Polymer Vol. 37 No. 12, pp. 2373–2377, 1996

0032-3861/96/$15.00+0.00

Transport and mechanical properties of PET/Rodrun 3000 blown films

O. Motta
Chemical Institute, Faculty of Engineering, University of Catania, Via le A. Doria 6, 95125 Catania, Italy

and L. Di Maio, L. Incarnato and D. Acierno*
Department of Chemical and Food Engineering, University of Salerno, Via Ponte Don Melillo, 84084 Fisciano (Salerno), Italy
(Received 12 June 1995; revised 19 September 1995)

Blends of different ratios of poly(ethylene terephthalate) (PET) and a thermotropic liquid crystalline polymer (TLCP) composed of 40 mol% of polyethyleneterephthalate and 60 mol% of *p*-hydroxybenzoic acid (Rodrun 3000) have been processed in a laboratory-based film-blowing extrusion apparatus. Gas permeability measurements have been performed on the films in order to evaluate the effect of the mesophase on the transport behaviour of PET films. The transport properties of the blends are dependent upon the state of dispersion of the minor phase; thus, scanning electron microscopy has been conducted on the film surfaces to observe the morphological structure of the TLCP developed during the extrusion process. Moreover, the mechanical properties of the films at 2, 10 and 30% (w/w) TLCP contents have been examined in both the transverse and flow directions. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(ethylene terephthalate); Rodrun 3000; blown films)

INTRODUCTION

Considerable attention in recent years has been focused on blends of thermoplastic and thermotropic liquid crystalline polymers (TLCPs). It is well known that TLCPs offer the potential of enhanced properties and improved processability owing to their highly anisotropic molecules which organize in ordered domains and orient easily during flow. Blend properties are significantly affected by the degree of dispersion, the shape, size and orientation of the TLCP, and the interfacial adhesion between the two phases[1–4]. In fact, the blend properties are intimately related to the morphological structure which develops during the processing operations.

The investigations reported in the literature[5–16] indicate that most of the binary blends of thermoplastic polymers and TLCPs are essentially incompatible. The adhesion between the phases of a TLCP/thermoplastic blend is often poor because of the intrinsic incompatibility between the two materials. The lack of adhesion between phases greatly reduces the mechanical properties of the blend.

It is, however, worth emphasizing that the incompatibility between the two phases influences the rheological behaviour of the blends. In fact, the TLCP phase can act as a lubricant layer for matrix flow, thus inducing a large drop in the viscosity of the matrix[6–12].

Furthermore, polymer blending is a useful means to alter the transport properties of polymeric materials. The study of transport phenomena in polymer blends is motivated not only by the need to use blend structures as barrier resins and selective permeation membranes, but also the need to characterize the polymeric solid state[17].

The aim of the following work was to study the influence of Rodrun 3000 on the properties of poly(ethylene terephthalate) (PET) blown films. In particular, the alteration of the gas transport properties of the PET matrix due to the presence of the TLCP phase has been considered. Studies on the barrier performances of thermotropic liquid crystalline copolyesters have shown that these materials exhibit excellent gas barrier properties[18,19].

Since the transport behaviour of PET/TLCP blends depends on the volume fraction, particle sizes and particle shapes of the dispersed phase, morphological analysis has been conducted on the films. Moreover, tensile mechanical tests have been performed on the films at different percentages of Rodrun 3000.

EXPERIMENTAL

Materials

The thermoplastic polymer used in this work was polyethyleneterephthalate (PET) with an inherent viscosity of 0.6 $\mathrm{dl\,g^{-1}}$ from Montefibre. The thermotropic liquid crystalline polymer was a copolyester composed of 60 mol% of *p*-hydroxybenzoic acid and 40 mol% of polyethyleneterephthalate known as Rodrun 3000 from Unitika. The materials were vacuum dried at 130°C for 16 h prior to use.

---

* To whom correspondence should be addressed

Table 1 Permeabilities and permselectivities for pure PET and blends of PET and Rodrun 3000

Sample	$10^{14}P_{CO_2}$ (cm^3 (STP) cm cm^{-2} s^{-1} Pa^{-1})	P_{CO_2}/P_{N_2}	$10^{14}P_{O_2}$ (cm^3 (STP) cm cm^{-2} s^{-1} Pa^{-1})	P_{O_2}/P_{N_2}
PET	5.15	22.0	0.96	4.11
98/2 blend	3.51	30.0	0.67	5.76
90/10 blend	2.96	21.4	0.54	4.28
70/30 blend	1.55	17.2	0.25	3.6

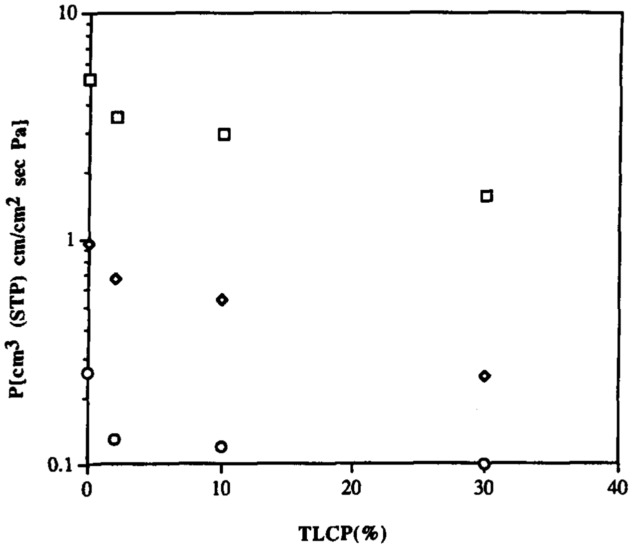

Figure 1 Permeability coefficient *versus* blend composition for PET/Rodrun 3000 at 30°C: (□) CO_2; (◇) O_2; (○) N_2

The films were prepared using a Brabender extruder ($L/D = 400/20$) connected to a 20 mm film-blowing head and a Haake take-up system. Blends with 2, 10 and 30% (w/w) Rodrun 3000 contents in PET were prepared.

The extrusion was performed at 15 rev min^{-1} (screw speed). The temperature was set at 250 and 270°C at the hopper and the barrel, respectively, while the temperature of the melt at the extrusion die was controlled at 280°C. The draw ratio and the blow ratio were approximately fixed at 15 and 3, respectively. In this way, a 30–40 μm film thickness was produced. During the process a continuous flow of nitrogen was supplied into the hopper to prevent moisture sorption.

Methods of investigation

Permeability tests were carried out at 30°C by means of a Lyssy GPM 200 quasi-isostatic apparatus on films of PET and blends at 2, 10 and 30% of the TLCP. Film permeability was measured with respect to a mixture of CO_2, O_2 and N_2 (1 : 1 : 1) at 30°C under steady state conditions. The permeabilities reported are the averages calculated for five tested samples.

Differential scanning calorimetry (d.s.c.) was performed on a Mettler TC 11 to evaluate the transition temperatures and the enthalpies of crystallization and fusion of the PET and blend films. The heating rate was 10°C min^{-1} and the materials were scanned from 30 to 300°C.

Mechanical tensile tests were performed on an Instron 4301. The films, cut into specimens 20 mm wide and 40 mm long, were tested in both the flow and transverse directions. The crosshead speed was 20 mm min^{-1}.

Scanning electron micrographs were obtained using a Cambridge 360. Prior to examination, the film surfaces were coated with gold using a high vacuum gold sputterer to improve the conductivity.

RESULTS AND DISCUSSION

Permeability measurements with respect to a mixture of CO_2, O_2 and N_2 were performed at 30°C on PET films and blends at 2, 10 and 30% (w/w) of Rodrun 3000 in PET. The permeability and permselectivity data are reported in *Table 1*. It is clear how the addition of the TLCP increases the barrier properties of PET. The effect of Rodrun 3000 in modifying the barrier properties of PET is clear even at small amounts of the TLCP: blending PET with only 2% (w/w) of the TLCP can decrease the permeability down to around 30% with respect to pure PET. This positive effect is sustained with increasing TLCP concentration in the blend, but processing gets difficult as the blown film becomes weak and unstable. Thus, a limit to the TLCP content in the blends was set at 30% (w/w), even though it may be possible to achieve higher contents by adjusting the processing conditions.

In *Figure 1*, the results are presented in terms of the semilogarithmic plot of permeability *versus* TLCP content. The non-linear relationship between the logarithm of the permeability and blend composition suggests that the system is incompatible.

Weinkauf and Paul[20] have shown that the permeabilities of TLCP films are an order of magnitude lower than those of pure PET films, and this result has been attributed essentially to an extraordinarily low gas solubility. The ordered domains of the nematic mesophase, with their efficient chain packing, are impenetrable barriers to the molecules of gases. Moreover, the impermeable regions impose a more tortuous path upon the steady state permeation of the penetrant across the polymer film[17], producing a reduction in space available for diffusion and a longer path that the penetrant has to take in order to get around the impermeable regions.

The length of the effective diffusional path is strongly dependent upon the size and shape of the impermeable phase, so this involves the details of the blend morphology.

Morphological studies conducted on the surfaces of the films have shown that two distinct phases are recognizable in this system for all the compositions analysed, as expected from the non-linear correlation between permeability and composition.

From scanning electron microscopy (SEM), the

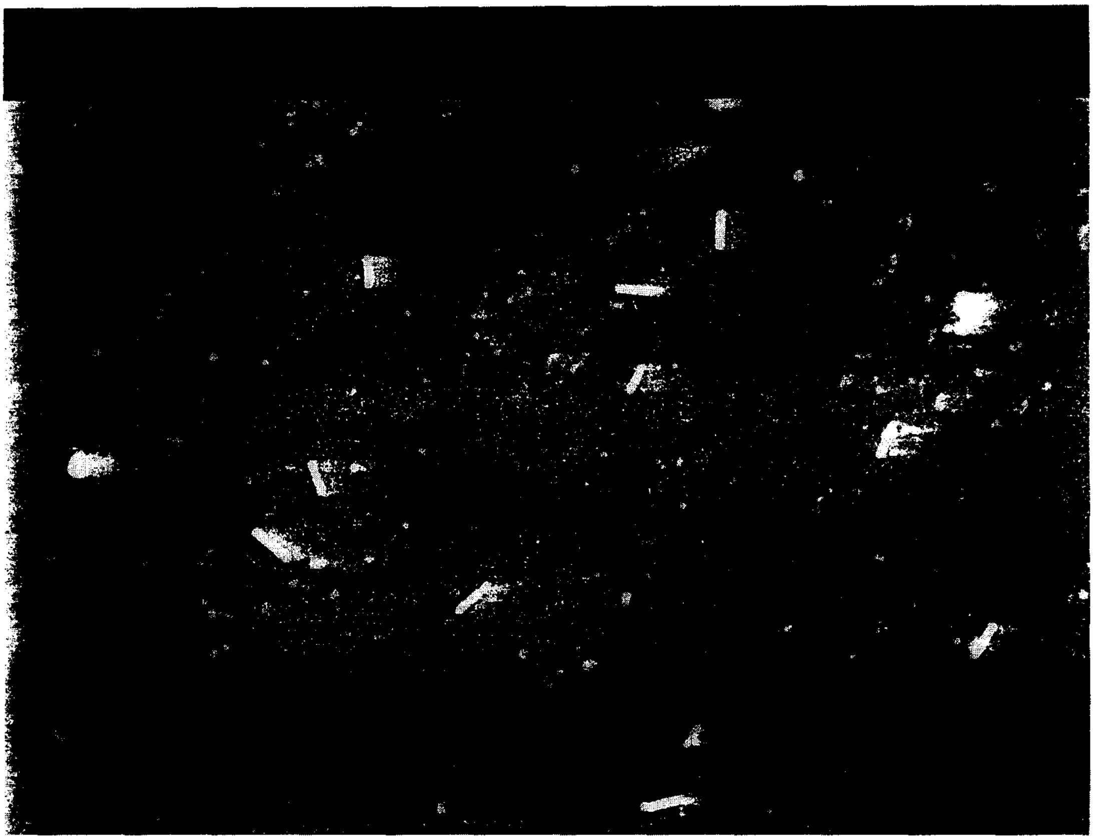

Figure 2 Scanning electron micrograph of the film surface of the 98/2 PET/Rodrun 3000 blend

Figure 3 Scanning electron micrograph of the film surface of the 70/30 PET/Rodrun 3000 blend

Table 2 Tensile properties of the system PET/Rodrun 3000 in the direction of flow

Sample	E (MPa)	σ_v (MPa)	σ_b (MPa)	ϵ_b (%)
PET	1256	28	25	100
98/2 blend	1180	26	22.5	105
90/10 blend	1264	27	22.6	94
70/30 blend	1570	36	36	2

Table 3 Tensile properties of the system PET/Rodrun 3000 in the direction transverse to flow

Sample	E (MPa)	σ_v (MPa)	σ_b (MPa)	ϵ_b (%)
PET	1130	23	24.5	135
98/2 blend	1050	22.5	21.5	120
90/10 blend	980	20	20.5	150
70/30 blend	1110	21	20	155

second phase (Rodrun 3000) appears to be distributed unevenly in the PET matrix and in the form of spheroidal domains and short fibres. In particular, in the 98/2 blend the TLCP is present essentially as small droplets a few micrometres in diameter, and some short fibrils around 1 μm in length and 0.1 μm in diameter are even detectable, as shown in *Figure 2*. In the 90/10 blend the extent of fibril formation and their dimensions are higher than those in the 98/2 blend. In both blends the non-uniform dispersion of the TLCP can be attributed to the low concentration of the second phase and/or to the processing conditions utilized. Increasing the TLCP content to 30% (w/w) leads to a better dispersion of the minor phase. At this composition the morphology of the blend still consists of a droplet and fibril dispersion of the TLCP in the matrix. However, owing to the higher concentration of Rodrun 3000, it is possible to find some regions where only fibrils ($L/D \approx 18$) of the TLCP phase are detectable, as shown in *Figure 3*. In all cases the second phase appears to be well anchored to the matrix, indicating good adhesion between the two phases.

The permselectivities for PET and blends containing Rodrun 3000 are listed in *Table 1*. There is a trade-off between decreased permeability and increased permselectivity for the 98/2 blend and a decrease in both permeability and permselectivity for the 70/30 blend. The 90/10 blend shows a decrease in permeability, while the permselectivity is essentially unchanged with respect to the matrix.

In order to verify whether the addition of the TLCP had some effects on the crystallinity of PET, we performed calorimetric tests on the films. The thermal behaviour of the films is similar to that of extruded blends reported in a previous paper[11]. The glass transition and the melting point of PET are detectable for all blend compositions investigated and do not show a significant shift upon the addition of the TLCP. This is a clear indication of the incompatibility of the system, revealed also from the morphological analysis. The differences between the heat of melting (ΔH_m) and the heat of crystallization (ΔH_c), calculated with respect to the weight of PET in the film during the first heating scan, are 15.9 $\mathrm{J\,g^{-1}}$ for pure PET and 17.1, 18.1 and 22.8 $\mathrm{J\,g_{PET}^{-1}}$ for the 98/2, 90/10 and 70/30 blends, respectively. From these results it appears that the presence of Rodrun 3000 leads to a slight increase in the crystallinity of PET, and this can be attributed to a nucleating effect of the TLCP dispersed in the PET matrix, as reported in the literature[21].

An increase in crystallinity usually leads to a reduction in permeability. The sorption, in fact, only occurs in the amorphous phase of the polymer. However, crystallinity reduces permeability not only by reducing the volume of the amorphous phase but also by increasing the tortuosity of the diffusion path for the penetrant[22], as for the TLCP domains discussed above.

For the system analysed, the increase in PET crystallinity can contribute to the reduction in permeability of the PET in the blends, but the presence of the nematic domains of the TLCP is presumably responsible for the remarkable gas barrier properties which have been observed.

Tensile tests were performed on specimens of PET and blends at 2, 10 and 30% (w/w) of Rodrun 3000 to study the mechanical properties of the films. In *Tables 2* and *3*, the results of the tensile tests performed on samples in both the transverse and flow directions are reported.

The inclusion of low percentages of Rodrun 3000 (2 and 10% (w/w)) does not modify significantly the mechanical behaviour of the PET matrix in either direction.

Increasing the TLCP content to 30% (w/w) results in a blend which is characterized by a mainly brittle behaviour in the flow direction. Such a behaviour is similar to that[7] of pure Rodrun 3000. As shown in *Table 2*, the 70/30 blend shows a dramatic reduction in the ultimate elongation value and an increase in the elastic modulus (E) and ultimate strength (σ_b).

The difference in mechanical behaviour in the flow direction of the 70/30 blend with respect to the blends at 2 and 10% (w/w) of the TLCP is essentially due to the larger number and higher aspect ratio of the fibrils in the 70/30 blend, as shown from the SEM analysis.

On the other hand, samples of the 70/30 blend tested in the direction transverse to flow show ductile behaviour like the PET sample and the blends at lower concentrations (2 and 10% (w/w)) of the TLCP. Such differences in the mechanical behaviour of the 70/30 blend in the two directions indicate that there is molecular orientation within the fibrils mainly along the flow direction. Baird and Sun[23] have reported that a fibrillar morphology does not guarantee an increase in the mechanical properties but a molecular orientation is needed.

In this regard, a preliminary investigation on the molecular orientation of Rodrun 3000 in the 70/30 blend was conducted by means of the usual X-ray diffraction method for oriented materials. The X-ray diffraction pattern, collected using a cylindrical camera with monochromatized CrKα radiation, confirmed that molecular orientation of the nematic phase parallel to the flow direction had occurred.

CONCLUSIONS

In this work, films of PET and blends of PET/Rodrun 3000 at 2, 10 and 30% (w/w) of the TLCP were obtained by means of a laboratory-based film-blowing apparatus.

In terms of the transport properties, the effect of the inclusion of the TLCP in the PET matrix is to reduce the permeability even at low concentrations of the TLCP.

Moreover, tensile tests performed along the transverse and flow directions on films of PET and 98/2, 90/10 and 70/30 blends revealed that the mechanical behaviour of the PET matrix is sustained in the blends at 2 and 10% (w/w) of the TLCP in both directions. On the other hand, the 70/30 blend is characterized by a brittle behaviour in the flow direction and a ductile behaviour in the transverse direction. Such a difference is closely linked to the morphology of the second phase, indicating that there is a deformation and molecular orientation of the TLCP fibrils mainly along the flow direction.

ACKNOWLEDGEMENT

This research was supported by the National Research Council of Italy, Special Project RAISA, Subproject 4, Paper no. 2604.

REFERENCES

1 Siegman, A., Degan, A. and Kenig, S. *Polymer* 1985, **26**, 1325
2 Kiss, G. *Polym. Eng. Sci.* 1987, **27**, 410
3 Weiss, R. A., Huh, W. and Nicolais, L. *Polym. Eng. Sci.* 1987, **27**, 684
4 Jung, S. H. and Kim, S. C. *Polym. J.* 1988, **20**, 73
5 Starita, J. M. *Trans. Soc. Rheol.* 1972, **16**, 339
6 Blizard, K. G. and Baird, D. G. *Polym. Eng. Sci.* 1987, **27**, 653
7 Nobile, M. R., Amendola, E., Nicolais, L., Acierno, D. and Carfagna, C. *Polym. Eng. Sci.* 1989, **29**, 244
8 Kholi, A., Chung, N. and Weiss, R. A. *Polym. Eng. Sci.* 1989, **29**, 573
9 Zhuang, P., Kyu, T. and White, J. L. *Polym. Eng. Sci.* 1988, **28**, 1095
10 Nobile, M. R., Acierno, D., Incarnato, L., Amendola, E., Carfagna, C. and Nicolais, L. *J. Appl. Polym. Sci.* 1990, **41**, 2723
11 Incarnato, L., Nobile, M. R., Frigione, M., Motta, O. and Acierno, D. *Int. Polym. Process.* 1993, **8**, 191
12 Incarnato, L., Motta, O. and Acierno, D. in 'Liquid Crystalline Polymers' (Ed. C. Carfagna), Pergamon, Oxford, 1993, p. 211
13 Sukhadia, A. M., Done, D. and Baird, D. G. *Polym. Eng. Sci.* 1990, **30**, 519
14 La Mantia, F. P., Valenza, A., Paci, M. and Magagnini, P. L. *Polym. Eng. Sci.* 1990, **30**, 7
15 Limtasiri, T. and Isayev, A. I. *J. Appl. Polym. Sci.* 1991, **42**, 2923
16 Joseph, E. G., Wilkes, G. L. and Baird, D. G. *Polym. Eng. Sci.* 1985, **25**, 377
17 Paul, D. R. and Newman, S. in 'Polymer Blends', Vol. 1, Academic Press, New York, 1978, Ch. 10
18 Chiou, J. S. and Paul, D. R. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 1699
19 Weinkauf, D. H. and Paul, D. R. *J. Polym. Sci., Polym. Phys. Edn* 1991, **29**, 329
20 Weinkauf, D. H. and Paul, D. R. in 'Liquid Crystalline Polymers' (Ed. C. Carfagna), Pergamon, Oxford, 1993, p. 219
21 Joseph, E. G., Wilkes, G. L. and Baird, D. G. in 'Polymeric Liquid Crystals' (Ed. A. Blumstein), Plenum Press, New York, 1984, p. 197
22 Van Krevelen, D. W. in 'Polymer Properties', Elsevier, Amsterdam, 1990
23 Baird, D. G. and Sun, T. in 'Liquid Crystalline Polymers' (Eds R. A. Weiss and C. K. Ober), American Chemical Society, Washington, DC, 1990, p. 416