ELSEVIER

Polymer 42 (2001) 9593–9599

polymer

www.elsevier.com/locate/polymer

Blends of a thermotropic copolyester and a thermotropic copoly(ester–amide): structure and mechanical properties

F.J. Vallejo, J.I. Eguiazábal, J. Nazábal*

Departamento de Ciencia y Tecnología de Polímeros, Instituto de Materiales Poliméricos 'POLYMAT', Facultad de Ciencias Químicas, UPV/EHU, P.O. Box 1072, 20080 San Sebastian, Spain

Received 19 March 2001; received in revised form 4 June 2001; accepted 19 June 2001

Abstract

Rodrun 5000/Vectra B950 blends were obtained by direct injection moulding at two injections rates. The blends were partially miscible and unreacted under the processing conditions used. Higher orientations and properties were obtained at the lower injection rate due to the higher overall orientation obtained. The produced orientation and the negative volume of mixing of the blends led to a range of LCP materials with intermediate modulus and tensile strength and slightly higher ductility. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Rodrun 5000; Vectra B950; Blends

1. Introduction

Thermotropic liquid–crystal polymers (LCPs) have gained increasing interest in recent years, due to their excellent mechanical properties, good processability and low thermal expansion coefficient [1]. Moreover, when mixed with thermoplastics they are able to act as reinforcements, due to their fibrillar and highly stiff and resistant structure in the solid state [2–5].

The number of commercially available LCPs is limited [1], so that there is a clear need for the development of new materials with thermotropic behaviour. Blending offers a valuable method to produce new LCPs due to their simplicity and comparatively low cost. The modulus of elasticity and the tensile strength of blends of two LCPs appear different from those usually found in conventional thermoplastic blends. Thus, they were synergistic in two immiscible blends [6,7], slight synergisms were observed in a partially miscible blend [8], and a practically linear behaviour was seen in a miscible blend [9].

Moreover, LCPs are usually copolyesters or copoly-(ester–amides), so that chemical interchange reactions can take place between the blend components during processing or thermal treatment in the melt state. In fact, although exceptions also exist [9], blends of two LCPs, Vectra A950 (VA) containing 2,6-hydroxynaphthoic acid (HNA) and *p*-hydroxybenzoic acid (HBA) with Vectra B950 (VB) containing only HNA [7,10], as well as of other LCPs with different HNA and HBA contents [11,12] have shown the development of interchange reactions. These reactions have also been considered [7,10] as responsible for the increased orientation of the LCPs in the blends.

The phase structure [6–9,11–14] and the rheological behaviour [6,8,11,13,15–19] of LCP/LCP blends have been often studied, but despite their high level, their mechanical properties have seldom been studied, and many of the works are patents [20–23]. In the open literature, only the mechanical properties of blends of two ethylene terephthalate–HBA copolyesters [9], VA with VB [7] and with Ultrax (a copolymer based on HBA, terephthaloyl and hydroquinone) [6] and only three compositions of another blend [8] have been studied.

Many other LCP blends are potentially interesting. For instance, the phase structure of Rodrun LC5000 (R5)/VB blends has been studied [14], but no systematic analysis of their mechanical properties has been carried out. This is despite the fact that R5/VB blends have been reported to be immiscible [14], and therefore likely to exhibit synergistic mechanical behaviour. Moreover, taking into account their chemical structures, transesterification reactions can take place between them, and this could also affect positively the mechanical properties of their blends.

In this work, R5/VB blends have been prepared across the full composition range by direct injection moulding. Different injection rates have been used because of their effects on molecular orientation and mechanical properties. The phase structure of the blends after the blending procedure

---

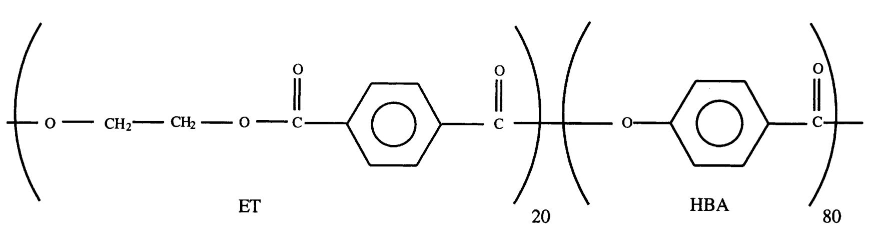
* Corresponding author. Tel.: +349-43-018-218; fax: +349-43-212-236. *E-mail address:* popnaetj@sq.ehu.es (J. Nazábal).

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00475-X

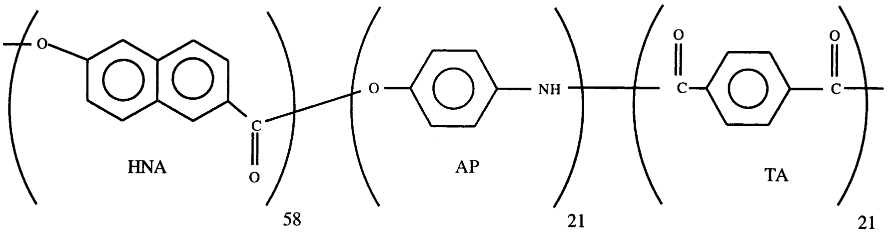
employed has been analysed by dynamic mechanical–thermal analysis (DMTA), and possible changes in the chemical structure have been studied by Fourier Transform Infrared Spectroscopy (FTIR). The mechanical properties of the blends have been determined by means of tensile tests and have been related to both their specific volume and orientation level as measured by X-ray diffraction.

2. Experimental

The polymers used in this work were Rodrun LC5000® (R5) from Unitika Ltd. and Vectra B950® (VB), commercialised by Celanese (Ticona). R5 is a copolyester based on *p*-hydroxybenzoic acid (HBA) and ethylene terephthalate (ET). VB is a copoly(ester–amide) composed of hydroxynaphthoic acid (HNA), aminophenol (AP) and terephthalic acid (TA). The chemical structures of R5 and VB are:



Rodrun LC5000



Vectra B950

Both LCPs were dried before processing for 8 h at 135°C in order to avoid moisture-induced degradation reactions during processing. The dried pellets were directly melt mixed and injection moulded over the entire composition range in a Battenfeld BA230E reciprocating screw injection moulding machine. A melt temperature of 300°C, a mould temperature of 20°C, and an injection pressure of 2450 bar were used. The low mould temperature was selected in order to obtain a high cooling rate and, thus, to improve the LCP orientation in the moulded specimens. The rapid cooling meant that a high injection pressure was required. In order to analyse the effect of the injection rate on the structure and properties of the blends, the moulding process was carried out at two injection rates, 1 and 7 cm^3/s.

The DMTA were carried out from 30 to 200°C in a Polymer Laboratories DMTA at a frequency of 1 Hz in the flexural mode and at a heating rate of 4°C/min. The samples were obtained in the orientation direction from the central section of the injection moulded tensile specimens. The chemical structure of the blends was studied by FTIR, using a Nicolet 5DXC spectrophotometer. Specific volume values were measured in a Mirage SD-120-L electronic densitometer with a resolution of 0.0005 cm^3/g using butyl alcohol as the immersion liquid.

The tensile tests were carried out using an Instron 4301 at a cross-head speed of 10 mm/min on 1.9 mm thick ASTM D-638 type IV injection moulded specimens. The specimens were gated at the outside end of the shoulder of the dumbbell-shaped moulding cavities. The mechanical properties (Young's modulus, E; break stress, σ_b; and ductility measured as the break strain, ε_b) were determined from the load-elongation curves. A minimum of eight specimens were tested for each reported value.

The WAXS diffraction patterns of some samples of the neat components and of the blends were obtained using a Statton flat camera (W.H. Warhus, Co.) and CuKα ($\lambda = 1.542$ Å) radiation. The samples (length = 20 mm) for X-ray diffraction were cut from the central section of the tensile specimens.

3. Results and discussion

3.1. Phase behaviour

The thermal transitions of the neat components and of the blends were not clearly observed by differential scanning calorimetry (DSC). Consequently, the thermal behaviour

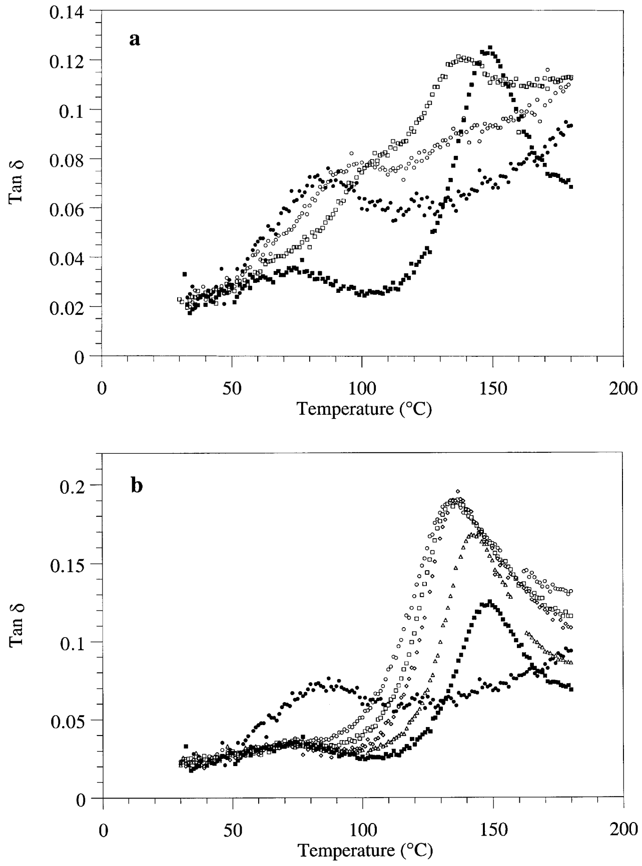


Fig. 1. Tan δ vs. temperature plots for: (a) R5 (●), VB (■) and the 80/20 (○) and 60/40 (□) blends and (b) R5 (●), VB (■) and the 40/60 (○), 30/70 (□), 20/80 (◇) and 10/90 (△) blends.

and the phase structure were analysed by DMTA, which is a more sensitive technique than DSC.

Fig. 1a shows the tan δ–temperature plots for neat R5 and VB and for the R5-rich blends, obtained at an injection rate of 7 cm^3/s. The residence time of the blends in the melt state was similar for both injection rates, so a possible effect on the phase structure can be neglected. As can be seen, the T_g of R5 was close to 85°C, while that of VB appeared near 150°C. The slight peak in the plot of VB near the T_g of R5 indicates the presence of a secondary transition probably due to the motion of the HNA unit. Its location seems to be invariant with the blend composition in spite of the fact that in previous DMTA studies [24] this transition was dependent on copolymer composition. The plots of the blends showed two tan δ peaks that overlapped in the 60/40 composition. The T_g values are collected in Table 1 together with those of the VB-rich blends that will be discussed later. Although an exact measurement of the T_gs from the maxima of the tan δ–temperature curves is difficult, the T_gs of the blends are intermediate between those of the pure components and approach each other slightly as the content of the two components of the blend equilibrates. This indicates the presence in the R5-rich blends of Fig. 1a of two mixed phases, each of them rich in one of the components.

Fig. 1b shows the tan δ–temperature plots for neat R5 and VB and for the VB-rich blends. As can be seen, and as was less clearly seen in Fig. 1a, the height of the tan δ peak of the VB is greater in the blends than in the neat components. This was accompanied by the fact that the E' drop in the glass transition region was also greater in the blends than in VB. This has been attributed in miscible blends [14] to changes in the liquid crystalline alignment of the blends compared to that of the neat components. The same phenomenon is also observed in the partially miscible blends of this paper. As can also be seen in Fig. 1b and Table 1, the T_g of the VB-rich phase of the VB-rich blends also decreased upon the addition of increasing amounts of R5. As stated above, this indicates the presence of some R5 in the VB-rich phase. However, no peak close to that of pure R5 appeared in the VB-rich blends. This is helped by the fact that the T_g of R5 is wide and weak, and therefore difficult to observe in the blends. The absence of the T_g of an LCP component of a blend is not unusual, even in sensitive DMTA measurements. For example, in extruded-injection moulded VA/Ultrax [6] and in directly injection moulded VA/VB [7] blends, the T_g of VA could not be observed. However, after a more careful observation of Fig. 1b, we realise that the minimum in tan δ of pure VB between 80 and 120°C does not appear in the blends. This effect is more clearly seen as the R5 content increases, and gives rise to tan δ peaks which are broader, as the composition tends to be equal amounts of both components. This suggests the presence of a single mixed phase, or microphase separation where the phase sizes are too small to be resolved by DMTA into separate peaks. Thus, although the VB-rich blends of Fig. 1b are close to miscibility, the presence of two partially mixed phases in the R5-rich blends of Fig. 1a indicates the existence of partial miscibility between R5 and VB.

The presence of wide single T_g peaks must be due to either partial miscibility or development of transesterification reactions during processing [7]. For this reason, FTIR analyses of the blends were carried out to check the possible development of interchange reactions between R5 and VB. The results are shown in Figs. 2a,b, where the experimental FTIR spectra of the 80/20 and 20/80 blends are compared with those calculated by combining the weighted spectra of

Table 1
Glass transition temperatures (T_g) of the pure components and of the blends at an injection rate of 7 cm^3/s

	T_g (°C)	
R5	84	–
80/20	89	138
60/40	99	137
40/60	–	134
30/70	–	135
20/80	–	136
10/90	–	143
VB	–	147

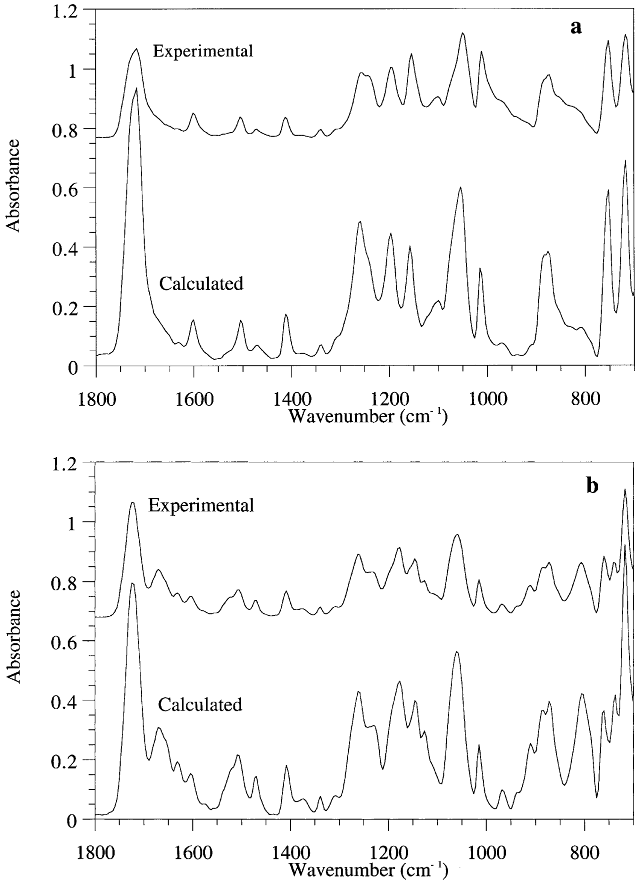


Fig. 2. Experimental and calculated FTIR spectra for the: (a) 80/20 and (b) 20/80 blends.

the pure components at each composition. The spectra of the 80/20 blend of Fig. 2a are representative of the R5-rich blends, and those of the 20/80 blend of Fig. 2b are representative of the VB-rich blends. As can be seen, the experimental and calculated spectra are practically identical in both composition regions. Therefore interchange reactions are not the reason for the T_g changes, indicating that the R5/VB blends are partially miscible.

3.2. Mechanical properties

The Young's modulus–composition relationships of the blends are shown in Fig. 3. As can be observed, in the blends injected at 1 cm^3/s, the modulus followed approximately the linear rule of mixtures; whereas in the case of the R5-rich blends injected at 7 cm^3/s, a very slight synergism (maximum approximately 4%) was seen. These modulus results agree with the tendency towards slight synergisms or linearity found in partially miscible and miscible LCP$_1$/LCP$_2$ systems [8,9].

The effect of the injection rate on the modulus is also shown in Fig. 3. As can be seen, the blends and the neat components injected at the low injection rate show modulus values higher than those of the high injection rate. This behaviour is common in LCPs, and is attributed [25–28] to the increase in the thickness of the oriented skin [29] as the injection rate decreases, although at decreasing injection rates the mechanical properties of the skin also appear to improve. The higher mechanical properties at low injection rates have also been attributed to cooling of the melt during flow that leads to a viscosity increase [27–30] and, therefore, both increased shear and molecular orientation.

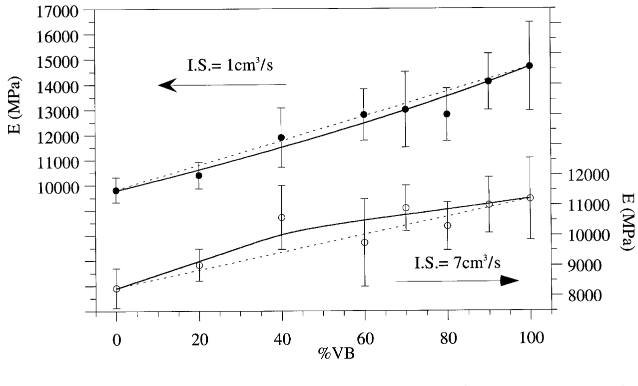


Fig. 3. Young's modulus of the blends injected at 1 cm^3/s (●) and at 7 cm^3/s (○) vs. composition.

To find out the reasons for the modulus behaviour, the orientation of the blends and of the pure components were measured. Additionally, the specific volume of the blends may change when some miscibility is present [31] and also influences the modulus values, and therefore, was also studied. The thickness of the skin could not be clearly determined, due to the presence in half of each specimen of four layers of different thicknesses.

The plot of the specific volume of the blends against composition is shown in Fig. 4. As can be seen, the difference in specific volume of the blends at the two injection rates is not significant. Hence a single curve is plotted. However, decrease in specific volume due to blending is clear at both injection rates. The decreases are quantitatively large enough (mean value 1×10^{-3} cm^3/g) [32] to lead to an increase in the modulus of elasticity. Therefore, the

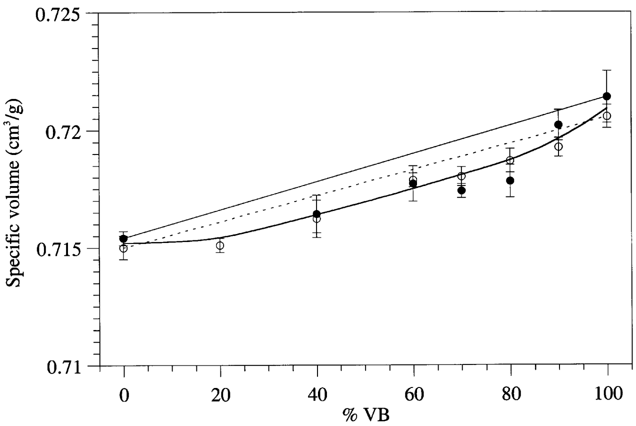


Fig. 4. Specific volume of the blends vs. composition. Symbols as in Fig. 3.

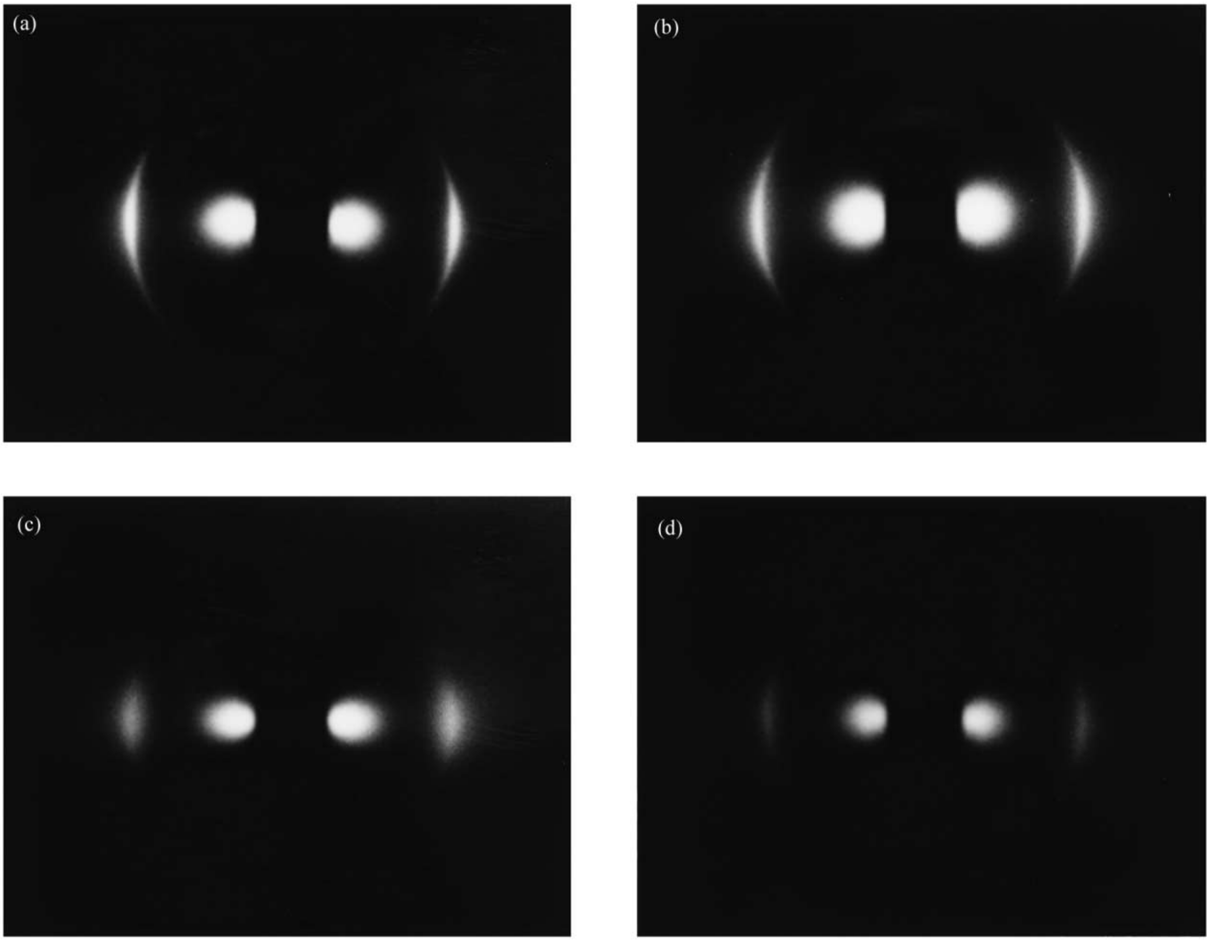


Fig. 5. X-ray diffraction patterns of: (a) R5, (b) 80/20 blend, (c) 20/80 blend and (d) VB injected at 1 cm^3/s.

decrease in specific volume upon blending will have a positive effect on the modulus of elasticity of the blends.

The possible differences in the overall orientation of the blends were analysed by X-ray diffraction. Some representative diffraction patterns for samples injected at 1 cm^3/s are shown in Fig. 5. As is seen from the arcing levels of the equatorial diffraction of the samples, the orientation is lower in R5 (Fig. 5a) than in VB (Fig. 5d). The diffraction pattern of the 80/20 R5/VB blend (Fig. 5b) indicates an orientation level similar or slightly lower than that of R5, while that of the 20/80 R5/VB blend of Fig. 5c approaches that of neat VB. Thus, the orientation of the blends could have a slight negative effect on the modulus values. The positive effect on the modulus of the negative volume of mixing should counteract the slight negative effect of the orientation, leading to the rather linear behaviour of the plot of modulus of elasticity at 1 cm^3/s of Fig. 3.

The influence of the orientation on the modulus values is also seen when the effect of the injection rate on the orientation is studied. Fig. 6 shows the diffraction pattern of the neat VB injected at 7 cm^3/s. The arcing is larger than that of the low injection rate of Fig. 5d. The same effect was less clearly seen in most of the blends. This indicates that, at high injection rates, there is a lower overall orientation in VB and in the blends, that agrees with their lower modulus.

The ductility of the blends is shown in Fig. 7. As can be seen, due to the brittle nature of the LCPs, the ductility is very low both for the neat components and for the blends. Moreover, it shows an overall positive deviation with

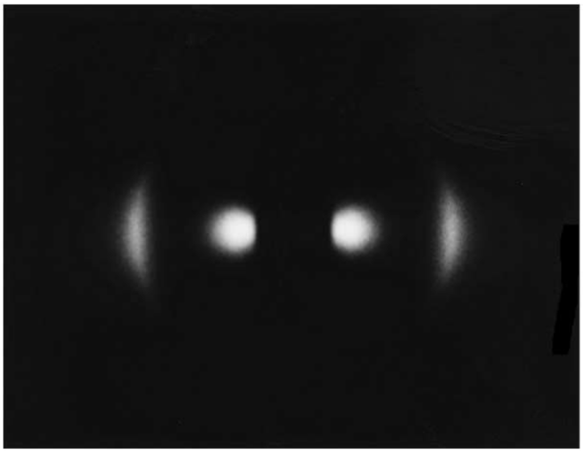


Fig. 6. X-ray diffraction pattern of VB injected at 7 cm^3/s.

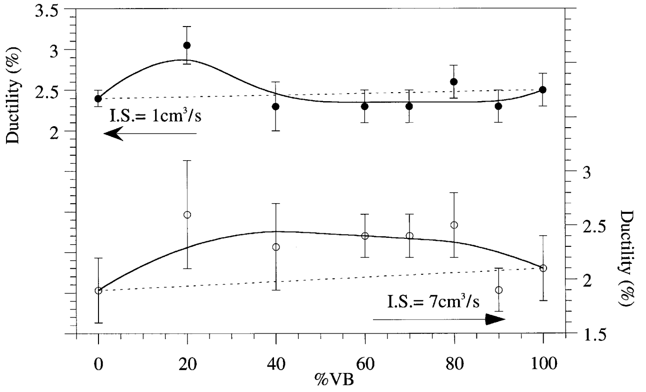


Fig. 7. Ductility of the blends vs composition. Symbols as in Fig. 3.

respect to the rule of mixtures between the values of R5 and VB at the high injection speed, and a mixed behaviour at the low injection speed. The high ductility value of the 80/20 blend at the low injection speed is a repetitive value (double amount of specimens tested), but it is not very significant, taking into account, the values of the rest of the blends and the lack of change of the measured morphological characteristics. The partial miscibility between the blend components and the improved interfacial adhesion probably led to the positive behaviour of Fig. 7.

As can also be seen in Fig. 7, the low injection rate leads to slightly higher ductilities. Ductility data of LCPs as a function of the injection rate are seldom reported in the literature and the relation between the injection rate and the ductility of LCPs is still not clear. This is because both a tendency for the ductility to increase [25] at lower injection rates, as in this work, and the opposite trend [27] have been seen.

The tensile strength plots of the blends are shown in Fig. 8. Its behaviour is rather parallel to that of the modulus. This is despite the fact that the ductility must affect the tensile strength in these brittle materials. The samples moulded at the low injection rate show clearly higher tensile strength, in agreement with their higher orientation and modulus behaviour and with the results obtained by other authors [25,27,33]. The tensile strength of the samples injected at 1 cm^3/s shows a slight negative deviation from the rule of mixtures (maximum approximately 10%), which can be attributed to the practically additive modulus (Fig. 3) and the generally slight negative deviation of the ductility (Fig. 7). The positive behaviour of both, the modulus and the ductility of the blends injected at 7 cm^3/s led to a positive deviation that reached a maximum of 25% in the R5-rich composition region. Thus, contrary to thermoplastic blends and to previous [6] clear positive synergisms in immiscible blends, and in agreement with other partially miscible blends [8], the partial miscibility of the blends leads to intermediate behaviours in the tensile strength and in the modulus of elasticity of these LCP blends.

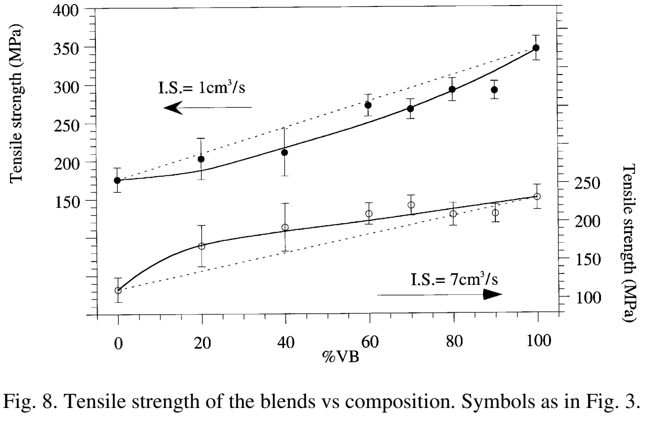


Fig. 8. Tensile strength of the blends vs composition. Symbols as in Fig. 3.

4. Conclusions

R5/VB blends are partially miscible. At the processing conditions of this work, the blends are unreacted as seen from FTIR spectra. Lower injection rates lead to clearly higher modulus of elasticity and tensile strength due to the overall greater orientation produced. The tensile strength values were close to those predicted by the rule of mixtures and were a consequence of the trends in the modulus and ductility. The modulus values of the blends at an injection rate of 1 cm^3/s were close to those predicted by the rule of mixtures. They were a consequence of the slightly smaller orientation of the components in the blends, partially counteracted by the positive effect of the negative excess volume of mixing.

Acknowledgements

The financial support of the University of the Basque Country (Project number G46/98) is gratefully acknowledged. F.J. Vallejo also acknowledges the University of the Basque Country (UPV/EHU) for the award of a grant. The authors also acknowledge Dr Iñaki Iribarren for the X-ray measurements.

References

[1] Brown CS, Alder PT. In: Folkes MJ, Hope PS, editors. Polymer blends and alloys. Glasgow: Chapman & Hall, 1993. Chapter 8.
[2] Vallejo FJ, Eguiazábal JI, Nazábal J. Polymer 2000;41:6311–21.
[3] Bastida S, Eguiazábal JI, Nazábal J. Polymer 2001;42:1157–65.
[4] La Mantia FP. Thermotropic liquid crystal polymer blends. Lancaster: Technomic Publishing Co., 1993.
[5] Acierno D, La Mantia FP. Processing and properties of liquid crystalline polymers and LCP based blends. Ontario: Chemtec Publishing, 1993.
[6] Akhtar S, Isayev AI. Polym Engng Sci 1993;33:32–42.
[7] Vallejo FJ, Eguiazábal JI, Nazábal J. Polym Engng Sci 2001 (in press).
[8] Kenig S, DeMeuse MT, Jaffe M. Polym Adv Technol 1991;2:25–30.
[9] Vallejo FJ, Eguiazábal JI, Nazábal J. Polym J 2001;33:128–32.
[10] Dreher S, Seifert S, Zachmann HG, Moszner N, Mercoli P, Zanghellini G. J Appl Polym Sci 1998;67:531–45.
[11] McLeod MA, Baird DG. Polymer 1999;40:3743–52.

[12] McCullagh CM, Blackwell J, Jamieson AM. Macromolecules 1994;27:2996–3001.
[13] Lin YG, Winter HH. Polym Engng Sci 1992;32:773–8.
[14] Hsieh T, Tiu C, Simon GP. Polymer 2000;41:4737–42.
[15] Hsieh TT, Tiu C, Simon GP, Andrews SR, Williams G, Hsieh KH, Chen CH. In: Shonaike GO, Simon GP, editors. Polymer blends and alloys. New York: Marcel Dekker, 1999. Chapter 12.
[16] Ding R, Isayev AI. J Thermoplast Compos Mater 1995;8:208–24.
[17] DeMeuse MT, Jaffe M. In: Weiss RA, Ober CK, editors. Liquid crystalline polymers, ACS Symp. Ser. No. 435, 1990. Chapter 30.
[18] McLeod MA, Baird DG. J Appl Polym Sci 1999;73:2209–18.
[19] Done D, Baird DG. J Appl Polym Sci 1990;30:989–95.
[20] Kiss G. US Patent 4,567,227, 1986.
[21] Matsumoto M, Kaneda T. US Patent 4,837,268, 1989.
[22] Froix MF. US Patent 4,267,289, 1981.
[23] Isayev AI, Subramanian PR. US Patent 5,070,157, 1991.
[24] Troughton MJ, Davies GR, Ward IM. Polymer 1989;30:58–62.
[25] Boldizar A. Plast Rubber Process Appl 1988;10:73–8.
[26] Hsiung CM, Tian J, Cakmak M. Int Polym Process 1993;8:164–77.
[27] Zülle B, Demarmels A, Plummer CJG, Kausch HH. Polymer 1993;34:3628–37.
[28] Kingma JA, Geijselaers H. In: Lemstra PJ, Kleintjens LA, editors. Integration of fundamental polymer science and technology, vol. 4. London: Elsevier, 1990. p. 361–6.
[29] Kenig S. Polym Compos 1986;7:50–5.
[30] Suokas E. Polymer 1989;30:1105–12.
[31] Hsieh TT, Tiu C, Hsieh KH, Simon GP. Korea Polym J 1998;6:44–52.
[32] Barlow JW, Paul DR. Polym Engng Sci 1981;21:985–96.
[33] Kenig S, Trattner B, Anderman H. Polym Compos 1988;9:20–6.