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Critical inter-particle distance dependence and super-toughness in poly(butylene terephthalate)/grafted poly(ethylene-octene) copolymer blends by means of polyarylate addition

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Abstract

New super-tough poly(butylene terephthalate) (PBT) materials were obtained modifying with 10 wt% polyarylate (PAr) a PBT/maleic anhydride grafted poly(ethylene-octene) copolymer (mPEO) blend with mPEO contents from 0 to 30 wt%. PAr was fully miscible in the PBT phase. The presence of mPEO did not influence either the nature or the crystallinity of the PBT–PAr matrix. The decrease in interfacial tension and particle size upon grafting of PEO, indicated that compatibilization took place. The maximum toughness obtained was very high (impact strength more than twenty-fold that of the PBT–PAr matrix). Moreover, it was attained with only 7.5% PEO maleinized at 0.63%, and was accomplished by an increase in stiffness of the blends. The successful modification of the matrix consolidates this method as a new one to improve impact toughness. The critical inter-particle distance (τ_c) appears as the parameter that control super-toughness in these blends, and it is proposed to depend on adhesion measured by means of the interfacial tension.

Keywords: Poly(butylene terephthalate); Metallocenic poly(ethylene-octene) copolymer; Inter-particle distance

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1. Introduction

Rubber toughening is the traditional way [1,2] to improve notched impact strength; it usually leads to notched toughness increases around three-fold that of the matrix in engineering polymers such as poly(butylene terephthalate) (PBT) [3] and polyamides [4]. Recently, however, notched impact strength improvements of the order of fifteen-fold that of the matrix have been obtained by compatibilization of thermoplastic/rubber blends. This is called super-toughness. Some examples of thermoplastics in which super-toughness was achieved are PBT [5–13], polyamides [14–19], amorphous copolyester [20–22], polyoxymethylene [13], poly(phenylene sulphide) (PPS) [13], poly(vinyl chloride) [23], high density polyethylene [24] and polypropylene [25]. Compatibilization is usually carried out by means of either modification of the rubber, or the use of non-commercial compatibilizers. Although notched impact strength values (ASTM D256) up to 1000 J/m have been achieved [26–28], the usual values are between 500 and 700 J/m.

Among the variables that influence the level of toughening, many studies focused on an optimum rubber particle size [2,4,27]. However, although the maximum particle size of the rubber (1 μm) to achieve super-toughness [17] was established in Nylon 6/rubber blends, it could not be determined [5,8,11] in other blends. This was because, among other factors, the optimum particle size depended on the rubber volume fraction. Nowadays, the inter-particle distance (τ) [16] is widely accepted as the parameter that controls super-toughness, which should appear when τ is below a critical value (τ_c).

τ_c was firstly considered to be a characteristic of a given matrix [16,21,24], but subsequent works showed that it depends on extrinsic parameters such as the test temperature [13,14,21,29], the strain rate [21,30,31] and the mode of deformation [21]. The dependence of τ_c on intrinsic parameters such as crystallinity [13], type [32] and modulus [11,33] of the rubber, the ratio between the modulus of the matrix and that of the rubbery dispersed phase (E_m/E_d)

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[5,8,11] and adhesion between the components [6–9,23], is less definitive because, besides the parameter being studied, another second parameter usually changes.

The dependence of τ_c on both the modulus of the dispersed phase (E_d) and on the modulus of the matrix (E_m) has been recently ruled out [8,9]. This is despite the fact that when the crystallinity of the matrix increased in PPS/rubber blends [13] τ_c decreased. Higher crystallinity should lead to higher E_m. However, the dependence of τ_c on interfacial adhesion has been proposed [6–9,23]. The possible dependence of τ_c on E_m/E_d [5,8,11] has been postulated using plots of τ_c against E_m/E_d for a number of polymer pairs. Thus, higher adhesion should lead to smaller τ_c, and higher E_m/E_d to larger τ_c.

With some exceptions [8,13,26,34], most of the studies on super-tough blends focus on the technique employed to compatibilize the blends; both to increase toughness and to study the intrinsic parameters on which τ_c depends on. However, few investigations have been carried out on the modification of the matrix. This is with the exception of PBT/mPEO and PBT/core-shell blends where the addition of phenoxy (Ph) [8] and polycarbonate (PC) [26], respectively, improved the toughness of the blends. The addition of Ph improved both the stiffness and toughness of PBT/mPEO blends, and was proposed as new way of compatibilization [8].

The purpose of this study is to additionally examine the effects of the modification of the matrix on the toughness of the PBT/mPEO blends. Moreover, provided similar modulus values to those of Ref. [8] were obtained, a new step could be taken to improve the knowledge of the parameters which τ_c depends. With these aims, the PBT matrix of PBT/maleinized poly(ethylene-octene) (mPEO) blends [5] was modified with polyarylate (PAr). It is known [35] that PAr is miscible with PBT and that, additionally, it should led to a higher modulus of elasticity. Provided super-toughness is obtained, the comparison of the τ_c of this work with those of previous works on PBT/PEO blends [5–9], will allow us to find out whether the E_m/E_d ratio affects τ_c or not.

90–10 wt% (PBT–PAr) blend with with mPEO contents from 0 to 30 wt% were obtained by melt blending by extrusion and subsequent injection moulding. The grafting levels of mPEO used were 0 and 0.63%. The blends were characterized by dynamic mechanical analysis (DMTA), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), contact angle measurements, and scanning electron microscopy (SEM). The mechanical properties were measured by means of tensile and notched impact tests. The results on the notched impact tests and the mean particle size of the blends were used to determine τ_c. The τ_c-adhesion and τ_c–E_m/E_d pairs of these blends were compared with those collected from previously studied PBT/PEO and thermoplastic/rubber blends.

2. Experimental

PBT used in this work was CRASTIN S600F10 (DuPont), PEO was ENGAGE EG8200 (DuPont-Dow) and PAr was U-Polymer (Unitika Ltd). The proportion of octene in the PEO was 24% by weight. PBT (4 h at 120 °C), PEO (6 h at 60 °C), and PAr (24 h at 80 °C) were dried to avoid possible moisture-induced degradation reactions in an air oven (PBT and PEO) and in vacuo (PAr). The mPEO was obtained by mixing 1 wt% maleic anhydride (MA) with 0.05 wt% peroxide initiator. The amount of grafted MA in the PEO was 0.63%. The PBT/PAr ratio of the blend was always 9/1, and the mPEO content changed from 0 to 30 wt%. Thus, a 90/10(0.63) blend contents a 90% PBT–PAr matrix, and 10% PEO of which a 0.63% is grafted with MA.

Blending was carried out in a Collin twin-screw extruder-kneader (type ZK25, L/D ratio 24, screw diameter 25 mm). Due to the high viscosity of PAr, a 70–30 PBT–PAr blend was first obtained. In a second extrusion step, the PBT–PAr 70–30 blend, the appropriate amount of PBT, and the mPEO were mixed. All the blends were processed at 250 °C and at a rotor speed of 50 rpm. The rod extrudate was cooled in a water bath, and then pelletized. Injection moulding was carried out in a Battenfeld BA230E reciprocating screw injection moulding machine to obtain tensile (ASTM D638, type IV, thickness 3.2 mm) and impact (ASTM D256, thickness 3.2 mm) specimens. The screw had a diameter of 18 mm and a L/D ratio of 17.8. The melt temperature was 260 °C (190 °C for the neat PEO) and the mould temperature 15 °C. The injection rate and pressure were 7 cm^3/s and 120 MPa, respectively.

The crystalline characteristics of the neat polymers and of the blends were studied by DSC using a Perkin–Elmer DSC-7 calorimeter and indium as reference. The samples were heated from 10 to 270 °C at 20 °C/min. The crystallization and melting temperatures and the enthalpies were determined from the maxima and the areas of the corresponding peaks, respectively. The enthalpy of fusion used for PBT was 142 J/g [36]. The phase structure was studied by DMTA analysis on a Polymer Laboratories DMTA that provided the plots of the loss tangent (tan δ) and the storage moduli (E') against temperature. The scans were carried out in single cantilever mode, at a constant heating rate of 2 °C/min, and at a frequency of 1 Hz, from -130 °C to roughly 110 °C.

The possible reactions between PBT–PAr and mPEO were studied by FTIR, using a Nicolet 5 DXC spectrophotometer. Contact angle measurements were carried out on a CAM 100 goniometer (KSV) on extruded and injection-moulded specimens, using water and ethylene glycol. The interfacial tension (γ_{12}) was calculated by the two-liquid Harmonic Method [37,38] by measuring the contact angle of two liquids on the surface of both polymeric components. The mean standard deviation of the measurement was 2–3°, which gave rise to an error in the interfacial tension values of approximately 20%.

The surfaces of cryogenically fractured specimens were observed by SEM after gold coating. A Hitachi S-2700 electron microscope was used at an accelerating voltage of 15 kV. The rubber particle diameter was measured in representative zones of the cryogenically fractured specimens. The weight-average particle size, $\bar{d}_w$, was calculated from a minimum of 200 particles by means of Refs. [2,39]

$$\bar{d}_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \qquad (1)$$

where n_i is the number of particles with size d_i, assumed to be spherical. The inter-particle distance, τ, was calculated by means of the equation [16]

$$\tau = \bar{d}_w\left[\left(\frac{\pi}{6\phi}\right)^{\frac{1}{3}} - 1\right] \qquad (2)$$

where ϕ is the volume fraction of the rubber.

The tensile tests were carried out using an Instron 4301 tensile tester at a cross-head speed of 10 mm/min and at 23 ± 2 °C on specimens according to ASTM D638 type IV. The Young's modulus was determined by means of an extensometer. The yield stress and ductility, measured as the elongation at break, were determined from the load-displacement curves. The elongation at break was determined from the crosshead travel rate, assuming a gauge length of 64 mm. Izod impact tests were carried out on notched specimens (ASTM D256) using a CEAST 6548/000 pendulum. The notches (depth 2.54 mm and radius 0.25 mm) were machined after injection moulding. A minimum of five tensile specimens and ten impact specimens were tested for each reported value.

3. Results and discussion

3.1. Phase structure

The phase structure of the blends was studied by DMTA. PBT/mPEO blends were composed of two pure amorphous phases, whatever the grafting level and the mPEO content [5]. Therefore, only the effects of the presence of PAr will be discussed. Fig. 1 shows the DMTA scans of the 90–10 PBT–PAr matrix (a); of the ternary blends with 10(0) (b); 10(0.63) (c); and 30(0.63) (d) PEO contents, as well as that of neat PEO (e). As can be seen in Fig. 1a, in agreement with previous results [35], the PBT–PAr matrix showed a single T_g at approximately 63 °C that is a temperature intermediate between that of PBT (58 °C, Ref. [5]) and PAr (204 °C, Ref. [40]). This indicated the fully miscible nature of the matrix.

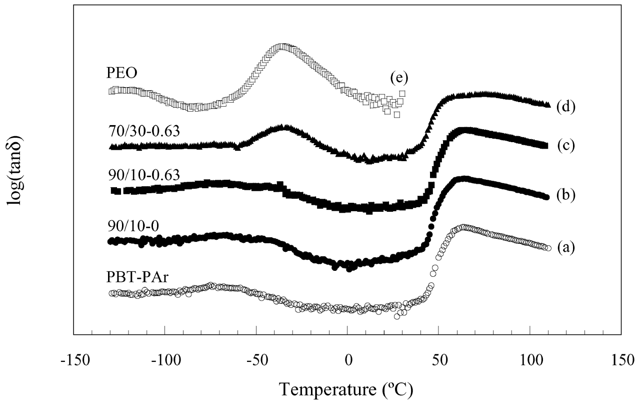


Fig. 1. DMTA scans of the 90–10 PBT–PAr matrix (a), of the blends with 10(0) (b), 10(0.63) (c), 30(0.63) (d) PEO contents and of the neat PEO (e). To aid clarity, the curves are shifted on the vertical axis.

As can also be seen in Fig. 1, the T_g of PBT–PAr, and as a consequence the nature of the matrix, did not significantly change either with the grafting level (curves b and c) or with the mPEO content (curves c and d). This indicates the presence of pure PBT–PAr matrix in all the blends studied. The T_g of PEO could be accurately determined only in the blend with 30% PEO(0.63) content, as a consequence of its low intensity. It appeared at almost the same temperature as in neat PEO, indicating the presence in all the studied blends of a pure PEO amorphous phase.

The crystalline characteristics of the blends were studied by DSC. Fig. 2 shows the DSC scans of the 90–10 PBT–PAr matrix (a), and those of the blends with 10(0) (b), 10(0.63) (c) and 30(0.63) (d) PEO contents. As can be seen, PBT crystallized during the DSC heating scan, indicating that it was not fully crystallized in the blends. Moreover, the crystallinity of PBT decreased from 33 in pure PBT to 28% in the blends. This took place whatever the mPEO content, therefore it had to be due to the presence of PAr in the PBT-rich amorphous phase, which may hinder the crystallization ability of PBT.

As can also be seen, the T_m of the matrix (227 °C) was almost that of the neat PBT (228 °C) [5,6]. Moreover, when the scans of the 90/10(0) and 90/10(0.63) blends (curves b and c) are compared and also those of the 90/10(0.63) and 70/30(0.63) blends (curves c and d), the T_m (as did the

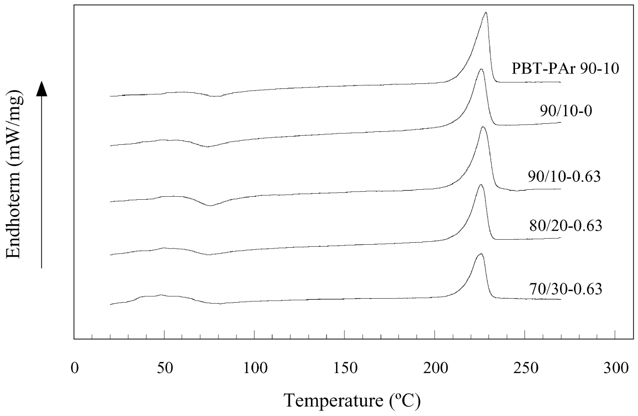


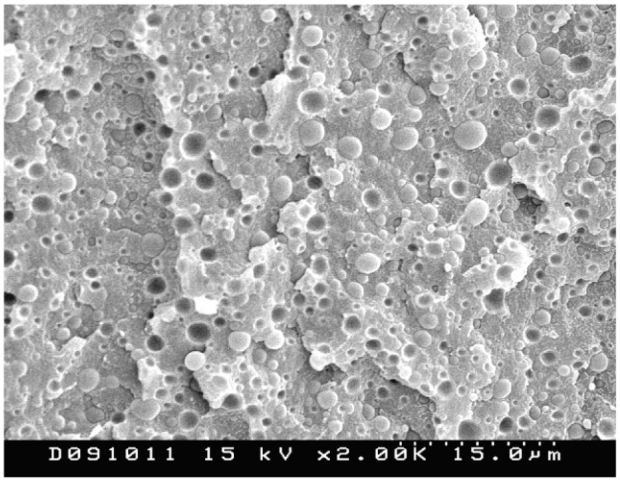
Fig. 2. DSC heating scans of the 90–10 PBT–PAr matrix (a), and of the blends with 10(0) (a), 10(0.63) (b) and 30(0.63) (d) PEO contents. To aid clarity, the curves are shifted on the vertical axis.

crystallinity of PBT) remained practically constant. This agrees with previous [5] results where neither the crystallinity level nor the T_m of PBT changed with either the grafting level or the mPEO content. The constancy of T_m indicated that the size of the crystallites did not change upon either PAr addition, grafting level of PEO or PEO addition.

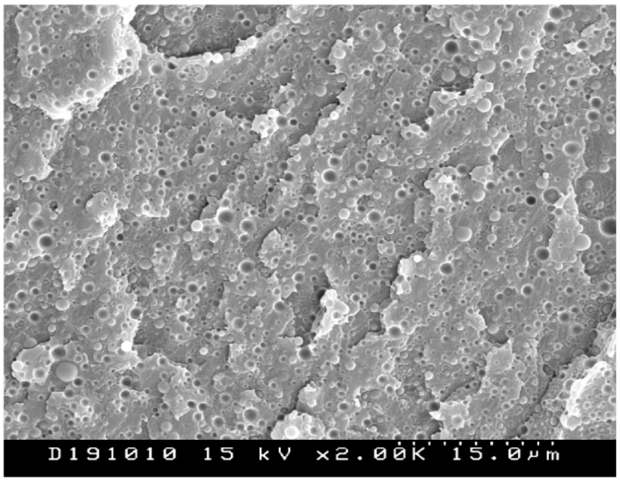
3.2. Morphology

The cryofractured surfaces of the injection moulded impact specimens were observed by SEM. A thin layer (below 150 μm) covered the specimens, but it will not be discussed because of its lack of effect on the mechanical properties. The morphology was always similar through the cross section.

Fig. 3 shows the typical cryogenically fractured surfaces of the impact specimens of the 90/10(0) (a) and 90/10(0.63) (b) blends. As can be seen, upon maleinization, the particle size clearly decreased (from 1.42 to 0.77 μm) indicating that compatibilization took place, probably as a consequence of either reactions or interactions. The occurrence of reactions was tested by FTIR. No sign of reactions was observed when the spectra of the blends were compared with that obtained by combining the weighted spectra of the pure components. This indicated that compatibilization probably took place through interactions between the PBT–PAr matrix and mPEO.



(a)



(b)

Fig. 3. Cryofractured surfaces of the impact specimens of the blends with 10(0) (a) and 10(0.63) (b) PEO contents.

In order to both prove the existence of compatibilization, and to have a quantitative measure of adhesion to discuss the τ_c results, the interfacial tension (γ_{12}) between PBT–PAr and both PEO(0) and PEO(0.63) was measured by means of the contact angle. The γ_{12} between PBT–PAr and PEO(0) was 2.00 mN/m, whereas between PBT–PAr and PEO(0.63) it was 0.60 mN/m. Therefore, the presence of mPEO decreased γ_{12}, indicating that it compatibilized the blend. If we compare this γ_{12} decrease upon compatibilization with that obtained through other compatibilization methods, the decrease observed in γ_{12} for these blends upon compatibilization with mPEO was similar to that obtained in (PBT-Ph)/mPEO [8] and PBT/PEO compatibilized with EGMA [9], but smaller [5] than that measured in PBT/mPEO blends and higher [6] than that of PBT/PEO-epoxy blends.

With respect to the effects of the PEO content on the morphology of the blends, the cryogenically fractured surfaces of the 80/20(0.63) and 70/30(0.63) blends are shown respectively in Fig. 4a and b. The morphology of the blend of Fig. 4a without PAr taken from Ref. [5] is also shown as a reference in Fig. 4c. As it is seen in Fig. 4a, the morphology of the 80/20(0.63) blend (as well as that of the blends with lower PEO contents) was rather homogeneous. However, at 30% PEO content, large rubber particles with some matrix inside were seen. The $\bar{d}_w$ (calculated by means of Eq. (1)) increased from 0.47 μm in the 95/5(0.63) blend to 1.36 μm in the 80/20(0.63). In the blend with 30(0.63)% mPEO of Fig. 4b, the complex morphology did not permit an accurate measurement of $\bar{d}_w$.

As can also be seen when Fig. 4a and c are compared, the particle size was fairly similar both in PBT/mPEO (particle size 1.30 μm) and in (PBT–PAr)/mPEO blends (particle size 1.36 μm). The main parameters that influence the particle size are both γ_{12} and the viscosity ratio $\lambda = \mu_d/\mu_m$ of the components of the blend, where μ_d and μ_m are respectively the viscosity of the dispersed phase and that of the matrix. The γ_{12} of the blends of this study (0.60 mN/m) is higher than that of the PBT/mPEO blends (0.25 mN/m) [5]. This should lead to a higher dispersed phase size. With respect to λ, that of PBT/mPEO blends was around 2. The presence of PAr should increase μ_m, because the torque of PAr at 300 °C was approximately 40 Nm [40], while that of PBT is smaller [41]. This increase in μ_m will make λ closer to unity, indicating a more effective blending and therefore a smaller particle size. Thus, the increase in particle size associated with the higher γ_{12} of this study, was probably

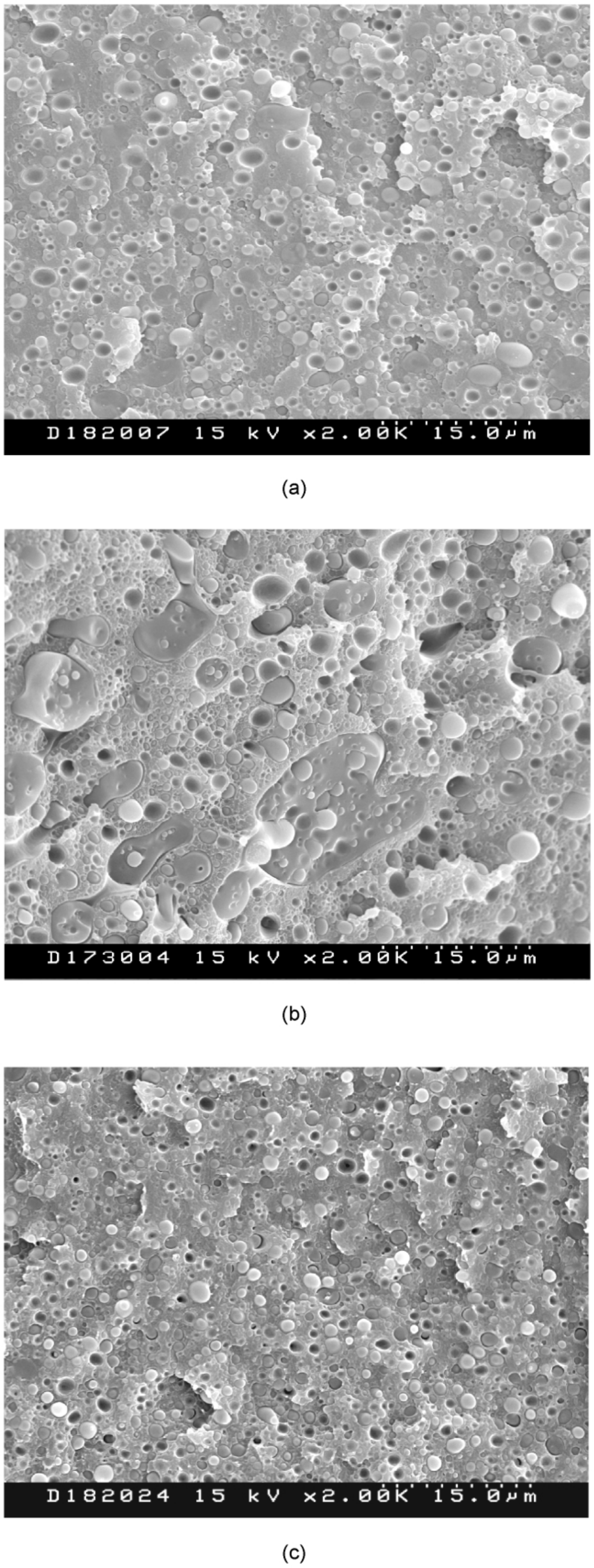


Fig. 4. Cryofractured surfaces of the impact specimens of the blends with 20(0.63) (a) and 30(0.63) (b) PEO contents. Fig. 4c corresponds to the blend with 20(0.63) content without PAr of Ref. [5].

counteracted by the decrease in the particle size because of the increase in μ_m.

As can also be seen in Fig. 4a, the surfaces of both the particles and the holes were clear, indicating that the adhesion level was poor. This is not worrying, as the fact that super toughness is achieved with apparently poor adhesion, is very common in compatibilized thermoplastic/rubber blends [5–7,16]. With respect to the larger interfacial tension of these blends with PAr compared with those without PAr, it could be seen as a negative result as regards compatibilization. However, it was seen that increasing compatibilization does not always lead to better mechanical properties if a minimum interfacial adhesion required to obtain a positive response is already present, as was found in the case of impact strength [5,9,42], and even in the case of ductility [9,12,19,43]. This will be discussed in Section 3.3.

3.3. Mechanical properties

Fig. 5 shows the Young's modulus and the yield stress as a function of PEO content of the blends both without (outline symbols, for the 10 and 20% PEO blends) and with (solid symbols) maleinization. The Young's moduli of the PBT/PEO(0.63) blends [5] (triangles) are also plotted in Fig. 5 as a reference. They were smaller than those of the blends with PAr because the lack of presence of the more rigid PAr solved in the matrix. The Young's modulus and the yield stress, as well as the rest of the mechanical properties, were plotted against the weight and volume composition due to the different densities of PBT (1.31 g/cm^3), PEO (0.87 g/cm^3) and PAr (1.21 g/cm^3). As can be seen, both the Young's modulus and the yield stress decreased when the mPEO content increased, as a consequence of the elastomeric nature of PEO. As can also be seen, the Young's modulus and the yield stress were almost the same before and after maleinization. This has been seen in other compatibilized polymer blends [4–6,8,9,44–46], and indicates that the adhesion level in the interphase has no influence on the low-strain tensile properties. Finally, the Young's moduli of the (PBT–PAr)/mPEO blends of this study were higher than those of the corresponding blends without PAr (broken line). This is due to the fact that, as could be expected and was sought in this study, the Young's modulus of both the PBT–PAr matrix and pure PAr, were higher than that of PBT. As indicated in Section 1, this will allow us to test whether E_m/E_d influences the τ_c of these thermoplastic/rubber blends.

The ductility of the blends is shown in Fig. 6 as a function of PEO content both with and without maleinization. As can be seen, the ductility of the blends remained practically constant and independent of the compatibilization level up to 10% PEO, where it started to decrease. In the case of mPEO, however, the ductility decrease started at 20% mPEO. This indicates that, although an increase in the

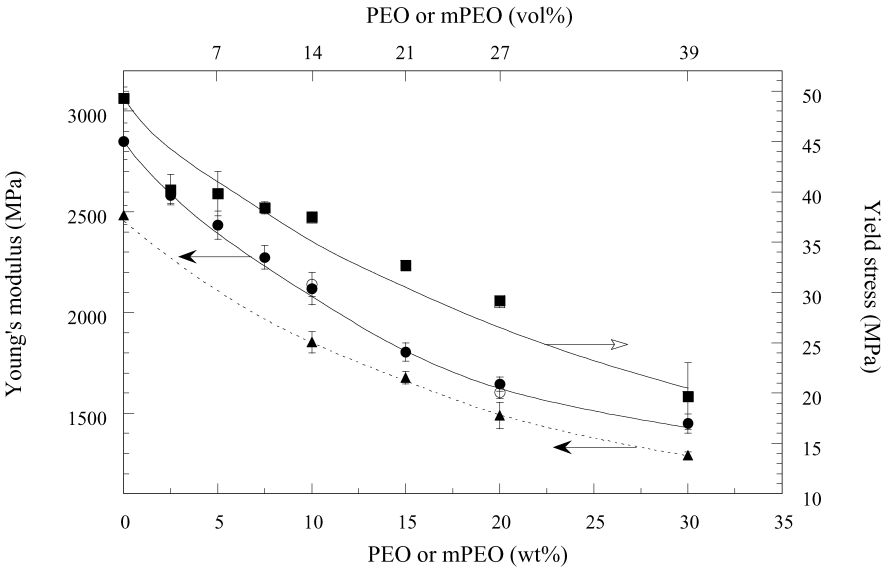


Fig. 5. Young's modulus (circles) and yield stress (squares) of the blends as a function of PEO content with (solid symbols) and without (outline symbols) maleinization. Filled triangles correspond to the Young's modulus of PBT/PEO(0.63) blends of Ref. [5].

notched impact strength was sought, compatibilization also improved ductility.

To test at what extent compatibilization in thermoplastic/rubber blends leads to ductility increases, a possible relation between the decrease in γ_{12} upon compatibilization, and increases in ductility was studied. With this aim, the PEO content at which ductility decreased in other PBT/PEO blends is given in Table 1 together with γ_{12}. The values of the blends with a modified PBT matrix, such as that of this study cannot be used, as the properties of the matrix may influence the PEO content at which fragility starts. As can be seen, the largest γ_{12} led to the ductility decrease to appear at the lowest PEO content, indicating that large γ_{12} leads to easier brittleness. The contrary did not take place, because the lowest γ_{12} did not lead to larger PEO contents for the onset of fragility. This may indicate that, as takes place in the case of impact strength [3,15,19] a minimum interfacial adhesion is necessary to obtain a positive ductility response; but provided it exists, additional adhesion increases do not lead to higher ductility.

Fig. 7 shows the impact strength of the blends as a function of PEO content both with and without maleinization. The impact strength values of PBT/PEO(0.63) blends [5] (filled squares) are also plotted in Fig. 7 as a reference. As can be seen, the impact strength of the blends without maleinization was very low. However, that of the blends with mPEO of this study increased greatly on PEO(0.63) addition, to roughly 1000 J/m. Further increases in the mPEO content did not significantly influence the impact strength. When the impact strength values of the maleinized

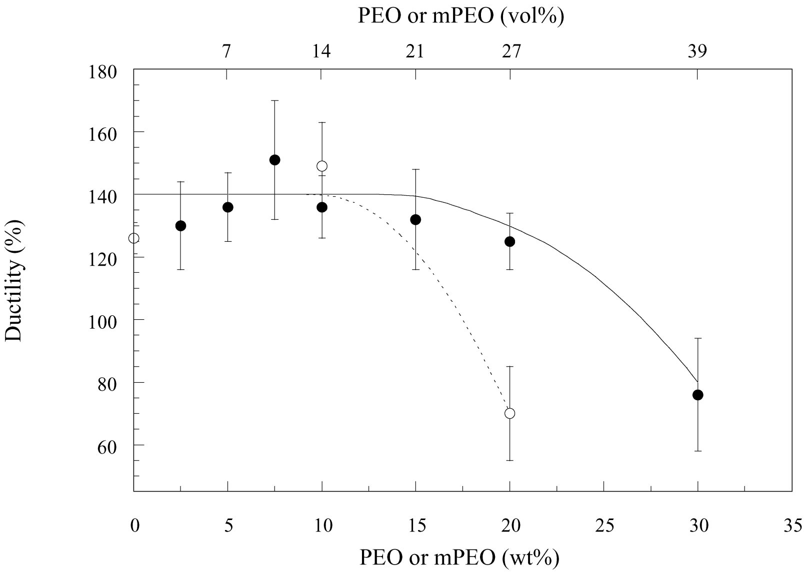


Fig. 6. Ductility of the blends as a function of PEO content with (●) and without (○) maleinization.

Table 1
PEO content at which ductility decreased and interfacial tension (γ_{12}) between compatibilized components

Blend	PEO content (%)	γ_{12} (mN/m)	Reference
PBT/PEO-epoxy	5	0.85	[7]
PBT/PEO-EGMA	20	0.59	[10]
PBT/mPEO	20	0.25	[5]

Table 2
Unbroken section of the specimen after impact testing

PEO (0.63) content (wt%)	Unbroken cross section (%)
7.5	20
10	25
15	31
20	35
30	42

blends of this study were compared with those of PBT/mPEO blends [5], the positive effect of the addition of PAr to the matrix was clear. This was because, not only the impact strength values obtained were 40% higher, but the minimum mPEO content to achieve super-toughness decreased upon PAr addition from 15 to 7.5%. This means that the increase in toughness is accomplished by an increase in stiffness (the modulus of elasticity was 2.3 GPa in the super-tough blends of this study, and 1.7 GPa in the blends without PAr).

Moreover, the reported impact strength values of Fig. 7 were minimum values, because the specimens did not break under the notched Izod impact tests. This is shown in Table 2, in which the percentage of unbroken cross section of the blends is collected. As can be seen, the proportion of unbroken cross section of the blend increased as the mPEO content increased.

The impact strength values of the (PBT–PAr)/mPEO blends of this study are among the highest in super-tough blends. To quantify this, the maximum super-toughness obtained in these blends is compared in Table 3 with those of other PBT/rubber-based blends, from the literature. The rubber content at which maximum super-toughness appeared and the modulus of elasticity of the blends are also given. As can be seen, the maximum value of impact strength corresponded to the blends of this work and to (PBT–PC)/core-shell blends [26], where incomplete fracture was not stated. The rubber content of Ref. [26] was also larger than in these blends, and therefore the modulus of elasticity was lower. Moreover, 20% of a high performance polymer such as PC was added to the matrix. As can also be seen, the third highest impact strength value also corresponded to a matrix modified blend. This demonstrates matrix modification as a new means to additional compatibilization. This is besides that obtained by either changing the rubber nature characteristics or chemical modification of already compatibilized thermoplastic/rubber blends.

The change from ductile to brittle behaviour below a critical inter-particle distance is accepted [47] to be due to plane stress conditions prevailing in microscopic scale. Fracture should start with cavitation followed by ductile tearing of the matrix. The changes from brittle to ductile behaviour can be discussed by means of the Ludwig–Davidenkov–Orowan theory [2] that predicts ductile fracture to occur when the break stress is larger than the yield stress. For this reason, in Table 4 the yield stress as well as the break stress of these blends are collected. As can be seen, the break stress is smaller than the yield stress at PEO contents equal or below 5 wt%. This indicates that fracture should be brittle. At PEO contents larger than 5 wt%, the break stress is mostly larger than the yield stress,

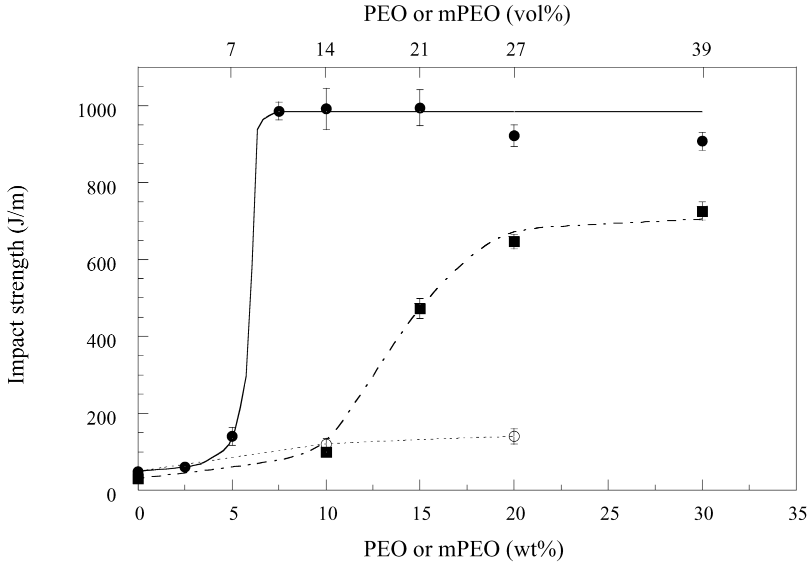


Fig. 7. Impact strength of the blends as a function of PEO content with and without maleinization. Symbols as in Fig. 6. Filled squares correspond to PBT/PEO(0.63) blends collected from Ref. [5].

Table 3
Rubber content at which maximum toughness appears, impact strength and stiffness of compatibilized PBT/rubber blends

Blends	Rubber content (wt%)	Impact strength (J/m)	Fracture	Modulus of elasticity (GPa)	Reference
(PBT–PAr)/mPEO	7.5	985	Incomplete	2.3	This work
(PBT–PC)/core-shell	20	1000	Not stated	1.7	[26]
(PBT–Ph)/mPEO	20	700	Incomplete	1.7	[8]
PBT/ABS/MGE	30	700	Not stated	1.7	[12]
PBT/PEO-EGMA	20	700	Incomplete	1.5	[10]
PBT/mPEO	20	640	Incomplete	1.5	[5]
PBT/PEO-epoxy	20	560	Incomplete	1.5	[7]
PBT/EGMA	25	605	Incomplete	1.4	[11]

indicating that fracture should be ductile/tough. Both the two behaviours and the limit between the two behaviours are in agreement with the observed impact behaviour.

The possible influence of γ_{12} on the impact strength attained is studied in Table 5, where the γ_{12} decrease upon modification and the increase in notched impact strength of the compatibilized blends with respect to both the uncompatibilized blends and the matrix are collected. As can be seen, the lowest γ_{12} decrease led to the lowest impact strength increase. However, the highest γ_{12} did not lead to the highest impact strength increase. The values of Table 5 suggest that as in the case of ductility; provided a minimum compatibilization level is attained, additional compatibilization (or γ_{12} decrease) would not improve properties. It must be noted that γ_{12} is not a direct measure of adhesion because γ_{12} is measured at ambient temperature and not in the melt. However, a low γ_{12} indicates interactions between the two components of the blends that should lead to adhesion at the interface.

3.4. Inter-particle distance

The dependence of the brittle-tough transition is usually studied in terms of either a minimum particle size or a critical inter-particle distance. In these blends, when a possible dependence on the particle size was studied, it was seen that blends with similar particle size showed both low toughness (90/10(0) blend, $\bar{d}_w = 1.42\ \mu m$) and super-toughness (80/20(0.63) blend, $\bar{d}_w = 1.36\ \mu m$). Thus, it appeared that the particle size did not control super-toughness in these blends. To find out whether τ determined the impact strength behaviour of (PBT–PAr)/mPEO blends, τ (calculated by means of Eq. (2)) is shown vs. impact strength in Fig. 8. Although the 90/10(0) blend (outline circle) has a different adhesion level, its impact strength is also plotted as a reference for low impact strength. As can be seen, a sharp increase in the impact strength of these blends took place when τ decreased below 0.43 μm. Thus, blends with $\tau > 0.45\ \mu m$ (95/5(0.63) blend) showed low impact strength, whereas blends with $\tau < 0.41\ \mu m$ (90/10(0.63) blend) showed super-tough behaviour. The τ value (0.45 μm) corresponding to the 95/5(0.63) blend was in the low impact strength region because its impact strength value was similar to that of the 90/10(0) blend. Therefore, τ_c appears as the parameter that controls the brittle-tough transition in these blends. Its critical value was considered to be 0.43 μm.

Table 4
Yield stress and break stress as a function of PEO content (average standard deviation 2–3%)

PEO (wt%)	0	2.5	5	7.5	10	15	20	30
σ_y (MPa)	49.3	44.8	41.6	38.4	37.5	32.7	29.2	19.7
σ_b (MPa)	41.4	40.2	39.8	41.4	37.8	34.7	31.2	18.5

If we compare the τ_c of this study with those of previous studies on super-tough PBT based [5,7–9,11] blends, which are collected in Table 6, we realize that the values are different. Extrinsic parameters such as test temperature or strain rate, thickness of the specimens, etc. were the same; therefore these changes in τ_c must be attributed to the change in intrinsic parameters. The intrinsic parameters that have been reported and proposed in the literature to influence τ_c, are the crystalline [13] and plasticizer [34] contents, the modulus of both the matrix and the rubber (E_m [8] and E_d [9,11], respectively), the E_m/E_d ratio [5,8,11] and adhesion [7–9]. The dependence of τ_c on E_m was neglected [8] because no correlation was seen between these parameters. With respect to E_d, although a possible dependence of τ_c on E_d was seen at low τ_c values [11], no general correlation was seen [9]. Moreover, when the τ_c–E_m and τ_c–E_d pairs of this study were added to the τ_c–E_m and τ_c–E_d figures of Refs. [8,9] respectively, the absence of correlation was confirmed. As a consequence, both E_m and E_d are ruled out as possible parameters that influence τ_c.

Considering the possible dependence of τ_c on either crystallinity [13] or plasticizer content; this is found [34], but both parameters are related to E_m/E_d (the higher the crystallinity or the lower plasticizer content, the larger is E_m/E_d). Moreover, the lack of direct influence of both parameters on τ_c is supported by the fact that, E_m/E_d is directly related to stress concentrations and thus fracture onset, but both crystallinity and plasticizer content are not. Thus, it is tentatively proposed that, the influence of both parameters on τ_c is through E_m/E_d. The influence of E_m/E_d on τ_c has also been proposed [5,8,11], since plots of τ_c–E_m/E_d pairs of a number of compatibilized thermoplastic/

Table 5
Decrease in γ_{12} on modification and corresponding increase in impact strength of compatibilized blends with respect to the uncompatibilized blends and the matrix

Blend	γ_{12} Decrease (%)	Impact strength increase with respect to that of the unmodified blend	Impact strength increase with respect to that of the matrix	Reference
PBT/PEO-epoxy	50	Four-fold	Eighteen-fold	[7]
(PBT–PAr)/mPEO	70	Ten-fold	Twenty-fold	This work
PBT/PEO-EGMA	66	Five-fold	Twenty-fold	[10]
(PBT–Ph)/mPEO	68	Six-fold	Forty-fold	[8]
PBT/mPEO	86	Six-fold	Twenty-fold	[5]

Table 6
τ_c Values of super-tough PBT/rubber blends

Blend	τ_c (μm)	References
PBT/EGMA	0.10	[11]
PBT/mPEO	0.33	[5]
(PBT–Ph)/mPEO	0.39	[8]
PBT/PEO-EGMA	0.39	[9]
(PBT–PAr)/mPEO	0.43	This work
PBT/PEO-epoxy	0.48	[7]

rubber blends were linear [5,8,11]. The $\tau_c - E_m/E_d$ values of this work followed the same trend. This strengthens the dependence of τ_c on E_m/E_d.

With respect to interfacial adhesion, its influence on τ_c was proposed [7–9] because, although some scattering was seen, the $\tau_c - \gamma_{12}$ plot showed a linear relation between both parameters [7–9]. When the $\tau_c - \gamma_{12}$ value of this work was added to this plot, it also fulfilled this, in principle, empirical relation. In the τ_c-adhesion plots of previous works [8,9], besides γ_{12}, other parameters as E_m/E_d also changed as the components of the blends changed. However, in the bibliography several new references [5,7–9] of PBT/PEO blends compatibilized with mPEO [5], epoxy [7], EGMA [9] and mPEO and phenoxy [8] are already present, and different τ_c were obtained. The studies were carried out at the same experimental conditions, and, therefore, both the extrinsic parameters and the intrinsic parameters relationated with the components (that are the same or only slightly changed) are excluded as possible reasons for the change of τ_c. Thus, the τ_c differences have to be attributed to adhesion. This influence is tested in Fig. 9, where the τ_c of PBT/PEO based blends compatibilized in different ways is plotted against adhesion measured by means of γ_{12}. As can be seen, the fairly lineal relation obtained (correlation 0.97) clearly indicated the dependence of τ_c on adhesion measured by γ_{12}.

4. Conclusions

Neither the presence of PEO nor the grafting level influenced the crystallinity of the PBT–PAr matrix or the phase nature of the two amorphous phases of the blends, which comprised a miscibilized PBT–PAr matrix and mPEO. The decrease in the interfacial tension in the blends upon grafting, measured by means of contact angle, led to a decrease in the particle size. The increase in the particle size upon PAr addition (attributed to the higher interfacial tension) appeared as counteracted by the increase in viscosity of the matrix that led to a decrease in the particle size.

The obtained super-tough PBT based (PBT–PAr)/mPEO blends were stiffer than the PBT/mPEO blends and showed toughness values among the highest in thermoplastic/rubber

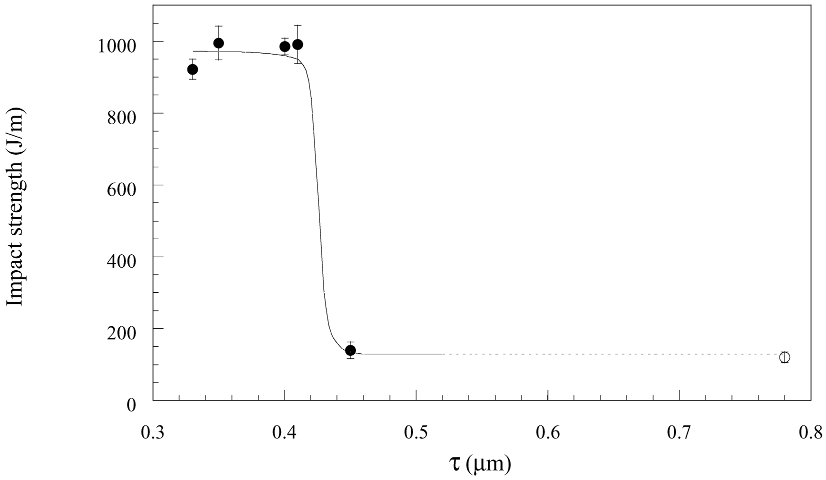


Fig. 8. Impact strength as a function of τ for (PBT–PAr)/PEO(0.63) (●) and of the 10(0) (○) blends.

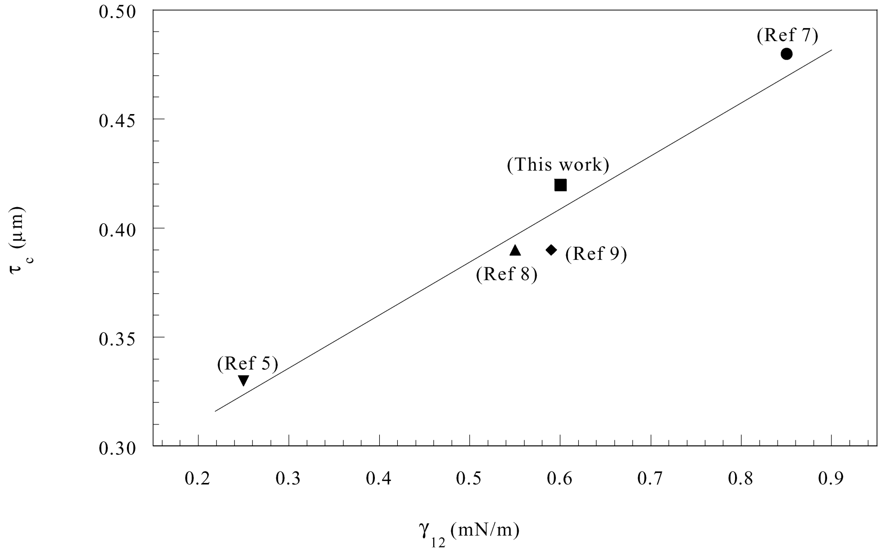


Fig. 9. τ_c as a function of adhesion measured by means of γ_{12} for PBT-based blends with PEO compatibilized with a) mPEO (▼), (b) epoxy (●), (c) EGMA (◆), (d) mPEO and Ph (▲), and (e) mPEO and PAr (■).

blends and higher than twenty-fold that of the PBT–PAr matrix with the addition of only 7.5% PEO(0.63). Thus, matrix modification is presented as a new method to improve the notched impact strength of already compatibilized thermoplastic/rubber blends.

τ is the parameter that controlled super-toughness in these (PBT–PAr)mPEO blends. The transition to super-toughness took place at $\tau_c = 0.43$ μm. The comparison of the τ_c of this work with those of other blends based on PBT and PEO (i.e. all parameters except adhesion mainly constant) showed that τ_c depended on adhesion measured by means of γ_{12}.

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References

[1] Bucknall CB. Toughened plastics. England: Applied Science Publishers Ltd; 1977.
[2] Gaymans RJ. In: Paul DR, Bucknall CB, editors. Polymer blends, vol. 2. New York: Wiley; 2000. [Chapter 25].
[3] Wang XH, Zhang HX, Wang ZG, Jiang BZ. Polymer 1997;38(7): 1569–72.
[4] Oshinski AJ, Keskkula H, Paul DR. Polymer 1992;33:268–83.
[5] Arostegui A, Gaztelumendi M, Nazabal J. Polymer 2001;42: 9565–74.
[6] Arostegui A, Nazabal J, J Appl Polym Sci to be published.
[7] Arostegui A, Nazabal J, Polym Eng Sci to be published.
[8] Arostegui A, Nazabal J. Polymer 2003;44:239–49.
[9] Arostegui A, Nazabal J. Polym J 2003;35:56–63.
[10] Arostegui A, Nazabal J. Polymer for Advanced Technologies, 2003; 14:400–8.
[11] Arostegui A, Nazabal J, J Polym Sci B (accepted for publication).
[12] Hale W, Lee J-H, Keskkula H, Paul DR. Polymer 1999;40:3621–9.
[13] Kanai H, Sullivan V, Auerbach A. J Appl Polym Sci 1994;53:524–41.
[14] Borggreve RJM, Gaymans RJ, Schuijer J, Ingen Housz JF. Polymer 1987;28:1489–96.
[15] Yu ZZ, Ou YC, Hu GH. J Appl Polym Sci 1998;69:1711–8.
[16] Wu S. Polymer 1985;26:1855–63.
[17] Majumdar B, Paul DR. In: Paul DR, Bucknall CB, editors. Polymer blends, vol. 1. New York: Wiley; 2000. [Chapter 17].
[18] Oshinski AJ, Keskkula H, Paul DR. J Appl Polym Sci 1996;61: 623–40.
[19] Chen H, Yang B, Zhang H. J Appl Polym Sci 2000;77:928–33.
[20] Yu ZZ, Lei M, Ou YC, Yang G, Hu GH. J Polym Sci B: Polym Phys 2000;38:2801–9.
[21] Wu S. J Appl Polym Sci 1988;35:549–61.
[22] Yu ZZ, Lei M, Ou Y, Yang G. Polymer 2002;43:6993–7001.
[23] Liu Z, Zhu X, Wu L, Li Y, Qi Z, Choy C, Wang F. Polymer 2001;42: 737–46.
[24] Bartczak Z, Argon AS, Cohen RE, Weinberg M. Polymer 1999;40: 2331–46.
[25] Stricker F, Thomann Y, Mülhaupt R. J Appl Polym Sci 1998;68: 1891–901.
[26] Brady AJ, Keskkula H, Paul DR. Polymer 1994;35:3665–72.
[27] Oshinski AJ, Keskkula H, Paul DR. Polymer 1992;33:284–93.
[28] Majumdar B, Keskkula H, Paul DR. Polymer 1994;35:5453–67.
[29] Jiang W, Liu CH, Wang ZG, An LJ, Liang HJ, Jiang BZ, Wang XH, Zhang HX. Polymer 1998;39:3285–8.
[30] Dijkstra K, ter Laak J, Gaymans RJ. Polymer 1994;35:315–22.
[31] Jiang W, Tjong SC, Li RKY. Polymer 2000;41:3479–82.
[32] Borggreve RJM, Gaymans RJ, Schuijer J. Polymer 1989;30:71–7.
[33] van der Sanden MCM, de Kok JMM, Meijer HEH. Polymer 1994;35: 2995–3004.
[34] Gaymans RJ, Borggreve RJM, Spoelstra AB. J Appl Polym Sci 1989; 37:479–86.
[35] Eguiazábal JI, Fernández Berridi MJ, Iruin JJ, Maiza I. J Appl Polym Sci 1996;59:329–37.
[36] Hage E, Hale W, Keskkula H, Paul DR. Polymer 1997;38(13): 3237–50.

[37] Wu S. In polymer interface and adhesion. New York: Marcel Dekker; 1982.

[38] Wu S. J Polym Sci Part C 1971;34:19–30.

[39] Irani RR, Callis CF. Particle size: measurement, interpretation and application. New York: Wiley; 1963.

[40] Bastida S, Eguiazábal JI, Nazábal J. Polymer 1996;37:2317–22.

[41] Sánchez P, Remiro PM, Nazabal J. Polymer 1993;50:995–1005.

[42] Li QF, Kun DG, Wu DZ, Lu K, Jin RG. Polym Eng Sci 2001;41: 2155–61.

[43] Hale WR, Pessan LA, Keskkula H, Paul DR. Polymer 1999;40: 4237–50.

[44] Tanrattanakul V, Hiltner A, Baer E, Perkins WG, Massey FL, Moet A. Polymer 1997;38:2191–200.

[45] Retolaza A, Eguiazábal JI, Nazabal J. Polym Eng Sci 2002;42(11): 2072–83.

[46] Torres N, Robin JJ, Boutevin B. J Appl Polym Sci 2001;81:2377–86.

[47] Bagheri R, Pearson RA. Polymer 2000;41:269–76.