–

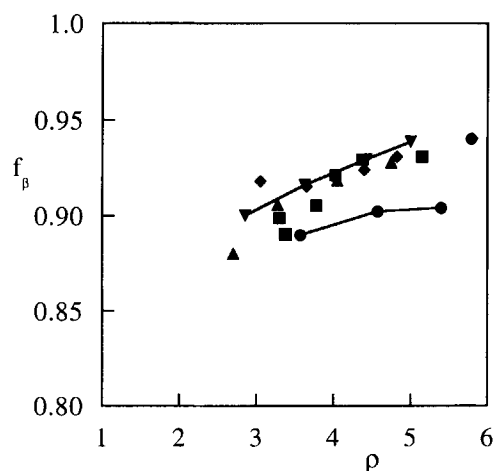


Figure 9 Second moment of the orientation function f_β of the β form crystals versus extension ratio ρ for different blend compositions. Symbols are the same as those in Figure 2.

15°C. This causes concern since the intensity on the meridian is both a function of the fraction of crystallinity corresponding to that reflection and of the orientation function.

The method employed here compares the integral of the azimuthal intensities of the 105 reflection of the α form with the 106 reflection of the β form. In order for this method to yield accurate results, it is required that the peak width of both reflections are constant. Only small deviations were observed and calculations showed that these differences have insignificant influence on the eventual result. To adjust for the 2θ dependence of intensity $I(\phi')$, azimuthal intensity profiles were obtained from an α -rich film (later designated as sample 3), from a β -rich film (later designated as sample 11), and from a sandwich of the two. The crystallinity was determined by DSC as described before. As the integrals of the azimuthal scans corresponded to known crystallinity, the 2θ dependent correction factor could be obtained.

Figure 10 shows the fraction of the crystallinity in the α form versus extension ratio for all compositions. Pure PBT samples exhibit high levels of α form crystallinity, while the β form crystallinity increases with PC content in the blend. The α fraction increases with extension ratio for samples with high PBT content, while the opposite is observed for samples with low PBT content.

No significant evidence was found to suggest orientation of the amorphous phase.

Strain Recovery Experiments

Two possible reasons can be given for this discrepancy between pure PBT and the blends with PC. First, it is conceivable that the PC dissolved in the PBT phase of the blends has an inhibiting influence on the formation of the α crystal form. This hypothesis is congruent with the melting behavior as found in the DSC study. No other signs of crystal imperfection due to the presence of PC in the PBT phase were found. Another possibility takes into account the completely reversible α to β transition exhibited at low strains. It has been shown that, upon applying higher strains, the β crystalline phase still reverts to the α crystal form, but to a lesser degree.³

To test this hypothesis, a number of samples of three different compositions were prepared by deforming under slightly differing procedures. Table II gives a detailed description of the stretching procedures employed and the resulting properties. In each case, the percentage strain recovery was measured as the difference between the length of the

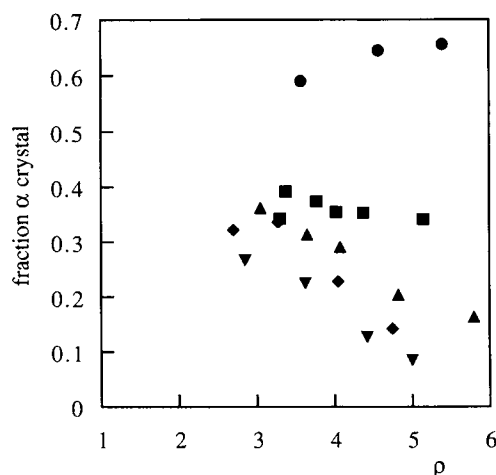


Figure 10 Fraction of the crystallinity in the α form versus extension ratio ρ for all different blend compositions. Symbols are the same as those in Figure 2.

sample while clamped and unclamped. Figure 11 shows the clear relationship between strain recovery and α fraction. The behavior in Figure 10 can therefore be explained by the higher extension retention after stretching of PC and of its blends with PBT. The extension retention decreases for blends with lower PC content. It needs to be noted that Figure 11 is completely analogous to the Figure 14 of α crystal fraction versus strain in the small strain elastic region as given in Reference 5. This is evidence that the α to β transformation of PBT is a phenomenon closely related to the small strain elasticity, regardless of the actual extension ratio.

A second reason for doing the strain recovery experiments was to find an explanation for the reinforcement effect in E' at low and high temperatures for blends with high PBT content as in pure PBT. The theoretical modulus of β crystal formed in the direction of the c -axis is significantly higher than for α crystals. Also, elastic recovery can relax some of the undetectable orientation in the amorphous phase or at the crystalline-amorphous interface. The values for E' at -150 , 110 , and 200°C found for the strain-recovered samples can be compared in Table II. It is found that strain recovery causes a significant decrease in the modulus of stretched PBT samples and to a lesser degree in the 50% PBT samples, but not for the 75% PBT samples. If transformation of the β form to the α form crystals would result in a decrease of the modulus, then the biggest change would have been found in the blends and none in pure PBT.

This indicates that morphology of the deformed blends plays a large part in the mechanical com-

Table II Deformation Conditions and Results from Relaxation Recovery Experiments

No.	%PBT ^a	T_{rel}^b	ρ	% rel ^c	$f(\alpha)^d$	$E'(-150^\circ)^e$	$E'(110^\circ)^e$	$E'(200^\circ)^e$
1	100	160 (40) ^f	4.60 (4.55) ^f	10.7	0.709 (0.645) ^f	7.09 (9.99) ^f	0.72 (0.79) ^f	0.288 (0.320) ^f
2	100	160 (40) ^f	3.60 (3.55) ^f	9.4	0.683 (0.591) ^f	5.11 (9.38) ^f	0.46 (0.56) ^f	0.194 (0.220) ^f
3	100	190	4.22	14.6	0.786	7.06	0.61	0.230
4	75	160	4.40	11.8	0.695	9.82	1.17	0.249
5	75	100	4.60	8.5	0.591	9.63	1.17	0.262
6	75	40 (1/3) ^g	4.90	4.3	0.394	10.7	1.23	0.293
7	75	40 (2/3) ^h (40) ^f	4.80 (4.70) ^f	6.1	0.441	10.8 (9.88) ^f	1.31 (1.20) ^f	0.285 (0.288) ^f
8	75	160	3.05	3.2	0.698	7.22	0.89	0.162
9	75	100 (40) ^f	3.15 (3.30) ^f	6.1	0.613	7.60 (6.26) ^f	0.96 (0.96) ^f	0.183 (0.200) ^f
10	50	160	4.72	2.5	0.132	8.57	1.66	0.193
11	50	100	4.82	1.4	0.125	8.38	1.58	0.203
12	50	40 (1/3) ^g	4.80	3.2	0.191	8.45	1.33	0.209
13	50	40 (2/3) ^h (40) ^f	4.75 (4.75) ^f	5.3	0.340 (0.142) ^f	9.85 (9.27) ^f	1.43 (1.75) ^f	0.206 (0.251) ^f
14	50	160	2.80	5.8	0.580	5.44	1.06	0.110
15	50	100 (40) ^f	3.20 (3.27) ^f	1.9	0.242 (0.336) ^f	5.92 (7.40) ^f	1.24 (1.48) ^f	0.140 (0.191) ^f

^a PBT content in the blend.

^b T_{rel} is the temperature at which the strain on the sample was removed.

^c Percent of total length after deformation relaxed after removal of strain.

^d f_α is fraction of α form crystal.

^e E' values in GPa.

^f Values in brackets are for samples made under the previous protocol that are closely related in extension ratio to results of samples reported here.

^g One-third of the stress on the sample was removed after deformation at 160°C, and the sample was subsequently cooled to 40°C.

^h Two-thirds of the stress on the sample was removed after deformation at 160°C, and the sample was subsequently cooled to 40°C.

position-dependent properties. It is unclear from these experiments what this influence is. However, it is clear that the α/β crystallinity ratio, the orientation of PC phase, increase in crystallinity, orientation of the PBT crystallites, and stress retention do not contribute to this reinforcing effect.

CONCLUSIONS

Blending PC with PBT significantly changes the deformation behavior and the properties of the deformed samples in a number of ways. Deformed blends with a PBT content of 50% or higher have higher E' than deformed pure PBT at low and ambient temperatures, while the mechanical properties of all blends are improved in the deformation direction. PBT crystallinity as measured by DSC increases significantly with deformation in pure PBT and blends; while, in the blends, relatively lower crystallinity is observed with increasing PC content. The melting temperature initially decreases slightly

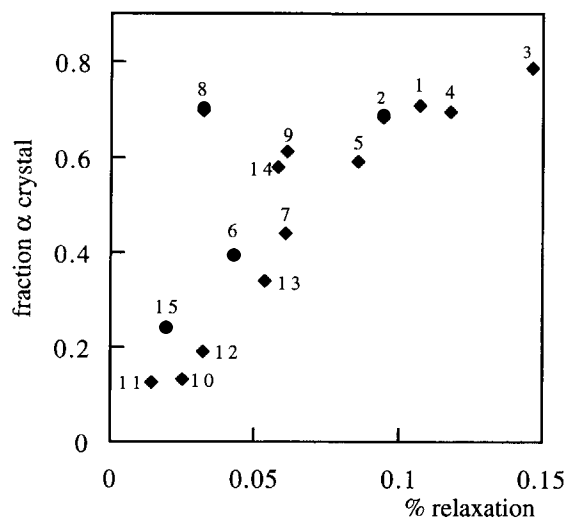


Figure 11 Fraction of the crystallinity in the α form versus strain recovery. Numbers in the figure correspond to the sample numbers in Table 2.

upon deformation, but increases through stress-induced crystallization. T_m decreases with decreasing PBT content.

The α fraction crystallinity decreases with decreasing PBT content, increases with extension for high PBT content, and decreases with extension for high PC content. Through strain recovery experiments after large deformation under different processing conditions, it was shown that the α fraction depends largely on the strain recovery after deformation. It was shown that this relationship is analogous with the α to β transition at 4–12% strain. This suggests that even at high deformations, the α to β transition is related to the elasticity of the sample. The presence of PC in the blends influences the recovery after deformation and gives rise to the large differences in α form fraction.

E' measurements for the strain recovered samples could not explain the larger increase of E' in PBT rich blends upon deformation.

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