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Compatibilization of PP/Vectra B "in situ" composites by means of an ionomer

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Abstract

Ionomer addition has been investigated as a compatibilizer for the immiscible polypropylene (PP)/Vectra B 950 (VB). Both modified and unmodified blends as a reference, with VB contents up to 30% were obtained by direct injection moulding. The crystallinity of PP/VB was barely influenced by the presence of the ionomer. The compatibilization leads to the presence of thinner fibres that broke during testing. Compatibilization reduced toughness, but at VB contents of 15 wt% or more, both the modulus of elasticity and the tensile strength significantly increased with respect to the uncompatibilized blends. The properties of both compatibilized and uncompatibilized blends, as a whole, were similar in the case of PP modified by either maleic anhydride or ionomer addition. However, favourable experimental conditions such as thinner specimens or higher compatibilizer content were used in the case of maleic anhydride modified PP. This indicates a more important positive effect on compatibilization by means of ionomer addition. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polypropylene; Vectra B; Ionomer

1. Introduction

The improvement of the mechanical properties of thermoplastic polymers is a research area of considerable interest in polymer science and technology [1,2]. One of the most recent procedures to reach this objective is to blend a thermoplastic matrix with liquid crystal polymers (LCPs) [3,4]. LCPs are able to deform into fibrillar structures, leading to the so-called "in situ" composites with improved mechanical properties, especially elastic modulus and tensile strength. Polypropylene (PP) is a very important, high consumption thermoplastic polymer. It shows a very positive combination of properties, including relatively high stiffness as well as good thermal and chemical resistance, as compared to other thermoplastics of similar price. Vectra B 950 (VB) is one of the most widely used commercial LCPs. Thus, the PP/VB blend appears to be an attractive possible "in situ" composite.

Numerous works on PP/LCP blends have been reported in the literature. Extrusion [5-16], extrusion followed by injection moulding [17-20] and direct injection moulding [21-22] have been used as processing methods. Some of these works were devoted to PP/VB blends, the morphology

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[7–9,11,13,17], mechanical properties [7,8,11,13,17] and thermal properties [7,17] being the most often studied aspects.

The mechanical properties of these "in situ" composites are generally limited by the intrinsic immiscibility of the blend components. For this reason, compatibilization is often attempted through improving the interfacial adhesion by different methods, mainly using maleic anhydridegrafted PP (PP-g-MA) [23-35], but also by adding ethylene or propylene copolymers with acrylic [36,39] or other compatibilizers [35,40–42]. Extrusion [30,34,35,37,39], extrusion followed by injection moulding [23,25,26,30, 32,33,36,38], extrusion followed by compression moulding [30], direct injection moulding [24], and direct injection moulding [28,29,31] after premixing the PP and the compatibilizer have been used as mixing methods. Some of these papers were devoted to compatibilized PP/VB blends and specifically to the morphology and mechanical properties [27,29,30] and to the interfacial properties [27]. The effects of maleic anhydride (10%), composition, and melt temperatures [30], and also the maleic anhydride content (5-50%)[27] have been studied in PP/VB blends by injection moulding. The effects of different draw ratios, and also composites obtained from several preextruded films by compression moulding [30], have also been studied.

The addition of ionomers is a compatibilization method

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that has given excellent results in PP/polyamide blends [43,44]. Moreover, the fact that VB is a copolyester-amide suggests the possibility of using ionomers to compatibilize PP/VB blends. This technique was used in this work. The thermal behaviour, morphology and mechanical properties of PP/VB blends compatibilized with a zinc salt of poly-(ethylene-*co*-methacrylic acid) (PEMA-Zn) were measured. The uncompatibilized materials were used as a reference. The blends were obtained by direct injection mixing, and were characterized by DSC and SEM. The mechanical properties were determined by means of tensile and impact tests. The improvements obtained were compared with those from the more common method of modification by maleic anhydride.

2. Experimental

The PP used in this work was Hostalen 1780-F, supplied by Hoechst. It had a melt flow index of 17.8 g/10 min (ASTM-D1238) with a 2.16 kg load at 230°C. Vectra B 950 (VB) (Hoechst) is a copolyester-amide based on 6hydroxynaphthoic acid (58%), terephthalic acid (21%) and aminophenol (21%). Its melt flow index was 28 g/10 min at 310°C with a 325 g load. The ionomer used as compatibilizer was an ethylene–methacrylic acid copolymer where methacrylic acid is partially neutralized with Zn (PEMA-Zn). It was supplied by Aldrich Chemical Co. Inc. (Cat No. 42,666-0). Its melt flow index, determined at 190°C and with a 2.16 kg load, was 14 g/10 min. Its melting temperature was 70°C.

VB and PEMA-Zn were dried before processing for 8 h at 135°C in an air circulation oven and for 8 h at 60°C in a vacuum oven, respectively. The dried pellets of the polymers were directly melt-mixed in a Battenfeld BA230E reciprocating screw injection moulding machine. A barrel and a nozzle temperature of 300°C, a mould temperature of 20° C, a injection speed of 7 cm³/s and an injection pressure of 2450 bar were used in the injection moulding process. The binary (PP/VB) blends of 95/5, 85/15, 80/20 and 70/30 by weight (3.3, 10, 14 and 22 vol% of VB) were obtained. As usual in ionomer addition [43,44], compatibilized blends were obtained with a PEMA-Zn content referred to the LCP content. PEMA-Zn was added at 20% of the VB content. This is the PEMA-Zn level that gave rise to the best improvement in properties with respect to the uncompatibilized blends in an initial study of the 70/30 blend. For comparative purposes, pure PP and VB were processed at the same conditions as the blends.

The phase structure was studied by Dynamic Mechanical analysis using a Polymer Laboratories DMTA that provided the loss tangent (tan δ) values against temperature. A heating rate of 4°C/min and a frequency of 1 Hz were used. The phase structure of the blends and of the components was also studied by differential scanning calorimetry (DSC) using a Perking–Elmer DSC-7 calorimeter. The samples

were first heated from 50 to 330°C at 20°C/min to remove the previous thermal history; then cooled to 50°C at the same scanning rate, and subsequently reheated as in the first scan. The glass transitions could not be analysed; that of PP because it was very weak and difficult to observe, and that of VB because it should appear approximately at 120°C [45] and was consequently masked by the wide melting peak of PP. No thermal feature of the PEMA-Zn copolymer was observed in the DSC scans carried out on compatibilized blends. The melting behaviour of VB could not be analysed because of the very small size of the endotherm, which could not be clearly identified in the PP-rich blends studied. PP crystallization was analysed in the cooling scan, and PP melting in the second heating scan. The crystallization and melting temperatures, and the enthalpies were determined from the maxima and from the areas of the corresponding peaks, respectively.

The density was measured in an electronic Mirage SD-120-L densitometer with a density resolution of 0.0002 g/ cm^3 using butyl alcohol as immersion liquid.

The interfacial tension between two polymers was calculated by the two-liquid Harmonic Method (Wu's method) [46–48] measuring the contact angle of two liquids on the surface of both polymers. The contact angle measurements were carried out on a CAM 100 goniometer (KSV) on injection moulded tensile bars, using water and ethylene glycol. The mean standard deviation of the measurements was $2-3^{\circ}$ which gave rise to an error in the interfacial tension values of approximately $\pm 20\%$.

The tensile tests were carried out using an Instron 4301 at a cross-head speed of 10 mm/min and at $23 \pm 2^{\circ}C$ on 1.9 mm thick ASTM D-638 specimens. The mechanical properties (Young's modulus, E; tensile strength; and ductility, measured as the break strain, ϵ_b) were determined from the load-elongation curves. In the plots of the mechanical properties both the weight and the volume composition are plotted due to the different densities of PP (0.8982 g/cm^3) and VB (1.3875 g/cm³). Impact tests (ASTM D-256) were carried out using a Ceast pendulum on injection moulded specimens, with a cross section of $12.7 \text{ mm} \times 3.2 \text{ mm}$. The notches (depth: 2.5 mm, radius: 0.25 mm) were machined after moulding. Eight specimens were tested for each reported value both in the tensile and impact tests. Scanning electron microscopy (SEM) was carried out on the surfaces of cryogenically fractured specimens after gold coating. A Hitachi S-2700 electron microscope was used at an accelerating voltage of 15 kV.

3. Results and discussion

3.1. Phase structure

According to previous results [17,29], and as usual in most thermoplastic/LCP blends, the PP/VB blends were composed of two almost pure PP and VB amorphous



Fig. 1. Tan δ vs. temperature for PP (||), VB (—), PEMA-Zn (\bigcirc), PP/PEMA-Zn (70/30) (\bigtriangledown) and VB/PEMA-Zn (70/30) (\times).

phases. In the case of the compatibilized blends, the phase structure was tested by means of DMTA which is usually more sensitive than DSC when unclear transitions must be detected. The DMTA scans of the pure PP, VB and ionomer, as well as those of the blends of PP and VB with a 30 wt% PEMA-Zn are collected in Fig. 1. As can be seen, in the scan of the VB/PEMA-Zn blend, two clear T_g peaks appeared at the T_g s of each pure component. This indicates the presence of two practically pure phases and of full immiscibility. In the case of the PP/PEMA-Zn blends, however, as seen in Fig. 1, no significant peak could be observed at temperatures close to the T_g of pure PEMA-Zn (40°C). This was likely taking into account the chemical nature of the components, and testifies to the presence of all the PEMA-Zn in the PP-rich phase.

The possible effects of the addition of Vectra and of the ionomer on the crystallization ability and crystallinity level of PP were studied, by comparing the crystallization and melting temperatures (T_c and T_m) and heats (ΔH_c and ΔH_m) of PP with those of the binary blends, and both of them with those of the compatibilized blends. The measured T_c and T_m are collected in Table 1 and the ΔH_c and ΔH_m are shown in Fig. 2.

Table 1

Crystallization (T_c) and melting (T_m) temperatures of PP in binary and ternary blends

% VB	$T_{\rm c}$ (°C)		$T_{\rm m}$ (°C)		
	PP/VB	PP/VB(PEMA-Zn)	PP/VB	PP/VB(PEMA-Zn)	
0	106	109	164	164	
5	103	101	166	163	
15	101	100.5	161.5	163.5	
20	109	100	162.5	163	
30	105	99	163.5	163.5	

As can be seen in Table 1, the addition of VB to the PP matrix did not significantly change its $T_{\rm m}$ s. However, the effect of the VB content on the T_c values was not clear. As can be seen, at low VB contents, the decrease in T_c , and as a consequence in the crystallization rate, and the increase at high VB contents were barely significant. This was because the estimated accuracy of the measurements was $\pm 2^{\circ}$ C. Moreover, no significant T_c change was seen in a previous work [17] in our laboratory. Similar misleading effects of the presence of LCP in the crystallization and melting behaviour of the matrix are often seen. For instance, in other works, the $T_{\rm m}$ remained constant [5,6,18,36] as in this work, slightly increased [7], or decreased [40]. The $T_{\rm c}$ both decreased [40] and increased [6]. This variability of the results indicates that there is no overall effect of the LCP on the crystallization-melting behaviour of PP or at least that the effect was slight.

With respect to the effect of the PEMA-Zn addition on the $T_{\rm m}$ and $T_{\rm c}$ of the PP matrix, and as seen in Table 1, no change of $T_{\rm m}$ was observed. However, whatever the ionomer content, the $T_{\rm c}$ decreased slightly more than in the binary blends. This was probably due to a dilution of the crystallizable species induced by the presence of PEMA-Zn that impeded the transport of PP chains to the crystallizable nuclei. The interaction between PP and PEMA-Zn may be an additional reason for the smaller $T_{\rm c}$ of compatibilized blends.

The ΔH_c and ΔH_m values of the binary (empty symbols) and compatibilized (filled symbols) blends are shown in Fig. 2. The plotted PP content differs from that of the nominal composition in the compatibilized blends due to the presence of ionomer presence. As can be seen, both the ΔH_c and ΔH_m of the binary blends were below the linear rule of mixtures (dotted lines). This indicated that, as in a former PP/VB work [17], the PP crystallization was



Fig. 2. Melting heat by DSC in the second scan of the PP/VB (\triangle) and PP/VB(PEMA-Zn) (\blacktriangle), and crystallization heat after the first scan of PP/VB (\bigcirc) and PP/VB(PEMA-Zn) (\blacklozenge).

hindered by the presence of LCP. In another work [7] the degree of crystallization of PP/LCP blends hold constant. Other authors even found increases in PP crystallinity with the addition of LCP [5,6,18,37]. These differences are probably due to the different processing procedures used.

As can also be seen, the ΔH_c and ΔH_m of the compatibilized blends (filled symbols) were slightly below those of the binary blends. This indicated that the additional effect of the ionomer presence was small. This effect of the ionomer was probably due to the same reasons as those stated in the case of the T_c decrease. The decrease in crystallinity because of compatibility is often seen [23,36], although not always [37].

Thus, the blends were composed of two amorphous phases, one practically comprised pure VB and the other PP and PEMA-Zn. The $T_{\rm m}$ and $T_{\rm c}$ of the blends did not significantly change due to the presence of either VB or PEMA-Zn. The crystallinity of the PP, however, decreased approximately 17% as a consequence of the presence of VB.

3.2. Morphology

Representative surfaces of the cryogenically broken unmodified tensile specimens of all the blends were studied by SEM and are shown in Fig. 3. Fig. 3a shows an overall view of the fracture surface of the 15% VB blend. The skin of the 5, 15, 20 and 30 wt% VB blends are shown in Fig. 3b–e, respectively, and the core of the 15% VB blend is shown in Fig. 3f. Fig. 4 shows the corresponding fracture surfaces of the compatibilized blends with the same PP/VB ratios as in Fig. 2.

Figs. 3a and 4a indicate a clear skin/core morphology. The skin became deeper as the LCP content increased, as was seen in other PP/LCP blends [17,21,25]. But as seen

when Figs. 3a and 4a were compared and in opposition to that observed [25-27] in PP-g-MA modified blends, the presence of ionomer had no discernible influence on the thickness of the skin.

As can also be seen in Figs. 3b–e and 4b–e, and as is typical in other LCP blends [49–51], the fibres in the skin became thicker as the LCP content increased. This thickening also took place in the core, and as seen before [25], in the 30% LCP compatibilized blend was accompanied by a slight orientation of the dispersed particles. Moreover, when the fracture surfaces of the binary (Fig. 3) and compatibilized (Fig. 4) blends were compared, the ionomer presence gave rise to a decrease in the fibre thickness. The diameter of the fibres changed from 2 to 18 μ m in the binary blends of Fig. 3c–e to 1–10 μ m in the compatibilized blends of the same compositions.

Most of the fibres of the compatibilized blends of Fig. 4c-e were broken; This phenomenon probably hides their longer shape compared with that of binary blends. The broken particles in compatibilized blends were also seen in PP/Vectra A 900 blends [36], PP/ Vectra A 950 and PP/VB blends [28,29]. This was in contrast to the very few broken fibres (30-120 µm long) of Fig. 3c-e, and proves that most of the fibres of the compatibilized blends were longer than the critical fibre length; thus allowing the fibres to make a better contribution to the resistance to external stresses. When the surface of the dispersed spherical phases of Figs. 3f and 4f were compared, no clear difference in roughness of the surfaces appeared. Therefore it seems that the adhesion level, despite the thinner fibres of the compatibilized blends did not clearly change as a result of compatibilization. The improved contribution of the fibres will give rise to an improvement in the



Fig. 3. Cryogenically broken surfaces of (a) the whole specimen of the 85/15 blend, (b) the skin of the 95/5, (c) 85/15, (d) 80/20, (e) 70/30 blends, and (f) the core of the 85/15 blend. The photographs were obtained by SEM at an angle of 30% from the perpendicular to the surface and correspond to the binary blends.

mechanical performance of these injection moulded "in situ" composites that will be discussed in the next section.

The presence of thinner fibres, probably with higher aspect ratios as a result of compatibilization, was also seen in PP/Rodrun blends [27,37], in PP/Vectra A 950 [25,28] and in PP/VB [27,29]. However, compatibilization helps fibrillation but it also decreases the particle size. Both facts are a result of the decrease in the interfacial tension between the components of the blends. This decrease in the

particle size gives rise to the presence of a maximum compatibilization limit that was also seen in compatibilized blends of PP/Vectra A [23-28]. The limit was marked by the fact that there is a minimum droplet diameter below which fibrillation does not take place.

The fibrillation of uncompatibilized blends is not always reached in injection moulding of thermoplastics/LCP blends [52]. It is known that the viscosity ratio, defined as $\lambda = \eta_d/\eta_m$, where η_d and η_m are the viscosities of the dispersed phase and of the matrix, respectively, is the main



Fig. 4. As in Fig. 3 for the PP/VB(PEMA-Zn) compatibilized blends.

[7,8,26,49,53–55], but not the only [10,11,15,34] parameter that determines fibrillation in unmodified thermoplastic/ LCP blends. The optimum λ range for fibrillation, assuming that it is the same for all thermoplastic/LCP blends, is a matter of discussion. It was proposed [56,57] that in shear flow, drop deformation can not take place at $\lambda > 3.8$ and when $\lambda < 0.1$ fibre formation becomes difficult. In another work [53], the best fibrillar morphology was obtained when $0.5 < \lambda < 1$. However, fibrillar morphologies in thermoplastics/LCP blends have been found in the case of $\lambda < 1$ [33,55,58–60], $\lambda \approx 1$ [8,61,62] or even $\lambda > 1$ [8,21,26]. With the aim of determining which of these three conditions held in these blends, the viscosities of PP and VB at 300°C and at a shear stress of 10^3 s^{-1} , of the order of that usual in injection moulding, were determined in a Göttfert Capillary rheometer. The values were 28 and 140 Pa s, respectively, for PP and VB; this gives rise to $\lambda = 5$. However, as shown previously, clear fibrillation with an aspect ratio mostly between 20 and 25 was obtained. A discussion in terms of the quantitative values of the fibre aspect ratio obtained would probably help the discussion of the best λ value for fibrillation.

Table 2 Interfacial tensions (mN/m) of PP–VB and PP(PEMA-Zn)–VB (the estimated experimental error is $\pm 20\%$)

PP/PEMA-Zn	Interfacial tension
100/0	4.6
98/2	3.7
95/5	4.7
90/10	1.5
70/30	1.5

Apart from the value of λ , another condition for fibrillation is a Weber number greater than 1 [63]. Thus,

$$2\dot{\gamma}\eta_0 b/\sigma > 1 \tag{1}$$

where η_0 is the viscosity of the matrix, $\dot{\gamma}$ the shear rate, *b* the particle diameter and σ the interfacial tension. In order to test whether this condition was fulfilled, the interfacial tensions in both the binary and ternary blends were measured by means of the contact angles between PP and VB, and also between PP + ionomer and VB. The values obtained are shown in Table 2 for different PEMA-Zn contents in the matrix. The σ values calculated for the binary and the ternary blends, with a VB content of 30% (6% PEMA-Zn in the matrix) were, respectively, 4.6 and 4.7 mN/m. When they were used to calculate the Weber number, the values obtained (150 and 500 for compatibilized and non-compatibilized blends, respectively), agreed with the observed fibrillation.

As can also be seen in Table 2, the σ value of the binary blend (4.6) is similar to that of the ternary blend, which has a PEMA-Zn content of the order of those used in this work (between 0 and 5.7%). This indicates that although there was compatibilization in the melt state, it was not large enough to significantly influence the interfacial tension in the solid state.

Finally, considering the reasons for the observed decrease in the interfacial tension in Table 2, either an interaction between PP/(PEMA-Zn) and VB, or a chemical reaction are possible. The first possibility was tested by means of the values of the interfacial tensions of PP-VB and modified PP-VB reported in Table 2. As can be seen, the interfacial tension of PP-VB was similar to that of the PP(PEMA-Zn)-VB at PEMA-Zn contents up to 10%; i.e. those of the blends of this work, and where the properties improved. Moreover, the measured interfacial tension decreased at higher PEMA-Zn contents, but the mechanical properties did not improve in an initial work. This is experimental evidence against the possibility of interactions. This also points to the occurrence of chemical reaction during processing, since VB is a copolyester-amide and the amide groups are susceptible to reaction with the CO groups of the PEMA-Zn [43,44]. However, no significant sign of reaction was observed when the FTIR results were compared. This indicated that, if chemical reaction takes place, its extent is small.

3.3. Mechanical properties

The overall mechanical behaviour of both the binary and compatibilized blends is shown in Fig. 5 by means of the stress-strain curves of the PP/VB and PP/VB (PEMA- Zn) blends, as well as that of pure PP as a reference. As can be seen, two kinds of curves were seen. The long ductile curves that correspond to the PP and the two 5% VB blends are referred to the lower abscissa, and show yielding and homogeneous drawing until fracture. The short brittle curves correspond to the rest of the blends and are referred to the upper abscissa. This change of shape is due to the presence of both rigid and brittle VB.



Fig. 5. Stress–strain curves of pure PP (○), 95/5 (□), 95/5(1) (■), 85/15 (◊), 85/15(3) (♦), 80/20 (△), 80/20(4) (▲), 70/30 (∇) and 70/30(6) (♥).



Fig. 6. Young's modulus of the PP/VB (\bigcirc) and the PP/VB(PEMA-Zn) (\bigcirc) blends vs. the VB content. In the compatibilized blends, the LCP content of the correspondent binary blend is plotted. The modulus values of binary (\blacksquare) and compatibilized (\Box) blends of Ref. [27] and of binary (\blacktriangle) and compatibilized (\bigtriangleup) blends of Ref. [29] are also plotted. The reference dashed tie line links the modulus values of PP and VB.

As can be seen in Fig. 5, the stress-strain curves of the binary blends with VB contents higher than 5% were different from those of the corresponding compatibilized ones. The compatibilized blends did not yield and showed higher modulus and stress values, which will be discussed later. They did not show the slightly decreasing stress plateau before breaking, which was observed in the case of the binary blends. The presence of the stress plateau may be due to debonding of the fibres from the matrix [17]. To verify this possibility, the density of the tensile specimens after three different strains and subsequent unloading was measured. The density of the tensile specimens that were



Fig. 7. Tensile strength vs. VB content (symbols as in Fig. 5).

deformed in the post-elastic range to 1.2, 2.7 and 4.5% were, respectively, 0.9565, 0.9525 and 0.9474 g/cm³. The decrease in density after releasing the increasing strains supports the presence of debonding, because cavitation in the PP matrix is not possible at so small strain.

Fig. 6 shows the Young's Modulus of both the binary and compatibilized blends as a function of the volume composition, together with the values of the same blends from other studies (triangles and squares) but with maleinized PP. In all cases, the empty symbols correspond to unmodified blends and the full symbols to compatibilized blends. As can be seen in the case of the binary blends of this work (empty circles), and as is usual in thermoplastic/LCP blends and more specifically in PP/Vectra A and B blends [21,25,29], the addition of VB gave rise mostly to an overall modulus increase, with values below those predicted by the linear rule of mixtures (dotted line). The low modulus of the 95/5 blend was similar to that of pure PP, probably due to the small fibre content as a consequence of the low small LCP presence in the skin.

With respect to the effect of the ionomer on Young's modulus of this work, the higher modulus values of the compatibilized blends (full circles) indicated a larger contribution of their LCP to the mechanical response. This larger contribution was a consequence of the larger aspect ratio of the fibres of the compatibilized blend. The mean modulus increase was 20% in blends with a VB content higher than 5 wt%. Smaller modulus increases were obtained in maleinized PP/Vectra A blends [23,28]. When the modulus values of this work were compared with those of the maleinized blends of Ref. [27] (squares) at the same compatibilizer content, the uncompatibilized values (empty squares) were higher than the values in this work, but the compatibilized ones were similar. The high uncompatibilized modulus value of Ref. [27] was probably due to the thinner specimens (1.5 mm against 1.9 mm in this work) and to the higher viscosity PP (fractional MFI against high MFI PP in this work) used that will probably lead to higher fibrillation and therefore to a larger effect of the compatibilizer. Taking into account these facts, the positive effect of the addition of PEMA-Zn will be probably be higher than that of maleinization.

In the case of the values of Ref. [29] (triangles), they were slightly higher than those of this work. However, it must be taken into account that the experimental conditions used in Ref. [29] gave a modulus of pure VB of 22 GPa against 11 GPa in this work and, more importantly, that the amount of compatibilizer was higher (10%) [64]. This indicated that, under experimental conditions, the addition of PEMA-Zn should be more effective than that of PP-g-MA.

The tensile strength of both the uncompatibilized blends of this work and those of previous maleinized PP/VB blends [27,29] are shown against composition in Fig. 7. The symbols are as in Fig. 6. As can be seen, the tensile strength of the 70/30 blend was the highest of the binary compositions studied, but it was lower than the tensile strength of



Fig. 8. Ductility of PP/VB (O) and PP/VB(PEMA-Zn) (•) vs. VB content. The reference dashed tie line links the ductility values of PP and VB.

pure PP. The high ductility of PP, together with its large strain hardening, gave rise to a tensile strength higher than that of the blends. Similar behaviours have been observed by different authors for blends of PP with LCPs such as Vectra A 950 [18,28], Vectra A 130 [21], Rodrun LC 3000 [28] and VB [29]. As can also be seen in Fig. 6, the tensile strength values of the compatibilized blends with VB contents higher than 5% increased with respect to those of the corresponding PP/VB blends a mean of 32%. This behaviour was due to the finer phase dispersion of the compatibilized blends, which was seen in Fig. 3a–d, and quantifies the positive compatibilizing effect of the ionomer on the blend. These increases are higher than those seen in maleinized PP/Vectra A blends [23,28].

Fig. 7 also shows that the tensile strength of the VB blends of this work and the effect of compatibilization, are higher than those of Ref. [27] (squares) at the same compatibilizer content. The tensile strength values of this work were also slightly higher than the corresponding ones of Ref. [29] (triangles), but the increment due to the compatibilization was higher in Ref. [29] (compatibilizer amount 10% against a maximum of 5.7% in this work). However, as stated when the modulus of elasticity was discussed, under similar experimental conditions, the addition of PEMA-Zn

will be probably more effective. This is because, when the possibility of fibrillation was studied by means of Eq. (1), the diameters obtained were far from those that correspond to droplets too small to deform into fibres.

The ductility of the blends is plotted in Fig. 8. As can be seen, the 5% VB blends remained ductile both in the case of the binary and also in the compatibilized blends. This was due to the low dispersed phase content, and also took place in both PP/Vectra A blends [36] and in filled PP [65]. When the LCP content increased to 15%, the low ductility of VB gave rise to a large ductility decrease to 5 and 2% in PP/VB and PP/VB(PEMA-Zn), respectively. This is common in thermoplastic/LCP blends [5,7,18,21,23,25]. Compatibilized blends show ductility values lower than those of the binary blends. This indicated a higher contribution of VB to the ductility that, taking into account the lack of significant change of the adhesion level after compatibilization, may be attributed to the longer length of the fibres in the compatibilized blends. This negative effect of compatibilization on the ductility of LCP blends has also been found in other works [23,25].

Finally, the effects of the LCP and of PEMA-Zn on the *impact strength* are seen in Table 3. As can be seen, the high notch sensitivity of PP contrasts with the low value for VB.

Table 3

Notched and unnotched Izod impact strength (J/m) values of binary and ternary blends (the standard deviation is in parenthesis)

%VB (w)	%VB (vol.)	Unnotched Izod impact strength		Notched Izod impact strength	
		PP/VB	PP/VB(PEMA-Zn)	PP/VB	PP/VB(PEMA-Zn)
0	0	852 (88)		10.9 (0.7)	
5	3.3	531 (72)	481 (84)	7.9 (0.6)	8.7 (0.5)
15	10.2	260 (82)	221 (90)	9.7 (0.5)	10.1 (0.7)
20	13.9	125 (20)	114 (42)	10.8 (0.5)	10.8 (0.8)
30	21.7	48 (20)	37 (5)	14.0 (1.4)	11.8 (0.9)
100	100	252 (56)	177 (36)		

This gave rise to the effects of immiscibility to be seen in the unnotched impact strength of the blends. This effect was not seen in the notched blends since the notching process embrittles the specimens. The machined notch that left out the oriented skin and the thick shape of the impact specimens are likely to be the reasons for the observed low notched impact values. The slightly lower unnotched impact strength of the compatibilized blends indicated that a controlled debonding is a clearly positive deformation mechanism when high toughness and impact strength are sought. This is often seen in other multicomponent materials [66,67], and took place more clearly in the more impact resistant binary blends.

4. Conclusions

The addition of an ionomer (PEMA-Zn) to PP/VB blends, barely decreased the crystallinity of the PP in the binary blends, but produced clearly finer fibre morphology. Upon fracture, the fibres of uncompatibilized blends were pulled out from the matrix, whereas those of compatibilized blends were mostly fractured. The improved morphology, gave rise to mean increases in the modulus (20%) and tensile strength (32%) in the blends with a VB content higher than 5%, comparable with those observed in two previous works on PP/VB blends compatibilized with maleinized PP. This, together with the less favourable experimental conditions for fibrillation of this work, indicated that at similar experimental conditions and compatibilizer content, the addition of PEMA-Zn is probably more effective than the previously used maleinized PP addition.

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References

- [1] Nielsen LE, Landel RF. Mechanical properties of polymers and composites. New York: Marcel Dekker, 1994 chap. 8.
- [2] Mallick PK. Fiber reinforced composites. New York: Marcel Dekker, 1988.
- [3] La Mantia FP. Thermotropic liquid crystal polymer blends. Lancaster: Technomic, 1993.
- [4] Acierno D, La Mantia FP. Processing and properties of liquid crystalline polymers and LCP based blends. Toronto: Chemtec Publishing, 1993.
- [5] Yongcheng Y, La Mantia FP, Valenza A, Citta V, Pedretti U, Roggero A. Eur Polym J 1991;27:723–7.
- [6] Tjong SC, Liu SL, Li RKY. J Mater Sci 1995;30:353-60.
- [7] Quin Y, Brydon DL, Mather RR, Wardman RH. Polymer 1993;34:3597-604.
- [8] Postema AR, Fennis PJ. Polymer 1997;38:5557-64.
- [9] Quin Y. J Appl Polym Sci 1994;54:873-80.

- [10] Heino MT, Seppälä J. J Appl Polym Sci 1992;44:2185-95.
- [11] Sukhadia AM, Datta A, Baird DG. Int Polym Process 1992;VII:218– 28.
- [12] Quin Y, Brydon DL, Mather RR, Wardman RH. Polymer 1993;34:1196–201.
- [13] Postema AR, Fennis PJ. Macromol Symp 1996;102:399-407.
- [14] Quin Y, Brydon DL, Mather RR, Wardman RH. Polymer 1993;34:1202–6.
- [15] Quin Y. J Appl Polym Sci 1995;54:735-42.
- [16] Sabol EA, Baird DG. Int Polym Process 1997;X:124-36.
- [17] Vallejo FJ, Eguiazabal JI, Nazabal J. Polym Engng Sci 1999;39:1726–35.
- [18] Heino MT, Seppälä JV, Kapanen C. J Appl Polym Sci 1992;44:1051– 60.
- [19] Heino MT, Vainio TP, Sepälä J. Polym Polym Comp 1993;1:439-49.
- [20] Kawagoe M, Nomiya M, Qiu J, Morita M. Polymer 1997;38:113-8.
- [21] Tjong C, Liu SL, Li RKY. J Mater Sci 1996;31:479-84.
- [22] Collier MC, Baird DG. Polym Compos 1999;20:423-35.
- [23] Heino MT, Seppälä JV. J Appl Polym Sci 1993;48:1677-87.
- [24] O'Donnell HJ, Baird DG. Int Polym Process 1996;XI:257-70.
- [25] Meng YZ, Tjong SC. Polym Compos 1998;19:1-10.
- [26] Tjong C, Li RKY, Meng YZ. J Appl Polym Sci 1998;67:521-30.
- [27] O'Donnell HJ, Baird DG. Polymer 1995;36:3113-26.
- [28] Datta A, Baird DG. Polymer 1995;36:505-14.
- [29] Datta A, Chen HH, Baird DG. Polymer 1993;34:759-66.
- [30] Sabol EA, Handlos AA, Baird DG. Polym Compos 1995;16:330-45.
- [31] O'Donnell HJ, Baird DG. Polym Engng Sci 1996;36:963-78.
- [32] Handlos AA, Baird DG. Int Polym Process 1996;XI:82-93.
- [33] Kozlowski M, La Mantia FP. J Appl Polym Sci 1997;66:969-80.
- [34] Tjong SC, Chen SX, Li RKY. J Appl Polym Sci 1997;64:707-15.
- [35] Bualek-Limcharoen S, Samran J, Amornsakchai T, Meesiri W. Polym Engng Sci 1999;39:312–20.
- [36] Chiou YP, Chiou KC, Chang FG. Polymer 1996;37:4099-106.
- [37] Miller MM, Cowie JMG, Tait JG, Brydon DL, Mather RR. Polymer 1995;36:3107–12.
- [38] Holtsi-Miettinen RM, Heino, MT, Seppälä JV. J Appl Polym Sci 1995;57:573–86.
- [39] Miller MM, Cowie JMG, Brydon DL, Mather RR. Polymer 1997;38:1565-8.
- [40] Yazaki F, Tsubouchi Y, Yosomiya R. Polym Polym Compos 1993;1:183–8.
- [41] Xu QW, Man HC, Lau WS. Compos Sci Technol 1999;59:291-6.
- [42] Xu QW, Man HC, Lau WS. Polym Plast Technol Engng 1998;37:253–9.
- [43] Willis JM, Favis BD, Lavaillé C. J Mater Sci 1993;28:1749-57.
- [44] Willis JM, Caldas V, Favis BD. J Mater Sci 1991;26:4742-50.
- [45] Bastida S, Eguiazabal JI, Nazabal J. J Appl Polym Sci 1995;56:1487– 94.
- [46] Wu SJ. J Polymer interface and adhesion. New York: Marcel Dekker, 1982.
- [47] Wu S. Polym Sci, Part C 1971;34:19-30.
- [48] Wu S. Polymer science technology, 12A. New York: Plenum, 1980.
- [49] Blizard KG, Federici C, Federico O, Chapoy LL. Polym Engng Sci 1990;30:1442–53.
- [50] Crevecoeur G, Groeninckx G. J Appl Polym Sci 1993;49:839-49.
- [51] Kwon SK, Chung IJ. Polym Engng Sci 1995;35:1137-44.
- [52] Subramanian PR, Isayev AI. Polymer 1991;32:1961-8.
- [53] Heino MT, Hietaoja PT, Vainio TP, Seppälä JV. J Appl Polym Sci 1994;51:259–70.
- [54] He J, Bu W, Zhang H. Polym Engng Sci 1995;35:1695-704.
- [55] Beery D, Kenig S, Siegmann A. Polym Engng Sci 1991;31:451-8.
- [56] Wu S. Polym Engng Sci 1987;27:335–43.
- [57] Elmendorp JJ, Van der Vegt AK. In: Utracki LA, editor. Two-phase polymer systems, Quebec: Hanser, 1991 chap. 6.
- [58] Verhoogt H, Willens CRJ, Van Dam J, Posthuma de Boer A. Polym Engng Sci 1994;34:453–60.
- [59] Bretas RES, Collias D, Baird DG. Polym Engng Sci 1994;34:1492-6.

- [60] Crevecoeur G, Groeninckx G. Polym Engng Sci 1990;30:532-42.
- [61] Champagne MF, Dumoulin MM, Utracki LA. Polym Engng Sci 1996;36:1636–46.
- [62] Beery D, Kenig S, Siegmann A. Polym Engng Sci 1993;33:1548–58.
- [63] Seo Y, Hong S, Hwang SS, Park TS, Kim KU, Lee S, Lee J. Polymer 1995;36:525–34.
- [64] Baird DG, Datta A. US Patent 5,621,041, 1997.
- [65] Guerrica-Echevarría G, Eguiazabal JI, Nazabal J. Polym Degrad Stab 1996;53:1–8.
- [66] Kim JK, Mai YW. Compos Sci Technol 1991;41:333-8.
- [67] Shiao ML, Nair SV, Garrett PD, Pollard RE. Polymer 1994;35:306– 14.