

Morphology Monitoring of PE/PBT Blends by Reactive Processing

I. PESNEAU, P. CASSAGNAU, A. MICHEL

Laboratoire d'Etudes des Matériaux Polymères et Biomatériaux, UMR CNRS 5627, Institut des Sciences et Techniques de l'Ingénieur de Lyon, Université Claude Bernard, Lyon I, 43, Boulevard du 11 Novembre 1918, 69 622 Villeurbanne Cedex, France

Received 4 November 1999; accepted 14 February 2001

ABSTRACT: Polyethylene (PE)/poly(butylene terephthalate) (PBT) blends were *in situ* compatibilized during a processing operation by the addition of a partially hydroxylated ethylene vinyl acetate copolymer (EVAh). This copolymer, obtained from ethylene vinyl acetate (EVA), was as compatible with PE as EVA was before modification. In the presence of EVAh, the dispersion of PBT in the PE matrix was finer, and the interfacial adhesion was improved. These results are relevant for the compatibilization of PE/PBT blends. Moreover, such blends present good toluene barrier properties. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3568–3577, 2001

Key words: polyethylene (PE); poly(butylene terephthalate) (PBT); compatibilization; reactive processing; permeability

INTRODUCTION

In recent years, polymer blends have been widely studied. They are classified into two main classes: compatible blends and incompatible blends. Previous studies indicate that compared with compatible blends, incompatible blends are useful for achieving synergism in some properties.¹ These properties are not single-value functions of the composition but may vary broadly with the morphology of the system. The ultimate behavior of incompatible polymer blends will depend, to a large extent, on the size and shape of the dispersed phase and the nature of the interface between the two phases.²

In immiscible blends, adhesion is often nearly nonexistent. This leads generally to very weak and brittle mechanical behavior. Methods to improve adhesion between two immiscible phases,

chemically and physically different, have been the subjects of considerable research activity. There exist two general routes for improving compatibility:

- Adding a compatibilizer capable of specific interactions with the blend constituents (generally a block or graft copolymer).
- Blending a suitable polymer (or functionalized polymers) capable of chemical reactions that lead to the *in situ* synthesis of a compatibilizer in the interfacial zone.

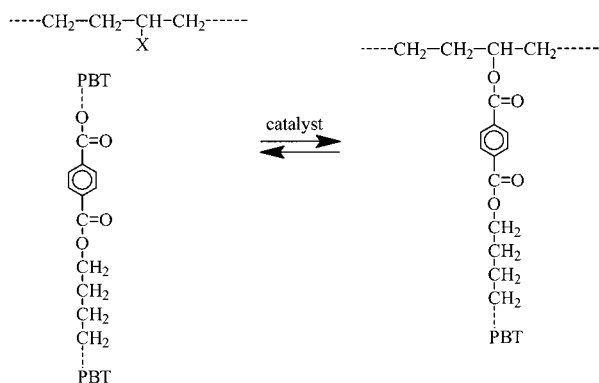
Transesterification reactions in polycondensate blends have been known for a long time.^{3,4} They generally lead to block copolymers that can act as compatibilizers. For a blend including one polymer with ester groups in the backbone and another polymer with pendant ester groups, transesterification leads to a graft copolymer that can act as a compatibilizer.^{5,6}

When chemical modification is carried out during processing operations, the reactions must be selective for side reactions to be avoided, and the

Correspondence to: A. Michel.

Contract grant sponsor: Institut Français du Pétrole.

Journal of Applied Polymer Science, Vol. 82, 3568–3577 (2001)
© 2001 John Wiley & Sons, Inc.



Scheme 1 Reactions between PBT and EVA ($X = \text{OCOCH}_3$: redistributive transesterification), PBT and EVOH ($X = \text{OH}$: alcoholysis), and PBT and EVAh ($X = \text{OCOCH}_3$ or OH : redistributive transesterification or alcoholysis): the syntheses of PBT-*g*-EVA, PBT-*g*-EVOH, and PBT-*g*-EVAh copolymers.

kinetics must be compatible with the residence time, which is typically about 1 min for a continuous process such as extrusion. Uncatalyzed transesterification reactions are not easy at temperatures lower than 280–300°C, but they can be induced and accelerated from 150°C by the presence of a catalyst.^{7–12} Transesterification reactions can be promoted by acid and base catalysts, but these compounds promote degradation at processing temperatures. A wide variety of metal alkoxides are also used (the most popular being sodium and potassium alkoxides). Recently, our work has shown that dibutyltin oxide (DBTO) reacts with ester groups to form alkoxy–acyloxy distannoxanes.^{13–15} These compounds are good catalysts for transesterification reactions.

The aim of this work was to compatibilize polyethylene (PE)/poly(butylene terephthalate) (PBT) blends. A previous study has shown that the *in situ* synthesis of a poly(butylene terephthalate)-*graft*-ethylene vinyl acetate copolymer (PBT-*g*-EVA) can compatibilize these blends. The synthesis of this copolymer was performed by a transesterification reaction between the ester groups of PBT and the ester groups of ethylene vinyl acetate (EVA; see Scheme 1).

Polyolefin/polyester blends can be used for forming high-barrier materials for hydrocarbons.^{16–18} In this case, the use of the EVA copolymer for compatibilization is unsuitable because hydrocarbons are generally good solvents of this copolymer.

This article presents the evolution of the morphology of PE/PBT blends in the presence of partially hydroxylated EVA (EVAh) and a compari-

son with the previous results obtained with EVA. The influence of EVAh on the barrier properties was studied.

EXPERIMENTAL

Reagents

PE was kindly supplied by FINA (Finathene 3802). The evolution of elastic and viscous moduli versus frequency for this polymer is represented in Figure 1(a). EVA copolymers were commercial products (Atochem). Different weight compositions of vinyl acetate (VA) units were used: EVATANE 2803 with 28% VA units, EVATANE 1020 VN3 with 9% VA units, and EVATANE 1005 VN2 with 5% VA units. These copolymers are called EVA28, EVA9, and EVA5, respectively. Poly(butylene terephthalate) (PBT) was a DuPont product (Crastin S 600). It was dried under vacuum at 80°C for at least 4 h before processing to minimize hydrolysis in the melt. Figure 1(b) represents the evolution of its viscous and elastic moduli versus frequency at 240°C.

EVAh Synthesis

Usually, ethylene vinyl alcohol (EVOH) copolymer is obtained by the hydrolysis of EVA copolymer. Lambla and coworkers^{19–22} studied the transesterification reaction of pendant ester groups by paraffinic alcohols introduced into the molten polymer (alcoholysis reaction). Different alcohols and catalysts were tested. In our case, 2-ethyl 1-hexanol and DBTO were used as the alcohol and catalyst, respectively. These two compounds were commercial products (Aldrich). The reaction was carried out in a single processing step by discontinuous mixing in an internal mixer (Haake plasticorder equipped with a Rheomix 600 internal mixer). EVA9 (40 g; ca. 0.062 mol of ester groups), 0.062 mol of the alcohol, and 0.0031 mol of the catalyst were mixed before use and poured rapidly into the mixing chamber of the internal mixer. The temperature of the mixer chamber was set at 180°C, and the rotation speed was 50 rpm. The molten medium was mixed for 10 min; then, the blend was solubilized in hot tetrachloroethane and precipitated in methanol. We repeated this treatment twice to eliminate unreacted alcohol and 2-ethyl 1-hexyl acetate obtained as byproducts.

Liquid ¹H-NMR spectroscopy was carried out with a Bruker AC250 apparatus at 250 MHz. The

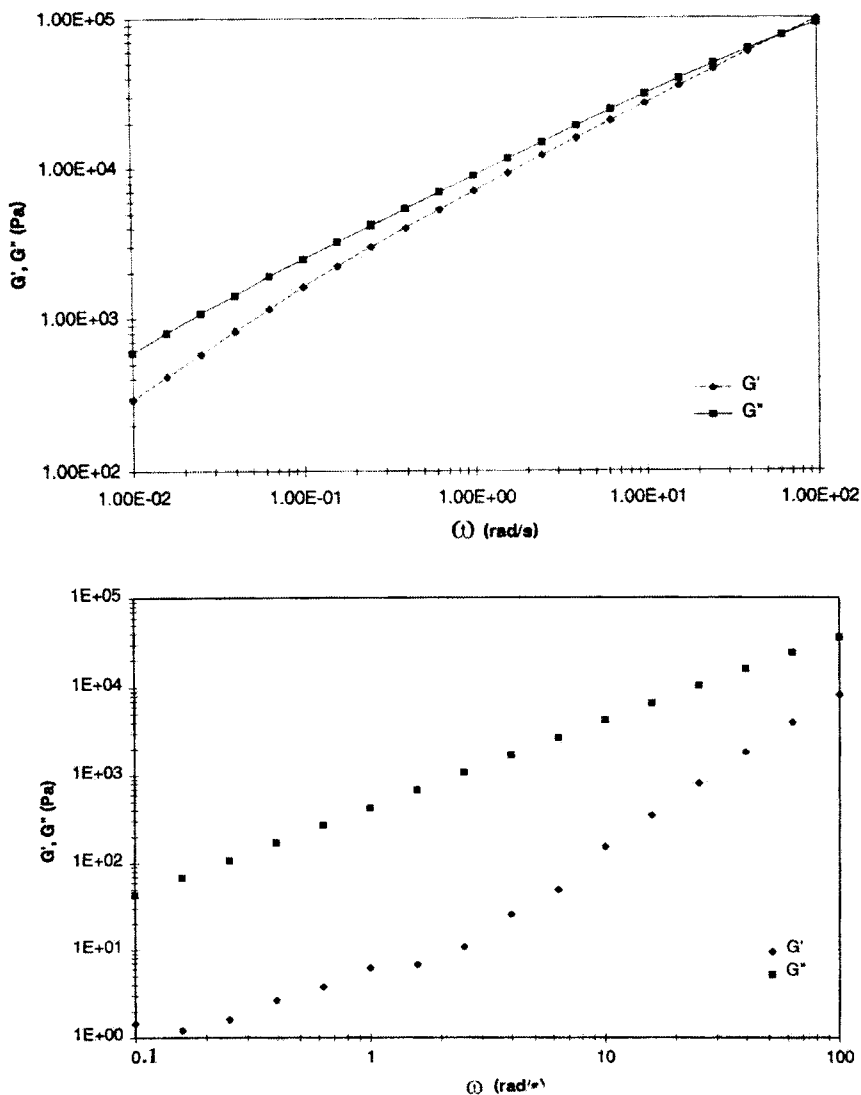


Figure 1 Elastic and viscous moduli versus frequency at 240°C for (a) pure PE and (b) pure PBT.

spectra were carried out in a tetrachloroethylene (TCE)/deuterated benzene (C_6D_6) mixture (2/1 v/v) at 373 K. Chemical shift values (δ , ppm) are given in reference to internal tetramethylsilane. The 1H -NMR spectrum of EVAh shows a resonance at 4.9 ppm assigned to the proton in the α position of the $-O-CO-CH_3$ group and a resonance at 3.5 ppm assigned to the proton α in the $CH\alpha-OH$ group. The integrals of those resonances give the extent of the reaction [ca. 50%; see Fig. 2(a)]. The ^{13}C -NMR spectrum confirms the presence of these two carbons with different substituents [$\delta = 74$ ppm for the acetate group and $\delta = 71.8$ ppm for the OH group; Fig. 2(b)].

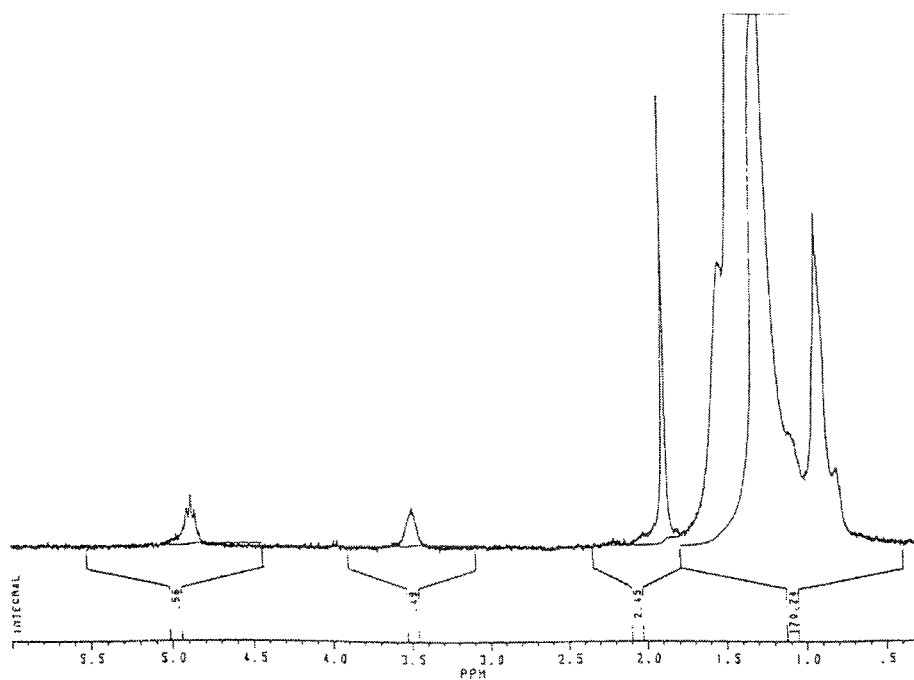
Blend Preparation

PE/EVA, PE/EVAh, and PE/PBT blends with (or without) EVA, EVAh, and catalyst were per-

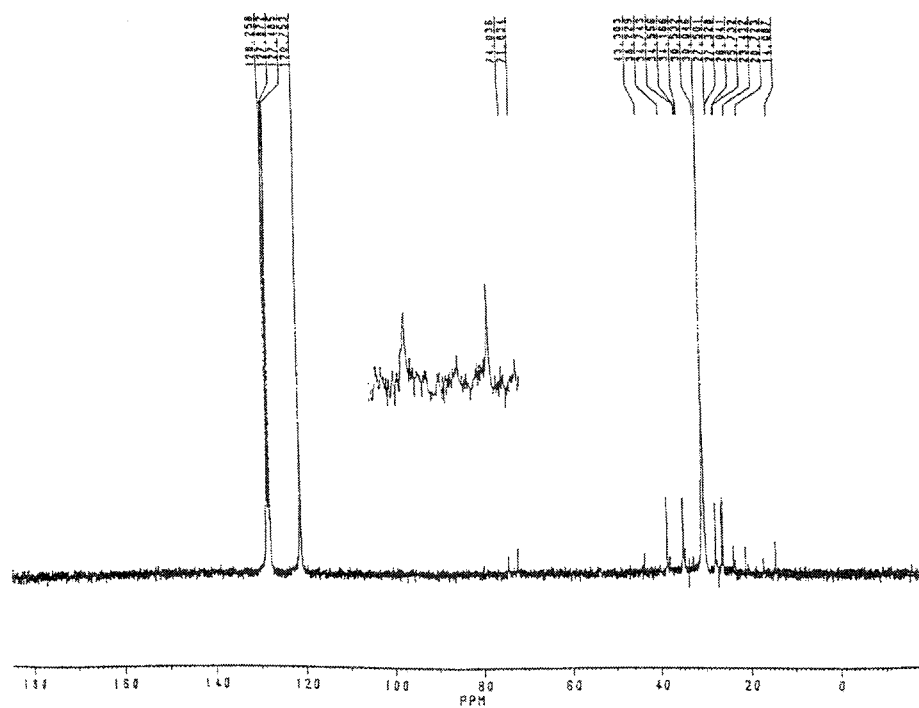
formed in the internal mixer. Samples (50 g) were mixed for 10 min at 230°C and 50 rpm.

Microscopy

The morphology of the blends was observed by scanning electron microscopy (SEM; JEOL JSM35). The samples were fractured in liquid nitrogen and then vacuum-metalized before analysis. In some cases, we extracted PBT, EVA, and EVAh before analysis to increase the contrast with the matrix (PE). In these cases, after being fractured in liquid nitrogen, the samples were put in a solution of phenol/tetrachloroethane (1/1 w/w) for the extraction of PBT and EVAh and in toluene for the extraction of EVA at 50°C over 24 h. These treatments removed all the nodules of the dispersed phases on the surfaces of the samples.



(a)



(b)

Figure 2 NMR spectra of EVAh in TCE/ C_6D_6 : (a) ^1H spectrum and (b) ^{13}C spectrum.

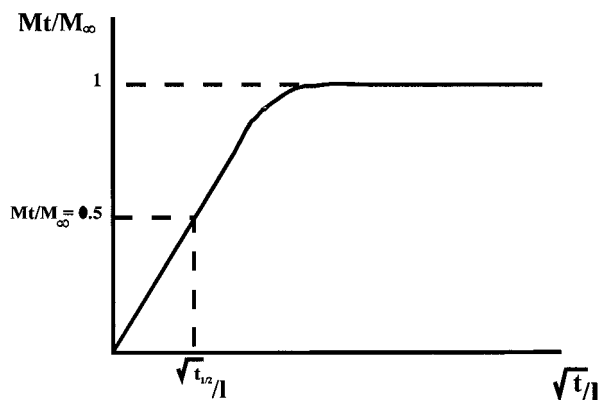


Figure 3 Permeability experiment: relative weight gain versus $t^{1/2}/L$.

Permeability

Solubility (S), diffusivity (D), and permeability (P) coefficients of toluene were determined. For this purpose, we studied the sorption behavior as a function of time. Samples of the different blends with known geometry (disc 38 mm in diameter and ca. 1.8 mm thick) were put in toluene at room temperature ($21 \pm 1^\circ\text{C}$). Data are plotted as the relative weight gain or loss, M_t/M_∞ , versus $t^{1/2}/L$ (Fig. 3), where M_t and M_∞ are the cumulative masses sorbed or desorbed at time t and time $t = \infty$, respectively, and L is the thickness of the sample; M_∞ is obtained in the practical sense when there is no sensible change in weight over a time interval comparable to the interval required to obtain that value.^{23–25}

From the second Fick equation, the mass sorbed by the sample at time t is given by eq. (1):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(-\frac{D(2n+1)^2\pi^2 t}{L^2}\right) \quad (1)$$

When the process is Fickian, the value t/L^2 for which $M_t/M_\infty = 0.5$ is given by eq. (2)

$$\left(\frac{t}{L^2}\right)_{1/2} = -\frac{1}{\pi^2 D} \ln\left(\frac{\pi^2}{16} - \frac{1}{9}\left(\frac{\pi^2}{16}\right)^9\right) \quad (2)$$

and, approximately,

$$D = 0.4939 \left(\frac{L^2}{t}\right)_{1/2} \quad (3)$$

S is obtained from the cumulative masses sorbed at equilibrium and $P = DS$.^{23–25}

Mechanical Properties

Mechanical properties were studied on compression-molded test specimens (type H3) with a universal tensile tester (Instron 1175) at a speed of 5 cm/min at room temperature (23°C).

RESULTS AND DISCUSSION

EVAh presents alcohol and ester groups that can promote the formation of PBT-*g*-EVAh through alcoholysis and redistributive transesterification reactions.

However, for the compatibilization of PE/PBT blends, EVAh chains have to present a partial miscibility with PE. In the first part of our work, we studied PE/EVA blends and their miscibility for different VA contents by SEM. We also verified that EVAh presents partial miscibility with PE. In a second part, PBT-*g*-EVAh copolymers were synthesized in PE/PBT blends. Its influence on the PE/PBT blend morphology and barrier properties was studied and compared with the influence of PBT-*g*-EVA.

Morphology Study

PE/EVA and PE/EVAh Compatibility

This study was carried out with SEM analysis. Ray and Khastgir²⁶ showed with rheological and morphological studies and DSC experiments that EVA28 presents partial miscibility in the amorphous phase with PE. Indeed, dynamic mechanical analysis shows an evolution of the α -relaxation temperatures associated with the glass transition of pure components. However, crystalline phases are incompatible and crystallize separately.

EVA with different contents of VA units can be found. Previous NMR studies carried out in our laboratory have shown that VA units are essentially isolated in EVA28, EVA9, and EVA5.²⁷ As a result, a decrease in the VA content leads to an increase in the number of ethylene units ($\text{CH}_2\text{—CH}_2$)_{*x*} between two VA units [$\text{CH}_2\text{—CH}(\text{OCOCH}_3)$]: *x* is about 8 for EVA28, 31 for EVA9, and 57 for EVA5. This evolution influences the miscibility between PE and EVA.

SEM micrographs were recorded on 80/20 PE/EVA blends with different EVAs (EVA28, EVA9,

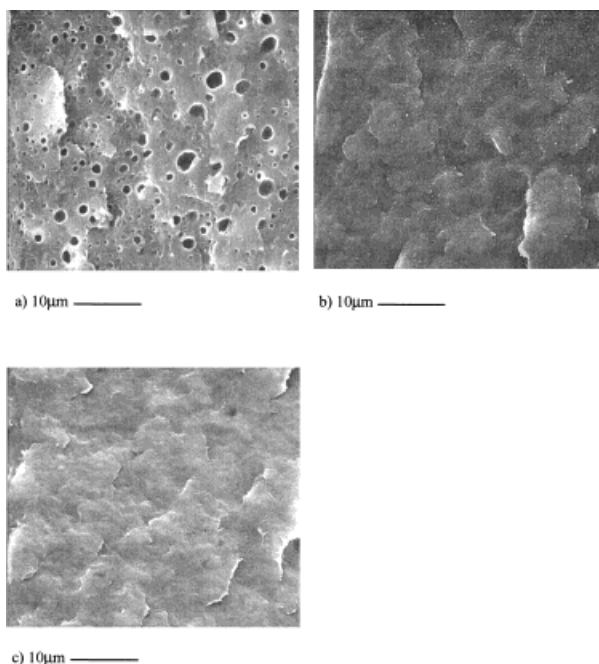


Figure 4 SEM micrographs (original magnification, 2000 \times) of 80/20 PE/EVA blends after the extraction of EVA: (a) EVA28, (b) EVA9, and (c) EVA5.

and EVA5). The micrographs presented in Figure 4 were obtained after the extraction of EVA. Blends with EVA9 and EVA5 led to the same results: the micrographs do not reveal the existence of two phases at the magnification used. Only the PE/EVA28 blend clearly presents two phases, EVA28 being the dispersed phase and PE the matrix. Micrographs of this blend reveal the presence of holes where EVA nodules were localized before extraction. The miscibility between PE and EVA9 and EVA5 is greater than that between PE and EVA28. These results show that the VA content has a great influence on PE/EVA miscibility.

To optimize both the miscibility of the chain with the PE phase and the transesterification reaction between EVAh and PBT, we synthesized EVAh from EVA9. The partial miscibility of this polymer with PE was studied by microscopy on an 80/20 PE/EVAh blend. Before SEM analysis, EVAh was extracted with phenol/tetrachloroethane. Figure 5 shows an example of the results obtained. As for EVA9, the micrographs do not reveal the presence of two phases. This copolymer (EVAh) presents partial miscibility with PE.

Morphology of the PE/PBT Blends

The incompatibility between PE and PBT can be directly seen on SEM micrographs. Because the

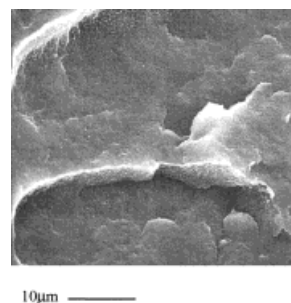


Figure 5 SEM micrograph (original magnification, 2000 \times) of an 80/20 PE/EVAh blend after the extraction of EVAh.

chemical structures of PE (nonpolar) and PBT (polar) are completely different, the two phases are directly seen on micrographs, and PBT did not need to be extracted. SEM micrographs recorded on PE/PBT blends clearly show a dispersion of fine spherical particles in a continuous matrix of up to 30 wt % PBT (Fig. 6). This dispersed phase is constituted by PBT. Indeed, micrographs of PE/PBT blends in which PBT was extracted reveal the presence of some voids that correspond to the place of PBT particles. The relative proportions of the components play a significant role in determining the morphology. As the PBT content

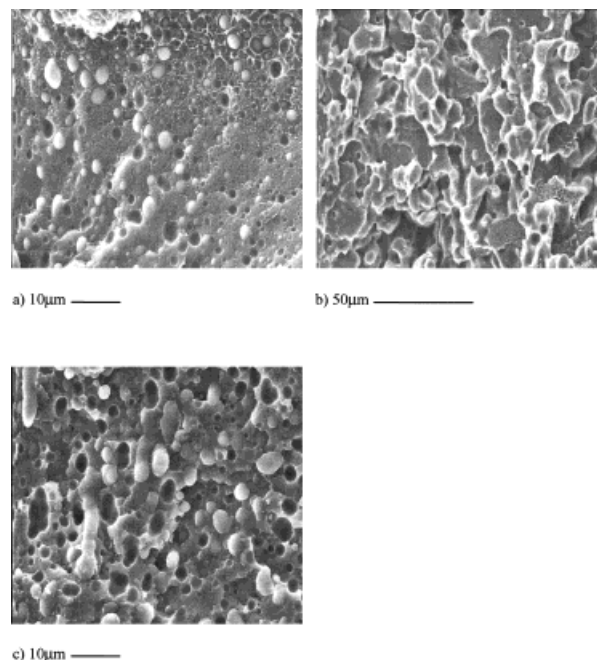


Figure 6 SEM micrographs of PE/PBT blends: (a) 70/30 (original magnification, 1000 \times), (b) 50/50 (original magnification, 400 \times), and (c) 20/80 (original magnification, 1000 \times).

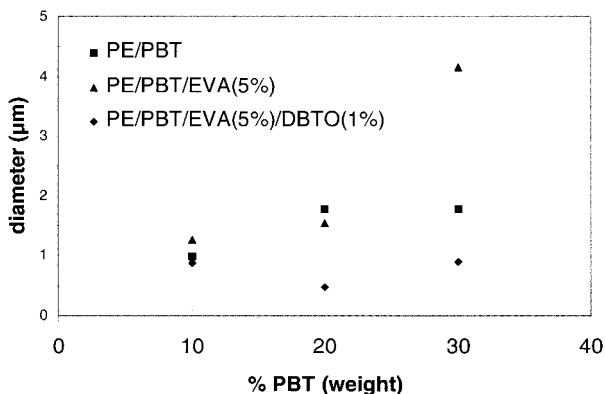


Figure 7 PBT particle size evolution for unreactive blends (PE/PBT and PE/PBT/EVA with 5 wt % EVA) and reactive blends (PE/PBT/EVA/DBTO with 5 wt % EVA and 1 wt % DBTO).

increases, the particle size increases. Above 40% PBT, the two phases are nearly cocontinuous. At higher contents of PBT, this polymer forms the matrix, and PE is the dispersed phase. The blends with less than 30 wt % PBT, no orientation of PBT particles is observed, and the average size of PBT particles can be determined (see Fig. 7). A slight increase is observed when the PBT content increases from 10 to 30 wt %. However, the distribution is broad, especially for 30% PBT.

Moreover, the incompatibility of PE and PBT is brought out because there is no evidence of adhesion between the two phases, the surface of PBT particles is perfectly clean, some microvoids can be observed around PBT nodules [Fig. 8(a)], and the fracture always takes place at the interface.

In the presence of 5 wt % EVA but without a catalyst, PBT-*g*-EVA cannot be synthesized and the blends are not compatibilized. Their morphology does not really change: PBT forms the dispersed phase as spherical particles in the PE ma-

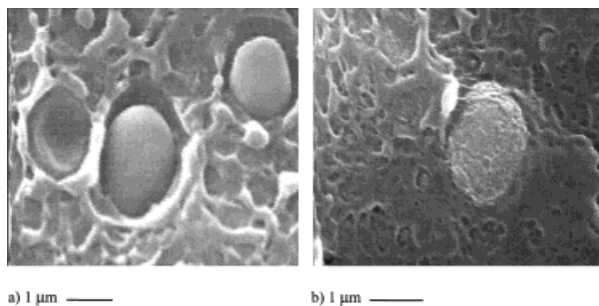


Figure 8 SEM micrographs (original magnification, 2000 \times) of (a) a 90/10 PE/PBT blend and (b) an 85/10/5 PE/PBT/EVAh blend.

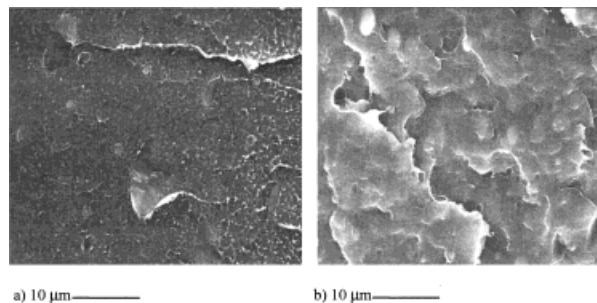


Figure 9 SEM micrographs (original magnification, 2000 \times) of (a) a 64/30/5/1 PE/PBT/EVA/DBTO blend and (b) a 65/30/5 PE/PBT/EVAh blend.

trix, adhesion between PE and PBT is poor, and the fracture takes place at the interface. The slight increase in particles size observed especially for the 65/30/5 PE/PBT/EVA blend (by weight; see Fig. 7) might be correlated with the variation of the viscosity ratio between the matrix and dispersed phase, a variation due to the presence of EVA in the PE matrix. This viscosity ratio influences particle coalescence and breaking and, therefore, blend morphology.^{28,29}

The addition of DBTO as a precursor of distannoxane, the true catalyst of the reaction, enables the synthesis of PBT-*g*-EVA by transesterification between ester groups of PBT and EVA.^{5,6} Therefore, 1 wt % DBTO was added to PE/PBT/EVA blends. The morphology of these reactive blends (PE/PBT/EVA/catalyst) is completely different from that of nonreactive blends (PE/PBT and PE/PBT/EVA). Figure 9(a) shows an example of these morphologies for a 65/30/5/1 PE/PBT/EVA/DBTO blend (by weight). The contrast between PE and PBT is very poor, and the adhesion seems to be better. The size of the particles determined from samples from which PBT was extracted is smaller than for nonreactive blends (Fig. 7). These improvements in dispersion and adhesion are consistent with the compatibilization of the blends through transesterification.

Influence of EVAh

EVAh was obtained by transesterification reactions between EVA9 and 2-hexyl 1-ethanol in the presence of DBTO, as previously stated. Of this EVAh, 5 wt % was introduced into PE/PBT blends.

In previous studies,^{13,14} we showed that DBTO reacts with ester groups to form distannoxane structures, the true catalyst of the transesterification reaction. Therefore, during the synthesis of

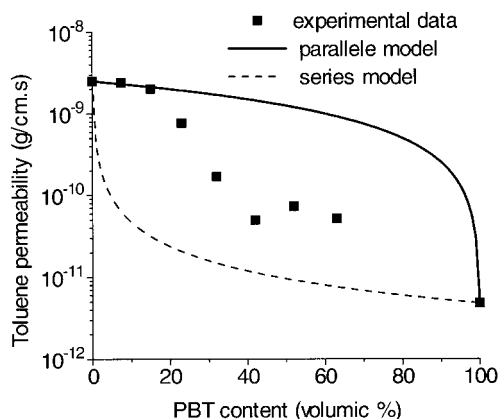


Figure 10 Toluene permeability versus PBT content.

EVAh, DBTO reacts with ester groups of EVA to form distannoxane structures. Hence, EVAh is constituted by 50% VA units and 50% hydroxylated VA units and distannoxane structures. The PE/PBT/EVAh blends contain the catalyst of transesterification, and the reactions between EVAh and PBT can occur during processing. Two types of reactions can take place: redistributive transesterification reactions between ester groups of PBT and ester groups of EVAh (acetate groups) and alcoholysis reactions between ester groups of PBT and hydroxyl groups of EVAh (hydroxylated acetate groups). DBTO, through distannoxane structures, catalyzes these two reactions,^{13,14,19–22} which lead to the synthesis of a PBT-g-EVAh copolymer (Scheme 1). The results of the morphology study show that this copolymer compatibilizes PE/PBT blends.

The morphology of the PE/PBT blends (Fig. 6) is completely modified by the presence of EVAh [Fig. 9(b)]. A finer dispersion is obtained, and interfacial adhesion is improved (see Fig. 8). As for PE/PBT/EVA/DBTO blends, the morphology of PE/PBT/EVAh is typical of compatibilized blends.

Barrier Properties

In recent years, the use of polymers in the packaging industry has increased steadily.³⁰ The high permeability of various gases and solvents through a single polymer layer can be avoided by the coprocessing and formation of multilayer materials. Although articles obtained by multilayer extrusion satisfy many of the needs of packaging applications, they still involve heavy commitments in capital investment, require difficult process optimization and process control, and have limited utility in the blow-molding process. One

alternative to this process could be based on the use of polymer blend systems.³¹ In this case, a high-barrier polymer is blended with a more permeable matrix. This is the case of polyolefin/polyester blends.^{16–18}

We studied the permeability of PE/PBT blends compatibilized with EVAh to determine the influence of this copolymer on barrier properties. First, we examined the influence of PBT in a PE matrix on the barrier properties for toluene.

The data obtained for different amounts of PBT are plotted versus the PBT content in Figure 10. As expected, permeability measurements show that the incorporation of PBT reduces toluene permeability. Increasing the PBT content results in a larger reduction of toluene permeability. The effects of this loading on P and the ratio P/P_1 (P_1 is the PE permeability) are listed in Table I. The smaller P/P_1 is, the better the barrier properties are. At a PBT small content, the reduction in toluene permeability is small. This reduction becomes important for 40 wt % PBT; SEM analysis shows that for this blend, the two phases are nearly cocontinuous. These experimental data were compared with theoretical models. The simplest ones correspond to multilayer materials, where the direction of permeation is perpendicular to the layer for the series model or parallel for the parallel model :

$$\frac{1}{P} = \frac{\phi_1}{P_1} + \frac{\phi_2}{P_2} \quad (4)$$

$$P = \phi_1 P_1 + \phi_2 P_2 \quad (5)$$

where P is the blend permeability, P_i is the permeability of polymer i , and ϕ_i is the volume fraction of polymer i .^{32–34}

Table I Toluene Permeability of PE/PBT Blends

PE/PBT Blend Composition (wt %)	P [(g/cm s) × 10 ¹²]	100 × P/P_1
100/0	2500 (P_1)	100
90/10	2400	96
80/20	2100	84
70/30	720	29
60/40	180	7.2
50/50	50	2.0
40/60	74	3.0
20/80	52	2
0/100	4.8	0.2

Table II Toluene Permeability of Reactive Blends

Blend Composition (wt %)	P [(g/cm s) $\times 10^{12}$]	$100 \times P/P_1$
PE	2500 (P_1)	100
PBT	4.8	0.2
80/20 PE/PBT	2100	84
75/20/5 PE/PBT/EVA	2900	116
74/20/5/1 PE/PBT/EVA/DBTO	2700	108
75/20/5 PE/PBT/EVAh	2100	84
70/30 PE/PBT	720	29
65/30/5 PE/PBT/EVA	2300	92
64/30/5/1 PE/PBT/EVA/DBTO	2400	96
65/30/5 PE/PBT/EVAh	250	10

The calculations based on eq. (4) are the upper bound and show a slow decrease in the permeation rate as a function of PBT content (Fig. 10). Equation (5), however, is the lower bound, representing the case in which PBT would exist as a continuous, undisturbed layer in PE. Experimental data for PE/PBT blends fall inside the range defined by the upper and lower bounds. Above 30 wt % PBT, the data show a clear trend toward the lower bound (Fig. 10). This can be explained by the cocontinuity of the two phases. A similar reduction in permeability could be obtained for a smaller PBT content if a laminar morphology was obtained.^{35,36}

The introduction of 5 wt % EVA into PE/PBT blends leads to an important increase in permeability (see Table II). For instance, the PE/PBT/EVA blend with 20 wt % PBT is more permeable than pure PE ($100 \times P/P_1 > 100$). This is due to the solubility of EVA in toluene. The introduction of a small amount of this polymer (5 wt %) leads to a loss of improvement due to 20 or 30% PBT. The addition of DBTO, which enables the synthesis of PBT-g-EVA, has only a weak effect on the barrier properties, which are always below the barrier properties of PE/PBT blends. On the con-

trary, the use of EVAh leads to decreased permeability, as expected. The presence of hydroxyl groups in the backbone of EVAh modifies the solubility of this polymer in toluene. For 75/20/5 PE/PBT/EVAh blends, the permeability is constant ($100 \times P/P_1 = 84$ for the PE/PBT and PE/PBT/EVAh blends). However, with 30% PBT, barrier properties are improved in the presence of EVAh ($100 \times P/P_1 = 10$ for the PE/PBT/EVAh blend and 29 for the PE/PBT blend). In these blends, PBT is dispersed as small spherical particles in the PE matrix, as previously stated, which is not the best morphology for high-barrier properties. For blends with a laminar morphology, higher barrier properties can be expected.

Mechanical Properties

The mechanical properties of the pure polymers and their blends are summarized in Table III. In the conditions used for the tests, PE is considerably deformed before breaking takes place. It presents a yield stress and a high elongation at break (760%). It is a ductile material. PBT, however, breaks without deforming. There is no yield

Table III Mechanical Properties of PE, PBT, and Their Blends

Blend	Young's Modulus (N/mm ²)	Yield Stress (N/mm ²)	Stress at Break (N/mm ²)	Strain at Break (%)
PE	610 \pm 60	20.1 \pm 0.4	33 \pm 1	760 \pm 70
PBT	2500 \pm 100		65 \pm 1	10 \pm 2
80/20 PE/PBT	740 \pm 60	17.8 \pm 0.3	22.9 \pm 0.8	550 \pm 20
75/20/5 PE/PBT/EVAh	700 \pm 30	20.3 \pm 0.3	17 \pm 2	360 \pm 40
70/30 PE/PBT	830 \pm 30	16.4 \pm 0.1	15 \pm 1	390 \pm 50
65/30/5 PE/PBT/EVAh	820 \pm 80	20.9 \pm 0.5	13.6 \pm 0.4	50 \pm 10

stress, and the elongation at break is small (10%). It is brittle.

In the PE/PBT blend, where PE remains the matrix and PBT is the dispersed phase, the ductility of the material is decreased in comparison with pure PE: the deformation of the material before breaking decreases. This deformation is more reduced in formulations with EVAh as in polymer blends that have been compatibilized, as previously seen. In these blends, the elongation at break is reduced, whereas the yield stress and Young's modulus increase. Therefore, for PE/PBT blends with PBT dispersed in the PE matrix, the improvement in interfacial adhesion between PE and PBT leads to a decrease in the ductility of the material.

CONCLUSION

The *In situ* compatibilization of blends by reactive processing is an important challenge. In this work, a reactive copolymer (EVAh) was used for compatibilizing PE/PBT blends. Its introduction into PE/PBT blends enabled the synthesis of PBT-g-EVAh via transesterification reactions. This copolymer promoted adhesion with the PBT phase through its PBT segment, whereas EVAh chains ensured adhesion with the PE phase.

Permeability measurements show these blends can form interesting materials with higher barrier properties for toluene than pure PE can provide.

REFERENCES

1. Kit, K. M.; Schultz, J. M.; Gohil, R. M. *Polym Eng Sci* 1995, 35, 680.
2. Lohfink, G. W.; Kamal, M. R. *Polym Eng Sci* 1993, 33, 1404.
3. Porter, R. S.; Jonza, J. M.; Kimura, M.; Desper, C. R.; George, E. R. *Polym Eng Sci* 1989, 29, 55.
4. Porter, R. S.; Wang, L.-H. *Polymer* 1989, 33, 2019.
5. Pesneau, I.; Llauro, M. F.; Grégoire, M.; Michel, A. *J Appl Polym Sci* 1997, 65, 2457.
6. Pesneau, I. Thesis, University Claude Bernard, Lyon, France, 1996.
7. Cassagnau, P.; Bert, M.; Verney, V.; Michel, A. *Polymer* 1993, 34, 124.
8. Otton, J.; Ratton, S.; Markova, G. D.; Nametov, K. M.; Bakhmutov, A. V.; Komarova, L. I.; Vinogradova, S. V.; Korshak, V. V. *J Polym Sci Part A: Polym Chem* 1988, 26, 2199.
9. Shah, T. H.; Bhatta, J. I.; Gamlen, G. A.; Dollimore, D. *Polymer* 1984, 25, 1333.
10. Tomita, K.; Ida, H. *Polymer* 1975, 16, 185.
11. Shah, T. H.; Bhatta, J. I.; Gamlen, G. A.; Dollimore, D. *J Macromol Sci Chem* 1984, 21, 431.
12. Otera, J.; Dan-oh, N.; Nozaki, H. *J Org Chem* 1991, 56, 5307.
13. Bonetti, J.; Gondard, C.; Petiaud, R.; Llauro, M. F.; Michel, A. *J Organomet Chem* 1994, 481, 7.
14. Espinasse, I.; Pétiard, R.; Llauro, M. F.; Michel, A. *Int J Polym Anal Characterization* 1995, 1, 137.
15. Lacroix, C.; Llauro, M. F.; Petiaud, R.; Bousmina, M.; Carreau, P. J.; Michel, A. *Polymer* 1996, 37, 2949.
16. Bataille, P.; Boissé, S.; Schreiber, H. P. *Polym Eng Sci* 1987, 27, 622.
17. Subramanian, P. M.; Mehra, V. *Polym Eng Sci* 1987, 27, 663.
18. Subramanian, P. M. *Polym Eng Sci* 1987, 27, 1574.
19. Lambla, M.; Druz, J.; Bouilloux, A. *Polym Eng Sci* 1987, 27, 1221.
20. Hu, G. H.; Lindt, J. T.; Lambla, M. *J Appl Polym Sci* 1992, 46, 1039.
21. Bouilloux, A.; Druz, J.; Lambla, M. *Polym Proc Eng* 1986, 4, 235.
22. Hu, G.-H.; Sun, Y.-J.; Lambla, M. *Makromol Chem* 1993, 194, 665.
23. Rogers, C. E. In *Polymer Permeability*; Comyn, J., Ed.; Academic: New York, 1980.
24. Crank, J. *The Mathematics of Diffusion*; Clarendon: Oxford, 1956.
25. Crank, J.; Park, G. S. In *Diffusion in Polymer*; Crank, J., Ed.; Academic: New York, 1968; Chapter 1.
26. Ray, I.; Khastgir, D. *Polymer* 1993, 34, 2030.
27. Llauro, M. F. Private communication, 1993.
28. Wu, S. *Polym Eng Sci* 1987, 27, 335.
29. De Loor, A. Thesis, University Claude Bernard, Lyon, France, 1994.
30. Akkapeddi, M. K.; Van Buskirk, B. *Polym Mater Sci Eng* 1992, 67, 317.
31. Lohfink, G. W.; Kamal, M. R. *Polym Eng Sci* 1993, 33, 1404.
32. Manson, J. A.; Sperling, L. H. *Polymer Blends and Composites*; Plenum: New York, 1976.
33. Hopfenberg, H. B.; Paul, D. R. In *Polymer Blends*; Paul, D. R.; Newman, S., Eds.; Academic: New York, 1978; Vol. 1, Chapter 10.
34. Brown, R. A.; Budd, P. M.; Price, C.; Satgurunathan, R. *Eur Polym J* 1993, 29, 337.
35. Fohfink, G. W.; Kamal, M. R. *Polym Eng Sci* 1993, 33, 1404.
36. Subramanian, P. M.; Mehra, V. *Polym Eng Sci* 1987, 27, 663.