Microfibrillar reinforcement of polymer blends

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The mechanical behaviour and morphology of films prepared from poly(ethylene terephthalate), poly(butylene terephthalate) and polyamide-6 blends subjected to zone drawing and annealing with fixed ends are studied. It is established that as a result of simultaneous physical (crystallization, relaxation, partial melting) and chemical (solid state exchange reactions and condensation) processes substantial structural changes take place in the blends which affect their mechanical properties.

(Keywords: polymer blends; compatibility; microfibrillar reinforcement; PET; PBT; nylon-6; compatibilizer)

Introduction

Physical or chemical modification of commercial polymers is one of the most promising routes for obtaining polymer materials with 'tailored' properties. Blending of two or more homopolymers is a typical example of physical modification. The homopolymer compatibility in the blends is of prime importance for their final properties. Compatibility is directly related to the chemical nature and crystallization ability of homopolymers as well as to the conditions of preparation and processing of the blends. Since polymers are in general incompatible, there is a constant search for means of improving their compatibility and/or suppression of incompatibility.

Poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT) and polyamide-6 (PA-6) differ in their crystallization ability. The higher chain flexibility of PA-6 and PBT leads to crystallization of these polymers at room temperature even after rapid quenching of their melts[1,2] while PET retains its amorphous structure for long periods after such treatment.

Numerous studies of the compatibility, morphology and properties of polymer blends based on thermoplastic polycondensates (polyamides and polyesters) have already been published[3–10]. However, these studies are directed mainly at elucidating structure–property relationships in the isotropic state. For this reason an investigation following the changes in the morphology of blends of PET, PBT and PA-6 subjected to zone drawing and annealing with additional thermal treatment, as well as the influence of this procedure on the mechanical properties of the blends, could contribute to the understanding of problems related to structure–property relationships in polymer blends.

Experimental

The polymers used were PET (Merge 1934F, Goodyear, $\bar{M}_n = 23\,400$), PA-6 (Capron 8200, Allied Co., $\bar{M}_n = 20\,600$) and PBT (RE6131, Dupont, $\bar{M}_n = 21\,300$). These polymers were finely ground (after cooling in liquid nitrogen) and then mixed in the solid state (1:1 and 1:1:1 w/w). Films of these blends and of the respective homopolymers were prepared according to the following procedure: a capillary rheometer, flushed with argon and heated to ~280°C, was loaded with powdered material. The melt obtained was kept in the rheometer for 5–6 min and then extruded through the capillary (1 mm diameter) on metal rolls rotating at ~30 rev min^{-1}. The rolls were immersed in a quenching bath of liquid nitrogen. In this way films of homopolymers and double and triple blends were prepared, their thickness (0.10–0.15 mm) and width (4–5 mm) depending on the extrusion rate and distance between the rolls.

It was established, by X-ray and calorimetric studies, that immediately after quenching, PET and the PET/PBT blend were completely amorphous while the films of PBT and PA-6 and the PET/PA-6, PBT/PA-6 and PET/PBT/PA-6 blends were partially crystalline.

All films were oriented according to the method of zone drawing[11–13] under the following conditions: moving speed of the heater, 10 mm min^{-1}; tension applied to the film, 15 MPa; temperature applied to the heating zone, 85°C (for PET, PBT and the PET/PBT blend) and 180°C (for the PA-6, PET/PA-6, PBT/PA-6 and PET/PBT/PA-6 blends). Samples with a draw ratio $\lambda = 3.7–4.5$ (*Table 1*) were thus prepared and were then subjected to isothermal annealing with fixed ends at 220 or 240°C for 5 or 25 h in vacuum.

Mechanical tests of the homopolymers and blends studied were conducted on a Zwick 1464 dynamometer at room temperature and a crosshead speed of 5 mm min^{-1}. Their Young's modulus (E), tensile strength (σ) and relative elongation at break (ε) were determined.

Wide angle X-ray scattering (WAXS) patterns of all samples were taken on a Siemens D 500 diffractometer using Ni-filtered Cu Kα radiation.

Results and discussion

Table 1 shows some mechanical properties of zone drawn films of PET, PBT, PA-6 and their blends (1:1 or 1:1:1 w/w) additionally subjected to annealing with fixed ends. It is seen that, except for the case of PBT/PA-6, all blends show relatively high values of E

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Table 1 Mechanical data of zone drawn (II) and thermally treated with fixed ends (1, 2, 3) PET, PBT, PA-6 and their blends (1:1 or 1:1:1 w/w)

		Zone drawing		Annealing		Mechanical data		
Sample	Composition	temperature (°C)^a	λ	T_a (°C)	t_a (h)	E (GPa)	σ (MPa)	ε (%)
PA-II	PA-6	180	3.7	–	–	4.5	342	31
PA-1		–		220	5	4.8	312	36
PA-2		–		220	25	2.7	95	55
PBT-II	PBT	85	3.8	–	–	3.2	141	24
PBT-1		–		220	5	4.4	156	46
PBT-2		–		220	25	2.2	106	61
PET-II	PET	85	4.0	–	–	9.3	221	9
PET-1		–		220	5	10.6	288	17
PET-2		–		220	25	11.4	316	12
PET-3		–		240	5	9.5	208	24
A-II	PET/PBT	85	4.3	–	–	8.4	244	26
A-1		–		220	5	8.9	237	30
A-2		–		220	25	6.6	145	116
A-3		–		240	5	5.8	126	137
B-II	PET/PA-6	180	4.2	–	–	8.8	330	36
B-1		–		220	5	9.3	346	31
B-2		–		220	25	9.8	275	29
B-3		–		240	5	7.8	159	160
C-II	PBT/PA-6	180	4.0	–	–	3.7	320	30
C-1		–		220	5	4.2	215	36
C-2		–		220	25	4.8	198	28
D-II	PET/PBT/PA-6	180	4.5	–	–	8.4	336	20
D-1		–		220	5	8.9	327	38
D-2		–		220	25	6.8	219	46
D-3		–		240	5	4.9	124	200

[a] All samples were annealed at the moving speed of the heater, 10 mm min^{-1}; tension applied, 15 MPa

and σ after zone drawing. These values are higher than the mean arithmetical values for the respective homopolymers (*Table 1*). After thermal treatment at $T_a = 220$°C for 5 h the E values slightly increase while σ remains almost unchanged; however, at $T_a = 220$°C for 25 h and particularly at $T_a = 240$°C for 5 h, E and σ greatly decrease. The PET/PA-6 blend is the sole exception from this trend—similarly to the PET homopolymer, at $T_a = 220$°C for 25 h, E reaches its maximum value in this case (*Table 1*). Annealing at 240°C results in the lowest values of E and σ both in homopolymers and blends. However, at this temperature a strikingly high deformation ability is observed with the PET/PBT, PET/PA-6 and PET/PBT/PA-6 blends (137, 160 and 200%, respectively) while the PBT/PA-6 blend shows an ε value lower than those of the homopolymers annealed under the same conditions (*Table 1*).

Figure 1 shows WAXS patterns of films of PET/PBT, PET/PA-6 and PET/PBT/PA-6 blends zone drawn and annealed at different temperatures. From the WAXS patterns of the zone drawn samples it can be concluded that they are highly oriented with chain alignment in the axial direction which explains the high mechanical properties of these samples. Furthermore, the drawing conditions (combined thermal and mechanical action) favour crystallization in the homopolymers and blends as indicated by the weak reflections in their WAXS patterns (*Figure 1*).

The changes in the WAXS patterns (increase in number and sharpening of the reflections) after additional treatment at 220°C for 5 h (*Figure 1*) suggest perfection and improved orientation of the crystallites in the draw direction. This perfection of the structure of the drawn blends is reflected in their mechanical properties, i.e. increase in E (*Table 1*). At $T_a = 240$°C, i.e. at a temperature higher than that required to melt PBT and PA-6, WAXS reflections indicating a return to the isotropic state of these polymers are observed while the orientation of the PET crystallites in the blends remains unchanged (*Figure 1*). As a result a composite-like structure arises, comprising an isotropic, semicrystalline matrix of PBT, PA-6 and their blends, reinforced with oriented, fibrillized semicrystalline PET. The presence of this reinforcing component in the polymer blends leads to the preservation of the shape and integrity of the samples at these annealing temperatures since macroscopic melting or softening of the films was not observed during annealing. On the other hand, the regeneration of the isotropic state of the homopolymers melting at lower temperatures reduces the number and fraction of taut tie molecules which in turn causes a decrease in E

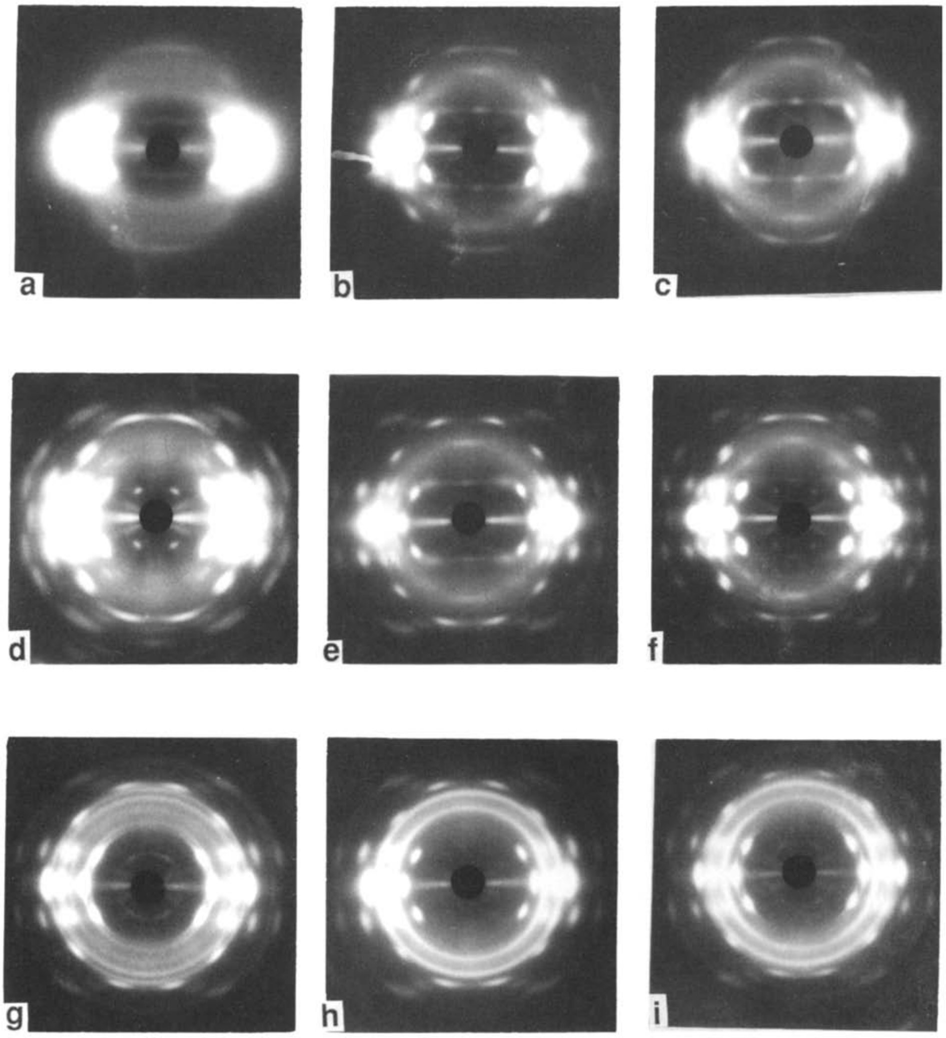

Figure 1 WAXS patterns of films of PET, PBT and PA-6 blends (1:1 and 1:1:1 w/w) zone drawn and annealed with fixed ends at 220 or 240°C for 5 h. Sample designation given in *Table 1*. Zone drawn: (a) A-II; (b) B-II; (c) D-II. Temperature = 220°C: (d) A-I; (e) B-1; (f) D-1. Temperature = 240°C: (g) A-2; (h) B-2; (i) D-2

and σ for these samples (*Table 1*). However, these values are higher by an order of magnitude than those of both undrawn homopolymers PA-6 and PBT ($E \sim 1$ GPa and $\sigma \sim 50$ MPa). It follows that PET microfibrils actually play the role of a reinforcing element just as glass or carbon fibres dispersed in isotropic matrices. The enhanced deformation ability of the same samples could be explained by additional orientation of the isotropic material during mechanical treatment. This orientation is possible, however, only if the highly oriented (fibrillized) PET fractions slip with respect to each other in the matrix consisting of PBT and/or PA-6. This assumption is confirmed by the fact that PET is characterized by a deformation ability that is 6- to 10-fold lower than that of the blends annealed at the same temperature (*Table 1*).

It is well known that chemical changes (condensation and exchange reactions) also take place in the bulk of linear polycondensates during annealing at high temperatures[14,15]. As a result, block or random copolymers are obtained from the starting polymer blends. Formation of copolymers enhances the compatibility of homopolymers in the blends and changes their structure.

It is interesting to distinguish the contribution of the physical processes from that of chemical processes in the formation of the supermolecular structure of drawn and annealed (at high temperature) blends of linear polycondensates. Some preliminary X-ray and calorimetric data of the blends studied look promising in this respect. Thus it was established that, unlike the case of homopolymers, thermal treatment above $T_a = 220°C$ results in a decrease of the size and volume fraction of PET crystallites in the oriented blends. These experimental data can be considered as indirect proof of the occurrence of chemical processes (mainly exchange reactions) in the blends[9,16]. It should be noted that these processes are favoured by the large interphase area as well as by the presence of a large number of entanglements under strain in the drawn samples since the stress points enhance the chemical reactions[17]. The copolymers formed at the interphase boundary, being in fact compatibilizers, could act similarly to the chemical agents covering the glass fibres used for the reinforcement of polymers. The presence of such a copolymer layer, i.e. a compatibilizer, will arrest dephasing and subsequent macroseparation of the polymer phases even under the action of additional external factors (temperature, mechanical stress, etc.). An experimental confirmation of this assumption resides in the fact that defibrillization or cleavage of the samples was not observed. Even at deformations of 140–200% (samples A-3, B-3 and D-3, *Table 1*) cleavage was not observed. Furthermore, the copolymer compatibilizer hampers the complete orientation of the isotropic material during the extension. For this purpose the isotropic matrix should be drawn to $\varepsilon = 300$–350% while the experimentally obtained ε values are within the range of 140–200% (*Table 1*).

On the basis of the above results it could be concluded that upon high temperature treatment of drawn PET, PBT and PA-6 blends, physical and chemical processes occur simultaneously. The former lead to a moderate increase in the volume fraction, perfection and orientation of polymer crystallites as well as to a partial or complete (at $T_a = 240°C$) regeneration of the isotropic state of the blend components melting at lower temperatures (PA-6 and PBT). As a result of the occurrence of solid state exchange reactions and condensation, copolymers are formed at the phase boundary between the two polymers. On the one hand they affect the homopolymer structure (decrease of crystallinity and crystallization ability, increase of the amorphous phase, etc.) and on the other hand they play the role of a chemical compatibilizer between the homopolymer phases, thus improving the compatibility and hampering dephasing of the polymer phases.

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References

1 Fakirov, S., Evstatiev, M. and Schultz, J. M. *J. Appl. Polym. Sci.* 1991, **42**, 575

2 Fakirov, S., Avramova, N. and Evstatiev, M. 'High Performance Polyesters and Polyamides Through Ultraquenching', Second Dresden Polymer Discussion, March 1990, Germany

3 Pillon, L. Z. and Utracki, L. A. *Polym. Eng. Sci.* 1984, **24**, 1300

4 Harraher, B. D., Angeli, S. R. and Runt, J. *Polym. Bull.* 1986, **15**, 455

5 Murff, S. R., Barlow, J. W. and Paul, D. R. *J. Appl. Polym. Sci.* 1984, **21**, 3231

6 Slagowski, E. L., Chang, E. P. and Tkacik, J. J. *Polym. Eng. Sci.* 1981, **21**, 513

7 Kamal, M. R., Sahto, M. A. and Utracki, L. A. *Polym. Eng. Sci.* 1982, **22**, 1127

8 Pillon, L. Z. and Laro, J. *Polym. Eng. Sci.* 1987, **27**, 984

9 Kimura, M. and Porter, R. S. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 367

10 Lefelar, J. A. *J. Polym. Sci., Polym. Phys. Edn* 1988, **26**, 1463

11 Kunugi, T., Ichinose, C. and Suzuki, A. *J. Appl. Polym. Sci.* 1981, **31**, 429

12 Kunugi, T., Akiyama, I. and Hashimoto, M. *Polymer* 1982, **23**, 1199

13 Kunugi, T., Domori, S. and Mikami, S. *Polymer* 1988, **29**, 814

14 Schultz, J. M. and Fakirov, S. 'Solid State Behavior of Linear Polyesters and Polyamides', Prentice Hall, Inc., Englewood Cliffs, 1990

15 Evstatiev, M. *PhD Thesis* Sofia University, 1988

16 Van Krevelen, D. W. in 'Properties of Polymers', Elsevier, Amsterdam, 1972

17 Dubner, W. S. *PhD Dissertation* University of Delaware, 1990