Compatibilization of a Poly(butylene terephthalate)/Poly(ethylene octene) Copolymer Blends with Different Amounts of an Epoxy Resin

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ABSTRACT: New toughened poly(butylene terephthalate) (PBT) materials were obtained by melt blending with 20 wt % poly(ethylene octene) (PEO) copolymer and different levels of a difunctional epoxy resin in a twin-screw extruder followed by injection-molding. The presence of neither PEO or epoxy influenced either the phase nature of the two amorphous phases of the blends or the crystallization process of PBT, despite the slight reaction of epoxy with PBT as stated by the observed torque increases. The addition of epoxy led to a decrease in the particle size that stopped due to the concomitant viscosity increase. Supertough PBT-based blends with an impact strength more than 18-fold that of PBT were obtained without previous chemical modification of any of the blend components at 1.0 wt % epoxy contents. The interparticle distance was the parameter that controlled notched toughness in these PBT/PEO blends. The adhesion at the interphase was the parameter on which the critical interparticle distance appeared to depend. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 260–269, 2004

Key words: resins; compatibilization; mechanical properties

INTRODUCTION

Poly(butylene terephthalate) (PBT) is an important engineering thermoplastic because of its good combination of properties,[1,2] such as rigidity, solvent resistance, and high rates of crystallization. The notched impact strength of PBT is very low, but it can be improved by the incorporation of elastomers.[3–8] Until recently, the impact strength improvements with unmodified elastomers were moderate, but in the last few years, increases in the impact strength between 10- and 20-fold have been achieved with the addition of functionalized elastomers to produce the so-called supertough PBTs. This is because the carboxylic and/or hydroxyl groups of PBT can react with a functionalized rubber during melt blending to produce grafted molecules that compatibilize the blend. This technique has been used to blend PBT with modified rubbers such as poly(ethylene octene) (PEO) copolymer,[9] ethylene–propylene–diene copolymer (EPDM),[10] ethylene–propylene copolymer (EPR),[11,12] polyethylene (PE),[13] poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS),[14–18] styrene–(ethylene-*co*-butadiene)–styrene (SEBS) copolymer,[19] and ethylene olefin rubber.[19] A PBT/phenoxy (Ph) blend was also modified with maleinized PEO.[20] The most common functional groups used for grafting these rubbers were maleic anhydride[9,11,20–24] and epoxy.[10,13,21,23]

Among the variables that influence the level of toughening, the rubber content, particle size, interface characteristics, and molecular weight and crystallinity of the matrix appear to be the most important. Some theories attribute the brittle–ductile transition to a competition between fracture stress and shear yielding stress[25] and, more recently, to the optimum particle size of the rubber.[3,22,26–28] A few years ago, Wu[29] proposed a model where supertoughness in rubber toughened blends is achieved when the interparticle distance (τ) between two neighboring particles is below a critical (τ_c) value. First, it was proposed that τ is characteristic of each matrix,[29–31] but later that it depends on the strain rate,[32] mode of deformation,[30] temperature,[19,30,33,34] plasticizer,[35] modulus ratio between the matrix and the dispersed phase,[9] crystallinity of the matrix,[19] and rubber type.[36] The studies on τ as the parameter that controls toughness have focused on polyamides,[29,30,34] PBT,[9,20] high-density PE,[31] and some engineering thermoplastics.[19]

PEO copolymer is a new polyolefin elastomer developed with a metallocene catalyst by Dow Chemical Co. (Schwalbach, Germany). PEO is characterized by narrow molecular weight and homogeneous octene distributions in the macromolecule backbone. More-

over, PEO has the advantage of thermoplastic process-ability as compared with conventional polyolefin elas-tomers (EPDM and EPR). As a consequence of the elastomeric nature of PEO, it has been used as an impact modifier for polypropylene (PP)[37–40] and PE,[31,38–40] and after maleinization, for poly-amides,[41–45] amorphous copolyester,[46] and PBT.[9,20]

PBT/PEO blends have been compatibilized[9] with maleinized PEO, with obtained impact strength values of 17- and 20-fold those of PBT with 15 and 20 wt % PEO, respectively, and with intermediate modulus de-creases (30 and 37% in the 15 and 20 wt % PEO blends, respectively). PBT/Ph blends were also modified by maleinized PEO.[20] It was proposed[9,20] that the relation between the modulus of elasticity of the matrix and that of the rubber could be a factor to achieve super-toughness and that adhesion also influenced.[20] The interactions between PBT and PEO could be also mod-ified with a difunctional epoxy resin as a compatibi-lizer because under melt conditions, the end groups of PBT will probably be able to react with the epoxy groups[10,21,47,48] and the PEO could be epoxidized to introduce the polar epoxy group into its macromole-cule backbone, as in the case of EPDM.[47] As the epoxy is difunctional, it could react simultaneously with PBT and PEO.

Our purpose in this study was to examine the pos-sibility of increasing the notched impact resistance of PBT by blending it with 20 wt % PEO, with difunc-tional epoxy at different contents as a compatibilizer. All of the components were mixed together in a twin-screw extruder and then injection-molded. The blends were characterized by differential scanning calorime-try (DSC), dynamic mechanical thermal analysis (DMTA), scanning electron microscopy (SEM), contact angle measurements, Fourier transform infrared (FTIR) spectroscopy, and torque measurements. The mechanical properties were measured by means of tensile and notched impact tests. The results on the mechanical properties were compared with those ob-tained with other compatibilizers. The obtained τ val-ues were used to discuss the parameters that influence τ_c in supertough thermoplastic/rubber blends.

EXPERIMENTAL

The PBT used in this work was Crastin S600F10 (Du-Pont, Mechelen, Belgium), and the PEO rubber was Engage EG 8200 (DuPont–Dow, Norgen, Switzerland). The proportion of octene in the PEO was 24 wt %. The reactive monomer used as a compatibilizer was a di-functional epoxy resin (DER 671, Dow Chemical Co.) with the following chemical structure:

The catalyst was ethyltriphenylphosphonium bro-mide (Aldrich, Milwaukee, WI). The PBT (4 h at 120°C), PEO (6 h at 60°C), and epoxy resin (6 h at 50°C) were dried before they were processed in an air oven to avoid possible moisture-degradation reac-tions. The PEO content in the blends was 20 wt %. The epoxy content with respect to a 100% PBT/PEO blend changed from 0 to 2.0 wt %. The catalyst (0.02 wt % with respect to a 100% PBT/PEO blend) was also always added to the epoxy. PBT/PEO-1.0 indicates that the amount of epoxy in the blend was 1.0 wt %. An 80/20 blend with an epoxy content of 1.0 wt % is indicated by 1.0%.

The torques of the pure PBT and PEO and that of the PBT/PEO 80/20 blend with and without epoxy resin were measured with a Brabender plasticorder at 235°C and 50 rpm. The operation was maintained for roughly 20 min until a constant torque was obtained.

Blending was carried out in a Collin twin-screw extruder-kneader (type ZK25, L/D ratio = 24, screw diameter = 25 mm). The set-up temperature was 225°C [slightly higher melting temperature (T_m)], and the rotor speed was 50 rpm. The rod extrudate was cooled in a bath of water and then pelletized. Injec-tion-molding was carried out in a Battenfeld recipro-cating-screw injection-molding machine to obtain ten-sile (ASTM D 638, type IV, thickness = 3.2 mm) and impact (ASTM D 256, thickness = 3.2 mm) specimens. The screw had a diameter of 18 mm and an L/D ratio of 17.8. The T_m was 250°C (neat PEO = 190°C), and the mold temperature was 60°C (neat PEO = 15°C). The injection speed and pressure were 7 cm³/s and 120 MPa, respectively.

The phase structure was studied by DSC with a PerkinElmer DSC-7 calorimeter. An indium sample was used as a reference. The samples were first heated from 10 to 270°C at 20°C/min, then cooled at the same rate, and reheated. T_m and enthalpy were determined in the first heating scan from the maxima and the peak area, respectively. DMTA was performed with a Poly-mer Laboratories dynamic mechanical thermal ana-lyzer that provided the plots of the loss tangent (tan δ) and the storage modulus against the temperature. The scans were carried out in bending mode at a constant heating rate of 2°C/min and a frequency of 1 Hz from −130°C until roughly 120°C.
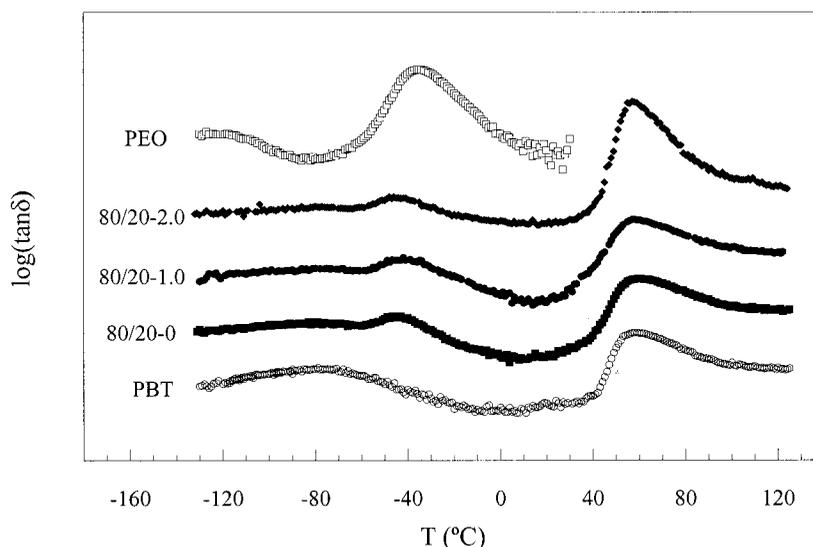
Figure 1 DMTA log(tan δ) versus temperature of neat PBT and PEO and the 80/20-*x* PBT/PEO-epoxy blends at 0, 1.0, and 2.0% epoxy contents. To aid in clarity, the curves are shifted on the vertical axis.

The possible reactions between PBT, PEO, and epoxy were studied by FTIR with a Nicolet 5 DXC spectrophotometer. The contact angle measurements were carried out on a CAM 100 goniometer (KSV) on injection-molded specimens with water and ethylene glycol. The interfacial tension was calculated by the two-liquid harmonic method[49,50] by the measurement of 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 with the following equation:

$$\bar{d}_w = \frac{\sum n_i d_i^2}{\sum n_i d_i}$$

from a minimum of 200 particles, where n is the number of particles with size d, with the assumption that the particles were spherical.

The tensile tests were carried out with an Instron 4301 tensile tester at a crosshead speed of 10 mm/min and at $23 \pm 2°C$. The mechanical properties [Young's modulus (E), tensile strength, and ductility, measured as the break strain (ϵ_b)] were determined from the load-displacement curves. E was determined with an extensometer. The elongation at break was determined from the crosshead travel rate with the assump-tion of a gauge length of 64 mm. Izod impact tests were carried out on notched specimens with a CEAST 6548/000 pendulum. The notch (depth = 2.54 mm and radius = 0.25 mm) was machined after injection-molding. A minimum of 5 tensile specimens and 10 impact specimens were tested for each reported value.

RESULTS AND DISCUSSION

Phase structure

The phase structure of PBT/PEO–epoxy blends was studied by DMTA because DSC did not provide information on the glass-transition temperature (T_g) behavior of PBT because it overlapped with the T_m of PEO. Figure 1 shows the DMTA scans of the blends with different epoxy contents and those of the pure components as a reference. As shown, the presence of epoxy did not change the position of the peaks. As a consequence, it did not influence the phase behavior of the blends. As is also shown, the secondary transition of PBT (at $-77°C$) remained constant with the epoxy content. That of PEO (at $-121°C$) could not be determined because of its low intensity. As also shown in the blends of Figure 1, the high temperature peak, which must have corresponded to the T_g of PBT, remained constant at 58°C. The T_g of PEO in the blend slightly decreased, probably due to the different processing conditions used for PEO and for the blends, as it took place in the PBT/maleinized PEO (PEO-*g*-MA),[9] (PBT–Ph)/PEO-*g*-MA,[20] and PP/PEO[38] blends. So, neither the presence of epoxy nor that of PEO or the catalyst influenced the nature of the two almost pure amorphous phases of the PBT/PEO blends.
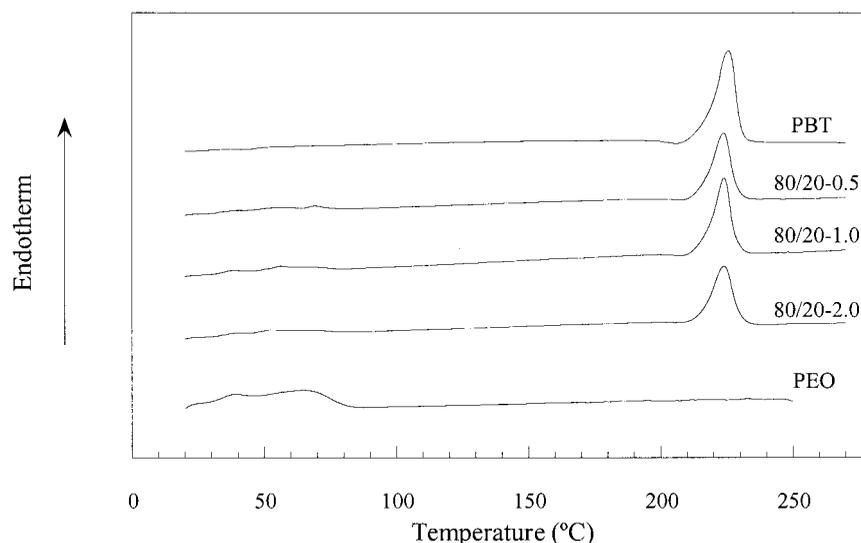
Figure 2 First DSC heating scans of the pure PBT and PEO and the 80/20-0.5, 80/20-1.0, and 80/20-2.0 blends. To aid in clarity, the curves are shifted on the vertical axis.

The melting behavior of PBT/PEO–epoxy blends was studied by DSC, and the correspondent results of the first scan are collected in Figure 2. As shown, no crystallization exotherm was observed despite the rapid cooling in the injection mold. As also shown in Figure 2, the T_m of PBT remained constant with the epoxy content and did not change with the addition of PEO. This indicates that neither the elastomeric phase nor the epoxy or catalyst disturbed the crystallization process of PBT. This result agreed with the melting behavior observed in PBT/PEO-g-MA[9] and (PBT–Ph)/PEO-g-MA[20] blends and with previous results in other semicrystalline matrix/elastomer blends.[37,39]

Chemical structure

We tested the possibility of reactions between any of the components of the PBT/PEO blend with epoxy by FTIR, comparing the FTIR spectra of the PBT/PEO blends with and without epoxy. No significant changes in the peaks characteristic of either PBT or PEO were observed between the two FTIR spectra, indicating that if chemical reactions took place, their extents were small.

However, torque measurements have been extensively used to detect the possibility of chemical reactions in the melt state.[51–53] This is because grafted or crosslinked reaction products lead to an abrupt torque increase that makes the torque behavior very sensitive to the occurrence of reactions. Therefore, the possibility of reactions was also studied by torque measurements. Figure 3 shows the torque behavior of the PBT/PEO 80/20 blends with 0, 0.5, 1.0, and 2.0% epoxy. As shown, the torque of the PBT/PEO blend decreased monotonously with mixing time. With both

0.5 and 1.0% epoxy addition, the initial torque was higher than that of the PBT/PEO blend, but then it followed the same trend as in the unmodified blend. However, the torque of the 80/20–2.0 blend, after a small initial decrease, held steady and then increased after about 5 min. The higher torque of the blends with epoxy indicated that a reaction took place between epoxy and either or both of the two components of the PBT/PEO blend. However, despite the different torque curves, the chemical structure of the 2.0% epoxy blends was rather similar to that of the two compatibilized blends. This was because the estimated time in the melt state in the extruder and in the injection machine of the blend was roughly 5 min, and the torques of the compatibilized blends after 5 min were rather similar.

To find out which component reacted with epoxy, the torques of PBT and PEO without and with 1.0% epoxy were compared, and the results are shown in Figure 4. As can be seen, the torque for PBT (outline circles) and PEO (outline triangles) decreased monotonously with the mixing time. However, in the case of PBT–epoxy (solid circles), the torque began to increase slightly after about 1.5 min, and after roughly 4 min, it remained higher than that of the neat component. The observed torque increases indicated that chemical reactions took place between the epoxy and PBT. As also shown in Figure 4, the difference between the torque curves of PEO and PEO–epoxy (solid triangles) was small and could have been due to the presence of epoxy. After mixing times longer than 10 min, the torque of PEO–epoxy decreased, probably as a consequence of thermal and/or mechanical degradation. Thus, with regard to the nonpolar nature of PEO, a reaction between PEO and epoxy was discarded.
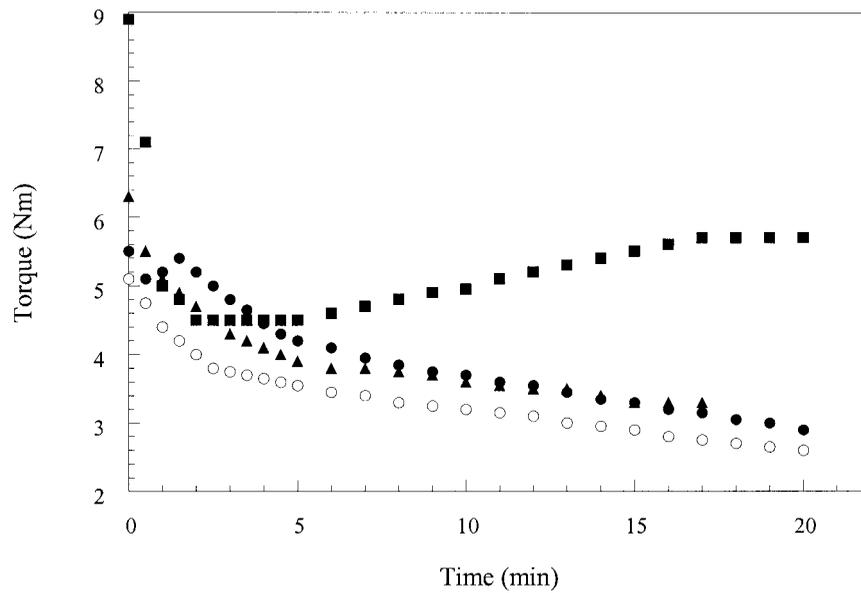
Figure 3 Torque of blending at 235°C versus time of 80/20-*x* PBT/PEO–epoxy blends with epoxy contents of (○) 0, 0.5 (▲), (●) 1.0, and (■) 2.0%.

The apparent lack of reactions shown by FTIR and the observance of reactions via torque measurements could have been due to the different processing conditions in the Brabender (where the torque was measured) and in the extruder followed by injection-molding (which produced the blends analyzed by FTIR). This was unlikely because the estimated residence time in the extruder and injection molder (roughly 5 min) was greater than that necessary for reactions to appear in the Brabender (roughly 3 min). However, the blends obtained in the Brabender after 20 min of mixing were also studied by FTIR. No sign of a chemical reaction was observed. This indicated that chemical reactions took place between the epoxy and PBT/PEO blends under the mixing conditions used but to a low extent, one not detectable by FTIR.

Morphology

The cryofractured surfaces of the injection-molded impact specimens were observed by SEM. A fine layer
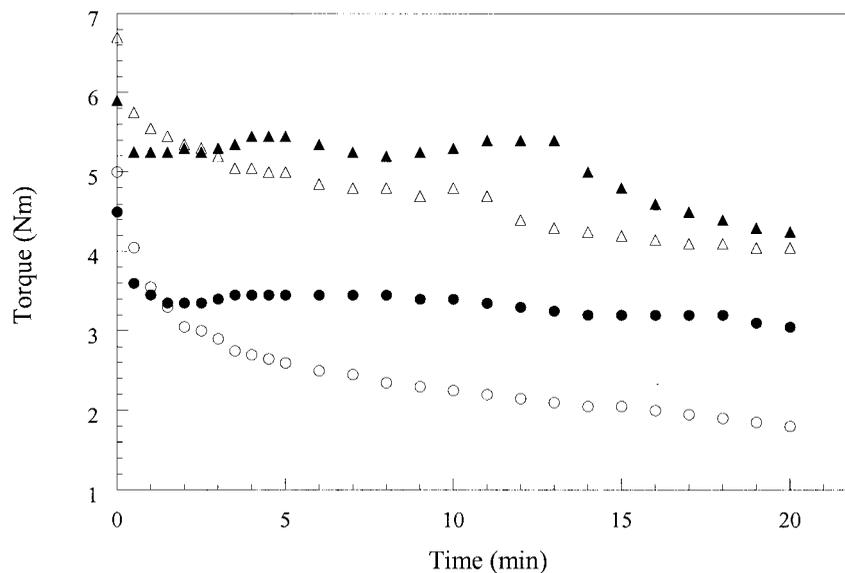
Figure 4 Torque of blending at 235°C versus time of (○, ●) PBT and (△, ▲) PEO without (outline symbols) and with 1.0% (solid symbols) epoxy content.
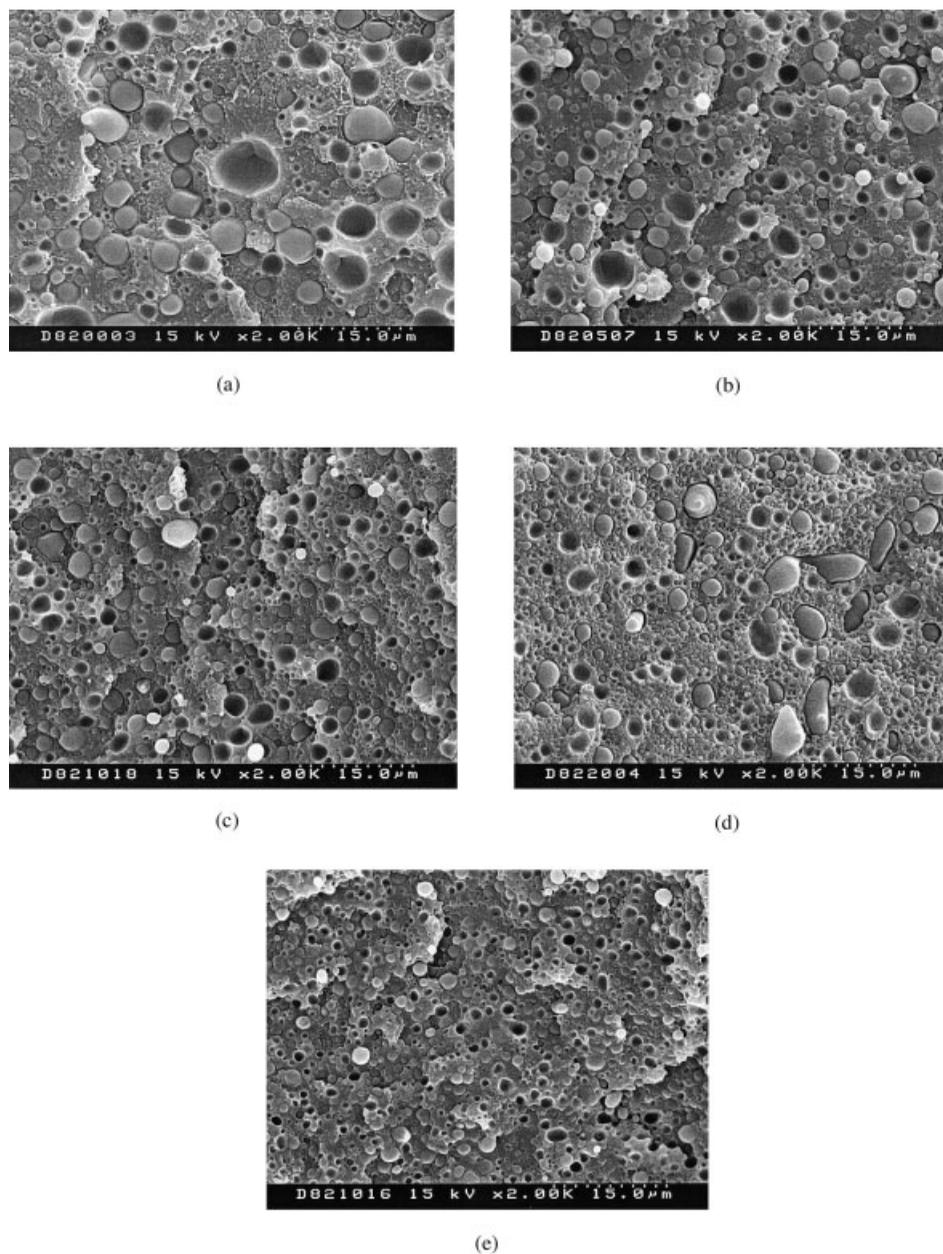
Figure 5 Cryofractured surface of the inner zone of injection-molded impact specimens of 80/20-*x* PBT/PEO–epoxy blends at (a) 0, (b) 0.5, (c) 1.0, and (d) 2.0% epoxy contents and (e) the outer zone at 1.0% epoxy content.

(ca. 100–150 μm) with elongated rubber particles covered the specimen, whatever the epoxy content. This fine layer has also been seen in PBT/PEO-*g*-MA,[9] (PBT–Ph)/PEO-*g*-MA,[20] and PET/SEBS-*g*-MA[54,55] blends. The possible effects of such a fine layer on the mechanical properties were negligible due to its low thickness, so it is not considered further in the discussion of the morphology. Across the rest of the transverse section, the morphology was slightly different close to the surface of the specimen compared to the core. This was probably due to the higher shear rate in the outer part of the specimen, close to the mold surface and relative to the core. This led to easier

coalescence in the interior and should have led to a larger dispersed particle size. Moreover, cooling was faster in the skin, and thus, the possibility of coalescence decreased. We refer to the two different zones as the outer and inner zones of the transverse section of the specimen.

The effect of the epoxy content on the morphology of the PBT/PEO 80/20 blends is seen in the SEM photographs of Figure 5. Figure 5 shows the cryogenically fractured surfaces of the inner part of the impact specimens of the blends at (a) 0, (b) 0.5, (c) 1.0, and (d) 2.0% epoxy contents. The morphology of the 80/20-1.5 blend was intermediate between those of the 80/20-1.0
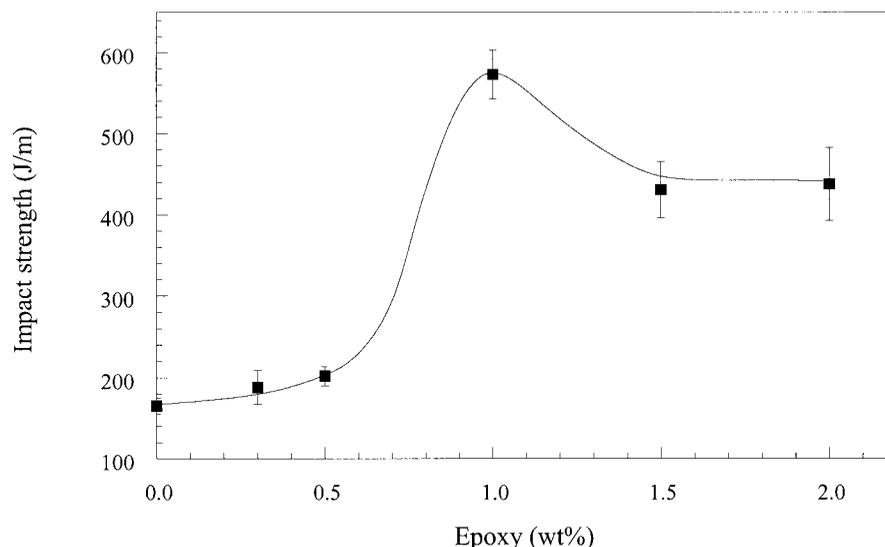
Figure 6   Impact strength of PBT/PEO 80/20 blends as a function of epoxy content.

and 80/20-2.0 blends. The morphology of the outer zone (roughly a third of the thickness of the specimen) of the 80/20-1.0 blend is shown in Figure 5(e). As shown when Figures 5(c) and 5(e) are compared, the morphology of the outside part was slightly finer than that of the inner part. This took place whatever the epoxy content, leading to the same trends as in the inner zone, so the morphology of the outer zone is not shown.

As shown in Figure 5(a,b), when 0.5% epoxy was added, the particle size clearly decreased. With the addition of 0.3% epoxy, the particle size decreased only slightly. The decrease in particle size from the binary to the 0.5% epoxy ternary blend indicated a smaller interfacial tension and that the compatibility of the PBT/PEO blend increased on the addition of epoxy. The change in the particle size was not so clear at higher epoxy contents, although the heterogeneity clearly increased.

The decrease in the rubber particle size observed up to 1.0% epoxy content agreed with the higher interactions at the interface expected as a consequence of the observed grafting reactions.[9,20,21,26,27,56,57] This is because larger epoxy contents should lead to an increase in the number of functional groups, leading to a higher probability of interaction. The similar particle size at high epoxy contents was unexpected. To study the lack of particle size decrease at 2.0% epoxy content and to confirm the stated improved compatibility of the blends, the interfacial tensions were measured by means of the contact angles between PBT and PEO and also between PBT–epoxy and PEO–epoxy. The interfacial tension between PBT and PEO was 1.70 mN/m, but between PBT–epoxy (1.0%) and PEO–epoxy (1.0%), it was 0.85 mN/m. This decrease in the interfacial tension between PBT and PEO indicated that the epoxy resin effectively compatibilized the

blends and was the reason for the observed particle size decrease. When the epoxy content further increased to 2.0%, the interfacial tension was the same as at 1.0% (0.86 mN/m). This agreed with the apparent unchanged particle size when the epoxy content increased from 1.0 to 2.0%.

This compatibility improvement had no observable effect on the apparent adhesion level between PBT and PEO. This was because the adhesion level appeared to be poor both in the binary and in the compatibilized blends because the surfaces of both the particles and the holes were clear and regular in all of the photographs of Figure 5.

Mechanical properties

E (1.5 ± 0.1 GPa) and the yield stress (32.5 ± 0.5 MPa) of the blends were independent of the epoxy content because the obtained differences were smaller than the standard deviation of the values. So, as in previous works,[9,20,26,33,55,58] the improved compatibility had no significant effect on these low-strain properties. As in the case of the modulus and the yield stress, the epoxy content had no significant influence on the ductility of the blends, which remained practically constant at a mean value of 35%, despite the improved compatibility of the binary blend that the contact angle results showed on the addition of epoxy.

The impact strength of the blends as a function of the epoxy content is shown in Figure 6. As shown, the impact strength did not change noticeably on the addition of 0.3 and 0.5% epoxy. However, as the epoxy content of the blend approached 1.0%, the impact strength increased rapidly up to at least 580 J/m. Further increases in the epoxy content led to a decrease in the impact strength to 440 J/m. This depen-

dence on the epoxy content did not appear in the case of the ductility values. This different behavior of ductility and impact strength indicated that either the adhesion needed to achieve large property values or the parameters that influenced the deformation ability of the blends in both tests or both of the these two factors operated differently in the low-speed tensile tests and in the high-speed impact tests.

The impact strength of the 1.0% blend was typical of supertough blends because it was more than 18-fold that of pure PBT and about 4-fold that of the blend without epoxy. Furthermore, the value of the 1.0% blend was a minimum value because the specimens did not break completely, and roughly 30% of the thickness of the specimen stayed unbroken. The decrease in the impact strength at high epoxy contents was attributed to the lower homogeneity observed in the particle size of these blends [Fig. 5(d)] compared with that of the 1.0% blends. The real increase obtained in the impact strength for the 1.0% blend (>580 J/m) was probably similar to the highest increase (640 J/m) obtained in PBT/PEO-*g*-MA blends that appeared at a 20% PEO content[9] and where a thinner area remained unbroken. Moreover, when the results of the two studies are compared, the simple experimental procedure used to obtain the blends in this study (direct mixing of the components by extrusion and injection) must be taken into account. This contrasts with the laborious preparation of the PEO-*g*-MA of ref. 9. The increase obtained in the impact strength of the blends of this study with respect to that of the matrix was smaller than that obtained in a modified PBT[20] but similar to those obtained in other thermoplastic/rubber blends, such as PBT/ABS,[4] and larger than those of nylon 6/PEO-*g*-MA[42] and nylon 6/epoxidized EPDM blends.[59]

All of the PBT/PEO–epoxy blends showed a stress-whitening, whose extent changed with the PEO and the epoxy content. The blends with low impact strength showed a stress-whitening zone only around the notch, whereas supertough PBT blends showed an intense stress-whitening along the whole fracture surface. Finally, it must be underlined that supertoughness was achieved under apparently poor adhesion conditions at the interface, as was shown by SEM. This indicated that as in other studies,[9,29] high adhesion was not a condition for supertoughness in these compatibilized rubber-toughened blends.

τ

It is known that the impact strength behavior is usually more related to the τ[29] than to the rubber content or particle size. For this reason, the impact strength results discussed are focused on this parameter and are also used to gain insight as to which parameters

influenced the τ_c value of the rubber-toughened thermoplastic blends.

The impact strength increase observed in thermoplastic/rubber blends should occur[29] when the τ between two neighboring particles is below τ_c. For randomly dispersed spherical particles, τ is measured as

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

where $\bar{d}_w$ is the weight-average particle diameter and ϕ is the volume fraction of rubber. The densities of PBT and PEO were 1.31 and 0.87 g/cm^3, respectively. τ_c should have been independent of the particle size and the volume fraction and characteristic of a given matrix.

To determine whether τ_c determined the impact strength behavior of the PBT/PEO–epoxy blends, the τ of these blends was calculated with eq. (1), and the values of impact strength against τ shown in Figure 7. As shown, the rubber content did not determine the impact behavior. This was because at the constant 20 wt % rubber content of the blends of this study, there were both supertough blends (1.0% epoxy) and blends with low notched toughness (0.3 and 0.5% epoxy). However, as also shown, at a τ around 0.47 μm, a sharp impact strength change took place. Thus, blends with τ values greater than 0.49 μm showed a low impact strength, whereas the same blend composition with a τ less than 0.45 μm was clearly supertough, and the impact strength was four-fold larger. Therefore, 0.47 μm was considered the τ_c of the blend of this study, and τ appeared to be the parameter that controlled toughness in these blends.

Although τ_c was considered[29] to be a characteristic of a given matrix, subsequent studies showed that the τ_c of a blend depends on extrinsic parameters, such as the test temperature,[19,30,33,34] strain rate,[30,32] and mode of deformation.[30] This could be expected as the deformation ability of both neat and multicomponent polymer materials is very dependent on these parameters. Intrinsic parameters, such as the crystallinity of the matrix,[19] type[31] or modulus[19] of the rubber, and relationship between the modulus of the matrix and that of the rubbery dispersed phase,[9,20] which apparently are less related to the deformation ability of the multicomponent polymer materials, have also been proposed as influences on τ_c. The adhesion between the matrix and the dispersed phase[20,60] has also been suggested. Studies of these factors, both extrinsic and intrinsic, that influence τ_c are useful for the selection of an appropriate rubber phase for the supertoughening of a given matrix. However, the conclusions of the studies on intrinsic parameters are not conclusive because usually, the change of one intrinsic parameter leads to the concomitant change of another. As a con-
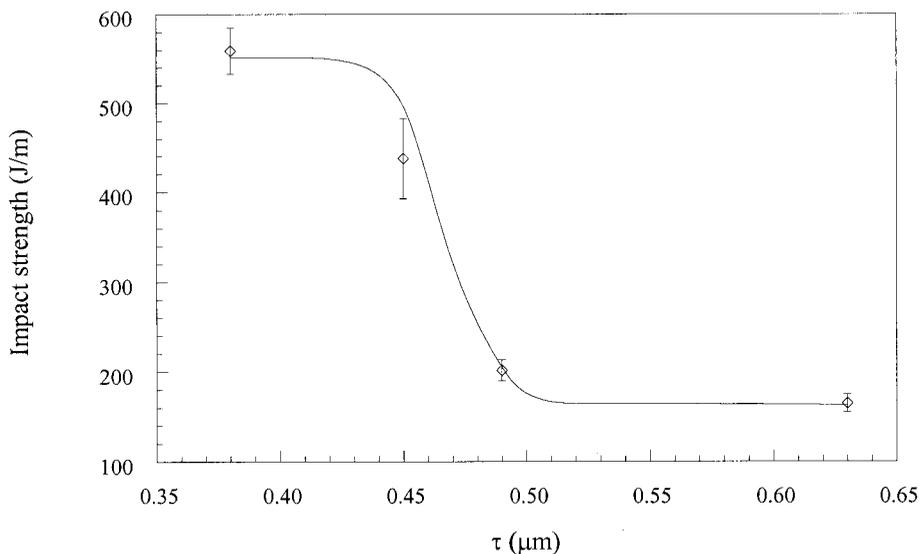
Figure 7 Impact strength of PBT/PEO–epoxy blends as a function of τ.

sequence, the observed changes in the τ_c could not unequivocally be attributed to a single parameter. For instance, when the adhesion between the matrix and the dispersed phase as a parameter that influenced τ_c, was studied in poly(vinyl chloride)/nitrile rubber (NBR) blends,[60] the adhesion was changed by means of the acrylonitrile content of NBR. However, obviously, the nature and properties of the dispersed phase also changed, and besides adhesion, this could also influence τ_c.

This study and that of ref. 9 also on PBT/PEO blends were carried out not only under the same extrinsic conditions (temperature, rate and type of deformation, etc.) and in the same experimental equipment but also under a number of intrinsic conditions. This was because the nature of the components, and as a consequence their properties, were practically the same in both works. The maleic anhydride (MAH) added to PEO in ref. 9 for supertoughness was 3 wt %, and the epoxy content of this study was 1.0%. For this reason, the comparison between the τ_c results of this work and that of ref. 9 provides an excellent opportunity to discuss the parameters on which τ depends. The τ_c of this work and that of ref. 9 were clearly different: 0.47 μm in this work and 0.33 μm in ref. 9. Therefore, given that all the extrinsic parameters, such as strain rate, temperature, and notch condition, were the same in the two studies, this clearly indicates that there was at least one parameter intrinsic to the blend that influenced τ_c.

The proposed intrinsic parameters that influence τ_c are the relationship between the modulus of the matrix and that of the rubber,[9,20] the modulus of either the rubber or the matrix, the crystallinity content of the matrix (32%), and (despite the low adhesion necessary to achieve supertoughness) the adhesion[20,60]

between the dispersed phase and the matrix. These parameters were the same in both works with the exception of adhesion. Therefore, the adhesion between the matrix and the dispersed phase must influence the τ_c value.

CONCLUSIONS

Neither the presence of PEO nor epoxy significantly influenced the crystallinity of PBT. Epoxy reacted with PBT as stated by the torque increases but to an extent not detectable by FTIR. The reaction must have also taken place in the blends, but due to its slight extent, it had no influence on the two amorphous phases of the blend, which appeared practically pure under the experimental conditions of this work.

The dispersed particle size decreased at increasing epoxy contents up to 1% epoxy content due to the decrease in the interfacial tension, indicating that epoxy compatibilized the blends. Larger epoxy contents did not change the particle size significantly (the interfacial tension also held steady), but the homogeneity of the blends decreased.

E and the yield stress of the 80/20 PBT/PEO blend did not change when epoxy was incorporated. However, impact toughness values 18-fold that of PBT, typical of supertoughness, were obtained in 80/20 PBT/PEO blends via the addition of 1.0% of unmodified commercial epoxy.

The τ_c of this study and that of a previous one on the same blend were different, and adhesion was the only parameter that differed. As a consequence, although it was not the only parameter, the τ_c value must have depended on the adhesion at the interphase.

References

1. Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G.; Kroschwitz, J. I. Encyclopedia of Polymer Science and Engineering; Wiley: New York, 1986; Vol. 12.
2. Van Berkel, R. W. M.; Van Hartigsveldt, E. A. A.; Van der Sluijs, C. L. In Handbook of Thermoplastics; Olabisi, O., Ed.; Marcel Dekker: New York, 1997; Chapter 20.
3. Gaymans, R. J. In Polymer Blends; Paul, D. R.; Bucknall, C. B., Eds.; Wiley: New York, 2000; Vol. 2, Chapter 25.
4. Hage, E.; Hale, W.; Keskkula, H.; Paul, D. R. Polymer 1997, 38, 3237.
5. Mohd Ishak, Z. A.; Ishiaku, U. S.; Karger-Kocsis, J. J Appl Polym Sci 1999, 74, 2470.
6. Brady, A. J.; Keskkula, H.; Paul, D. R. Polymer 1994, 35, 3665.
7. Benson, C. M.; Burford, R. P. J Mater Sci 1995, 30, 573.
8. Hourston, D. J.; Lane, S.; Zhang, H. X. Polymer 1995, 36, 3051.
9. Arostegui, A.; Gaztelumendi, M.; Nazabal, J. Polymer 2001, 42, 9565.
10. Wang, H. X.; Zhang, H. X.; Wang, Z. G.; Jiang, B. Z. Polymer 1997, 38, 1569.
11. Cecere, A.; Greco, R.; Ragosta, G.; Scarinzi, G.; Taglialatela, A. Polymer 1990, 31, 1239.
12. Vongpanish, P.; Bhowmick, A. K.; Inoue, T. Plast Rubber Compos Proc Appl 1994, 21, 109.
13. Takashi, A.; Angola, J. C.; Hiromu, S.; Takashi, I.; Yasushi, N. Polymer 1999, 40, 3657.
14. Hale, W.; Keskkula, H.; Paul, D. R. Polymer 1999, 40, 365.
15. Hale, W.; Keskkula, H.; Paul, D. R. Polymer 1999, 40, 3353.
16. Hale, W.; Lee, J. H.; Keskkula, H.; Paul, D. R. Polymer 1999, 40, 3621.
17. Hale, W.; Keskkula, H.; Paul, D. R. Polymer 1999, 40, 3665.
18. Lee, P. C.; Kuo, W. F.; Chang, F. C. Polymer 1994, 35, 5641.
19. Kanai, H.; Sullivan, V.; Auerbach, A. J Appl Polym Sci 1994, 53, 527.
20. Arostegui, A.; Nazabal, J. Polymer 2002, 44, 239.
21. Majumdar, B.; Paul, D. R. In Polymer Blends; Paul, D. R.; Bucknall, C. B., Eds.; Wiley: New York, 2000; Vol. 1, Chapter 17.
22. Keskkula, H.; Paul, D. R. In Rubber Toughened Engineering Plastics; Collyer, A. A., Ed. Chapman & Hall: London, 1994; Chapter 5.
23. Datta, S.; Loshe, D. J. Polymeric Compatibilizers; Hanser: Munich, 1996.
24. Grigoryeva, O. P.; Karger-Kocsis, J. Eur Polym J 2000, 36, 1419.
25. Ward, I. M. Mechanical Properties of Solid Polymers, 2nd ed.; Wiley: New York, 1983; Chapter 12.
26. Oshinski, A. J.; Keskkula, H.; Paul, D. R. Polymer 1992, 33, 268.
27. Oshinski, A. J.; Keskkula, H.; Paul, D. R. Polymer 1992, 33, 284.
28. Bucknall, C. B. In Polymer Blends; Paul, D. R.; Bucknall, C. B., Eds.; Wiley: New York, 2000; Vol. 2, Chapter 22.
29. Wu, S. Polymer 1985, 26, 1855.
30. Wu, S. J Appl Polym Sci 1988, 35, 549.
31. Bartczak, Z.; Argon, A. S.; Cohen, R. E.; Weinberg, M. Polymer 1999, 40, 2331.
32. Jiang, W.; Tjong, S. C.; Li, R. K. Y. Polymer 2000, 41, 3479.
33. Borggreve, R. J. M.; Gaymans, R. J.; Schuijer, J.; Ingen Housz, J. F. Polymer 1987, 28, 1489.
34. Jiang, W.; Liu, C.; Wang, H. Z. G.; An, L. J.; Liang, H. J.; Jiang, B. Z.; Wang, X. H.; Zhang, H. X. Polymer 1998, 39, 3285.
35. Gaymans, R. J.; Borggreve, R. J. M.; Spoelstra, A. B. J Appl Polym Sci 1989, 37, 479.
36. van der Sanden, M. C. M.; de Kok, J. M. M.; Meijer, H. E. H. Polymer 1994, 35, 2995.
37. Da Silva, A. L. N.; Rocha, M. C. G.; Coutinho, F. M. B.; Bretas, R.; Scuracchio, C. J Appl Polym Sci 2000, 75, 692.
38. Rana, D.; Lee, C. H.; Cho, K.; Lee, B. H.; Choe, S. J Appl Polym Sci 1998, 69, 2441.
39. Paul, S.; Kale, D. D. J Appl Polym Sci 2000, 76, 1480.
40. Kwag, H.; Rana, D.; Cho, K.; Rhee, J.; Woo, T.; Lee, B. H.; Choe, S. Polym Eng Sci 2000, 40, 1672.
41. Chen, H.; Yang, B.; Zhang, H. J Appl Polym Sci 2000, 77, 928.
42. Yu, Z. Z.; Ou, Y. C.; Hu, G. H. J Appl Polym Sci 1998, 69, 1711.
43. Yu, Z. Z.; Ou, Y. C.; Qi, Z. N.; Hu, G. H. J Polym Sci Part B: Polym Phys 1998, 36, 1987.
44. Yu, Z. Z.; Lei, M.; Ou, Y. C.; Hu, G. H. J Polym Sci Part B: Polym Phys 1999, 37, 2664.
45. Yu, Z. Z.; Ke, Y. C.; Ou, Y. C.; Hu, G. H. J Appl Polym Sci 2000, 76, 1285.
46. Yu, Z. Z.; Lei, M.; Ou, Y. C.; Yang, G.; Hu, G. H. J Polym Sci Part B: Polym Phys 2000, 38, 2801.
47. Jiang, W.; Wang, Z. G.; Liu, H. C.; Liang, H. J.; Jiang, B. Z.; Wang, X. H.; Zhang, H. X. Polymer 1997, 38, 4275.
48. Martin, P.; Devaux, J.; Legras, R.; van Gurp, M.; van Cuin, M. Polymer 2001, 42, 2463.
49. Wu, S. Polymer Interface and Adhesion; Marcel Dekker: New York, 1982.
50. Wu, S. J Polym Sci Part C: Polym Symp 1971, 34, 19.
51. Mondragon, I.; Nazabal, J. J Appl Polym Sci 1986, 32, 6191.
52. Kim, C. H.; Cho, K. Y.; Park, J. K. Polymer 2001, 42, 5135.
53. Liu, W. B.; Kuo, W. F.; Chiang, C. J.; Chang, F. C. Eur Polym J 1996, 32, 91.
54. Tanrattanakul, V.; Hiltner, A.; Baer, E.; Perkins, W. G.; Massey, F. L.; Moet, A. Polymer 1997, 38, 2191.
55. Tanrattanakul, V.; Hiltner, A.; Baer, E.; Perkins, W. G.; Massey, F. L.; Moet, A. Polymer 1997, 38, 4117.
56. Oshinski, A. J.; Keskkula, H.; Paul, D. R. J Appl Polym Sci 1996, 61, 623.
57. Wu, C. J.; Kuo, J. F.; Chen, C. Y.; Woo, E. J Appl Polym Sci 1994, 52, 1695.
58. Liu, Z. H.; Wu, L. X.; Kwok, K. W.; Zhu, X. G.; Qi, Z. N.; Choy, C. L.; Wang, F. S. Polymer 2001, 42, 1719.
59. Wang, X. H.; Zhang, H. X.; Jiang, W.; Wang, Z. G.; Liu, C. H.; Liang, H. J.; Jiang, B. Z. Polymer 1998, 39, 2697.
60. Liu, Z.; Zhu, X.; Wu, L.; Qi, Z.; Choy, C.; Wang, Z. Polymer 2001, 42, 737.