

Morphology Control of Polyester–Polyolefin Blends by Transesterification during Processing Operations in the Presence of Dibutyltin Oxide

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ABSTRACT: PE and PBT are known to be incompatible polymers. A grafted copolymer PBT-EVA has been generated as a compatibilizer *in situ* during the processing operation by redistributive transesterification between PBT and EVA in the presence of dibutyl tin oxide (DBTO). This copolymer has been isolated by selective extractions from PBT/EVA/DBTO (49.5/49.5/1% in weight) blend after processing in the melt. It has been evidenced by a ¹H-NMR study. This copolymer presents all the resonances of PBT and EVA sequences and some others that have been assigned specifically to grafting. To achieve these assignments, a model compound obtained by transesterification of EVA with methyl benzoate has been used. When the melt conditions enable synthesis of the grafted copolymer PBT–EVA *in situ* during processing operations, important changes in the morphology of PE/PBT/EVA/DBTO blends are observed. SEM analysis shows a decrease of PBT particle size and a good adhesion between the PBT and PE phase. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2457–2469, 1997

Key words: transesterification; dibutyltin oxide; distannoxane; copolymer; blend morphology

INTRODUCTION

A fascinating feature of blends in the polyester family is the potential for transesterification. As polyesters readily transesterify, near and above their melting points, interchange reactions commonly occur between constituents.^{1–7} The structure of the copolyesters resulting from the exchange reaction is a function of the reaction time. At short times the exchange reaction leads to the formation of block copolymers. As the reaction proceeds, the average sequence length of ester repeating units is shortening and the two types of polyester sequences are expected to be randomly distributed along the polymer backbone at least if

the initial blend is homogeneous.^{1,8} Such reactions are expected to induce morphological changes of blends and can be used for such a purpose. Partial miscibility reported in the literature, such as in the case of polyester/polycarbonate and polyester/polyarylate, results from transesterification reactions at the interface: interchange reactions enhance the miscibility of the blend.

Uncatalyzed transesterification reactions are not easy but they can be induced by polymerization catalytic residuals. Acid, base, and organometallic compounds are known to activate this type of reaction. This opens a new route to compatibility.

Dibutyltin oxide is known to promote transesterification reactions. For example, it is a precursor of distannoxanes, the true catalyst in the covalent cocrosslinking reaction of ethylene-*co*-vinylacetate (EVA) and ethylene-*co*-methylacrylate (EMA) polymer blends in the molten state. The crosslinking has been followed by rheological

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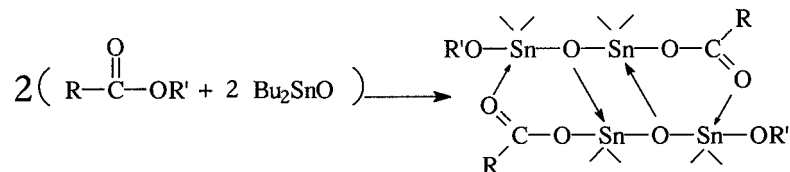
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Scheme 1 Reaction of DBTO with ester groups to give distannoxane.

measurements.^{9,10} The presence of methylacetate indicated that some redistributive (interchain ester-ester interchange reaction) transesterification occurred.¹¹ Moreover, it has been shown¹² both on model esters and polymers bearing pendant ester groups that esters react with preexisting $\text{-R}_2\text{Sn-O-SnR}_2\text{-O-}$ distannoxane structure of dibutyltin oxide and give dimeric 1-alkoxy, 3-acyloxy tetrabutyl distannoxanes by the following reaction (see Scheme 1).

Crosslinking of EVA (or EMA) alone in the presence of dibutyltin oxide are well explained by the formation of these moisture-sensitive dimeric distannoxanes.

1-Alcoxy, 3-acyloxy tetrabutyl distannoxanes incorporated in catalytic amounts in EMA/EVA polymer blends are also efficient in cocrosslinking of the polymer matrix. With dibutyltin oxide, where the catalytic distannoxane entity is readily produced *in situ* and borne by the polymer chain itself, the storage modulus is higher than with free distannoxanes.¹³ Moreover, exchange reactions at the tin sites between alcoxy and acyloxy ligands of these distannoxanes and free ester groups have been evidenced above 100°C.

All these previous results^{12,13} incite us to use dibutyltin oxide in catalytic amounts in a view to obtain grafted copolymers by transesterification as a route to compatibility between incompatible parent polymers.

To compatibilize polyethylene (PE)/poly(butylene terephthalate) (PBT) blends, the *in situ* synthesis of the PBT-*g*-EVA copolymer has been performed by transesterification reaction. As ester groups in EVA are pendant, the reaction leads to a grafted copolymer. The PBT graft is expected to promote adhesion with the PBT phase, while the EVA backbone, which has a similar structure with PE, ought to improve adhesion with PE. Ray and Khastgir¹⁴ have shown that ethylene vinyl acetate copolymer (EVA with 28% VA) is miscible with low-density PE in amorphous zones. They have studied morphology, thermal, and dynamic mechanical properties of PE/EVA28 blends with different contents of EVA (0/100, 30/70, 50/50, 70/30,

and 100/0). Thermal analysis (DSC) does not show any variation of melting temperatures, and the authors conclude that intermiscibility in the crystalline phase is improbable. But dynamic mechanical analysis shows an evolution of relaxation temperatures associated with the glass transitions, indicating that the polymers present a partial miscibility through the amorphous phase. Moreover, previous studies have shown that vinyl acetate units are essentially isolated. So when the VA unit content in EVA decreases, the number of ethylene units ($\text{CH}_2\text{-CH}_2$) between two vinyl acetate units ($\text{CH}_2\text{-CH(OCOCH}_3\text{)}$) increases (8.5 for EVA28 and 31.5 for EVA9) and then compatibility with the PE increases.¹⁵

In this article the results of the synthesis and characterization of the grafted copolymer PBT-EVA (PBT-*g*-EVA) and of its effect on morphology of PE/PBT blends are reported and discussed. As PE matrix does not play any part during the synthesis of the copolymer, and to simplify the system, the copolymer has been first synthesized and analyzed from PBT/EVA/DBTO blends. Then blends with PE as the matrix and where the copolymer is obtained (PE/PBT/EVA/DBTO) *in situ* during processing have been analyzed by scanning electron microscopy.

EXPERIMENTAL

Reagents

Dibutyltin oxide (DBTO) and methyl benzoate are commercial products (Aldrich).

PE was generously supplied by Fina (Finathene 3802). Ethylene-vinyl acetate copolymer (EVA) is supplied by Atochem (EVA 2803). Two weight compositions of vinyl acetate (VA) units in the copolymer were used: 28 and 9%. Poly(butylene terephthalate) (PBT) was also an Atochem product (Orgater TMNO). It was dried under vacuum at 80°C for at least 4 h before processing to minimize hydrolysis in the melt.

Table I Solubility of the Polymers

| | Toluene (Hot) | DCAA | TCE (Hot) |
|-----|---------------|-----------|-----------|
| EVA | soluble | insoluble | soluble |
| PBT | insoluble | soluble | soluble |

Reactions**Reaction between a Polymer (EVA) and a Model Compound (Methyl Benzoate)**

19.2 g of methyl benzoate and 40 g of EVA (9%) were mixed with 3.5 g of dibutyltin oxide in an internal mixer (Haake Rheocord Mixer). The temperature of the mixer chamber was set at 180°C, and the stirring speed was 50 revolution per minute (rpm).

The molten medium was malaxed for 10 mn; then the blend was solubilized in tetrachloroethylene, filtered off to eliminate a possible cross-linked phase, and precipitated with methanol. This treatment is repeated twice to eliminate unreacted methyl benzoate.

Reaction between the Two Polymers (EVA and PBT)

49.5 g of EVA and 49.5 g of PBT were mixed with 1 g of dibutyltin oxide in the internal mixer (Haake). The temperature was set at 230°C and the stirring speed was 50 rpm. The molten medium was malaxed for 20 mn.

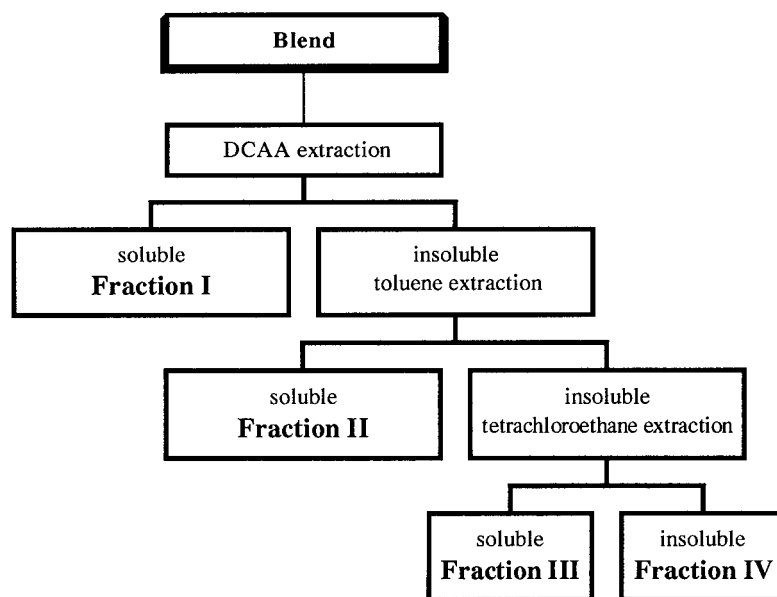
Extraction of the Copolymer

These extractions are similar to those realized by Pilati.¹⁶ Preliminary solubility tests showed that EVA was soluble in hot toluene and hot 1,1,2,2-tetrachloroethane (TCE), but insoluble in dichloroacetic acid (DCAA). PBT was soluble in DCAA at room temperature and in hot TCE, but insoluble in toluene (see Table I).

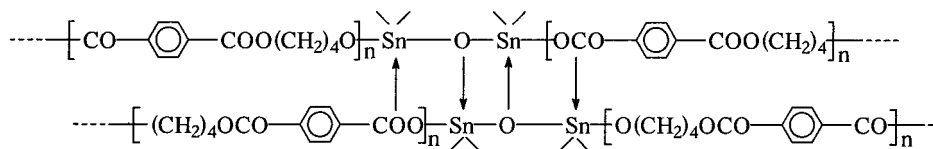
About 5 g of final blend was added to 100 mL DCAA and stirred at room temperature for 24 h. The suspensions were filtered off. The clear solution obtained was precipitated with water; the precipitate obtained was washed with water and dried until constant weight. This product was named Fraction I. The residue of the filtration was extracted with hot toluene in a Soxhlet apparatus for 3 days. The solution obtained was precipitated with methanol; the precipitate obtained, after being washed with methanol and dried, was named Fraction II. The residue of this second extraction was extracted with hot TCE in the Soxhlet apparatus for 3 days. The solution obtained was precipitated with methanol, washed, and dried. It constituted fraction III. The residue of this third extraction was named fraction IV. Due to the very small amount of this fraction, it was not possible to collect and characterize it. These extractions are summarized in Scheme 2.

Instrumental Methods

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



Scheme 2 Extraction of the copolymer from the blend after reaction in the melt, between the two immiscible polymers in the presence of DBTO.



Scheme 3 Distannoxane structure in PBT chains.

Different solvents were used according to the product analyzed: tetrachloroethylene/deuterated benzene (C_6D_6) mixtures (2/1 by volume) in the case of the modeling reaction, EVA, and fraction II, $CF_3COOD + CDCl_3$ (1/1 by volume) in the case of PBT, fraction I, and fraction III and tetrachloroethane in the case of EVA, modeling reaction, and fraction III. Chemical shifts values (δ) are given in ppm in reference to internal tetramethylsilane (TMS).

IR spectra were recorded on a Nicolet 20SX spectrometer. DSC measurements were carried out with a Mettler TA 3000 calorimeter. Samples of 20 mg encapsulated in aluminium pans were heated from ambient temperature to $270^\circ C$ at $10^\circ/mn$.

The blends investigated in the second part of this study were based on PE/PBT, and in some case EVA and DBTO. Blending of 50 g samples was performed using a Brabender Plasticorder at 50 rpm, for 10 min at $230^\circ C$. The morphology of these blends was examined by scanning electron microscopy (JEOL JSM35). The samples were fractured in liquid nitrogen and then vacuum metallized before analysis. In some case, the dispersed phase (PBT) was extracted 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 in weight) at $50^\circ C$ for 24 h. This allowed removal of all PBT particles on the surfaces of the samples.

RESULTS AND DISCUSSION

The first step of our work was the analysis of the copolymer. It was obtained from the reaction of EVA and PBT in the presence of DBTO as quoted in the Experimental section.

As PBT and EVA are incompatible, and if DBTO is supposed to be homogeneously dispersed in the blend, three different situations have to be considered. In the PBT phase, the rapid reaction of DBTO with ester sites in the backbone is expected to produce some polymeric distannoxane structures randomly distributed in the matrix (Scheme 3).

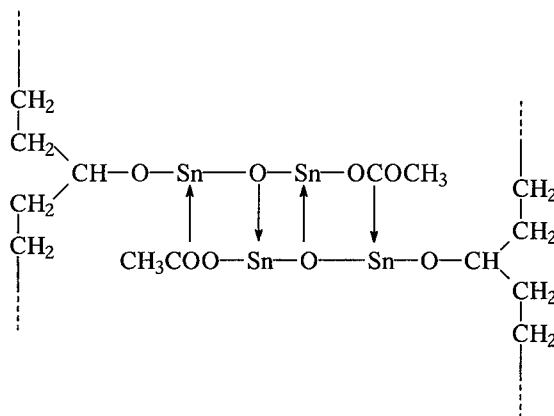
Owing to the low quantity of DBTO involved, these structures are not expected to be evidenced by 1H -NMR. Moreover, 1-alcoxy, 3-acyloxy distannoxane structures have shown to be highly moisture-sensitive hydrolysis, giving in this case some shortened PBT chains.

In the EVA phase, reaction of DBTO with pendant ester groups will produce a reversible cross-linking by the following interchain distannoxane link (Scheme 4).

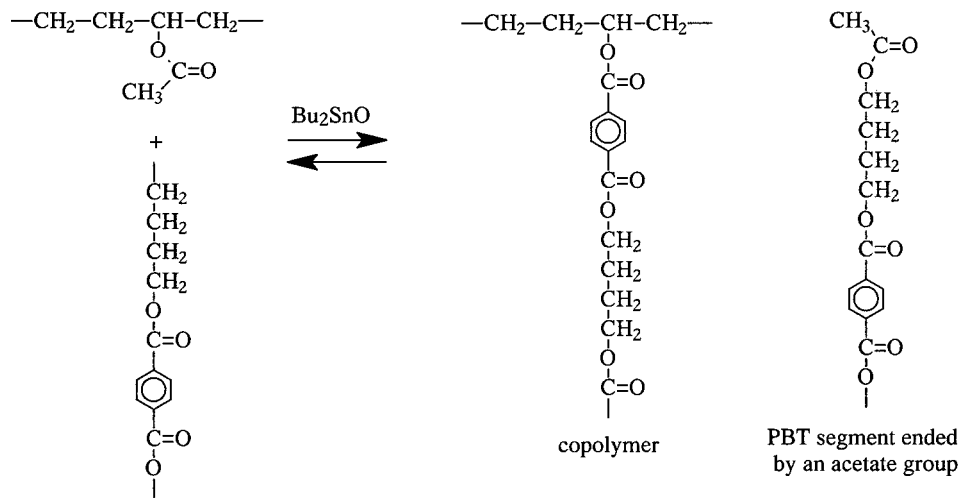
The exchange reaction of transesterification catalyzed by DBTO is expected to occur only at the interface of the two incompatible polymers and produce only a small amount of grafted copolymer (Scheme 5). For that reason, the copolymer is difficult to evidence in the blend and must be isolated before characterization. The difference in solubility of PBT and EVA was exploited for purposes of separation. By selective extractions different fractions (see Experimental) were obtained.

Identification of PBT-g-EVA through Separation and Characterization of the Fractions

The initial blend was composed of 50% (in weight) PBT and 50% EVA. After reaction in the melt in the presence of DBTO, successive extractions are performed as described above (Scheme 2) and give four fractions with the following weight distribution: fraction I: 46%, fraction II: 36%, frac-



Scheme 4 Distannoxane structure in EVA chains.



Scheme 5 Reaction between EVA and PBT.

tion III: 12% and fraction IV: 6%. Fractions I, II, and III were analyzed by FT-IR, DSC, and NMR.

Fraction I

This fraction, soluble in DCAA, is theoretically composed by the PBT phase of the blend.

The $^1\text{H-NMR}$ spectrum of fraction I is shown on Figure 1. The main resonances observed are three singlets at $\delta = 8.150$, 4.530, and 2.055 ppm corresponding to chemical shift values previously observed for aromatic (A) and methylenic (B and C) protons of pure PBT in the same solvent (see Scheme 6).

The IR spectrum for this fraction shows all the

characteristic PBT bands. DSC analyses were realized on a pure PBT blend of PBT/DBTO: 99/1 (in weight) and fraction I. The melting temperatures observed are respectively 238, 232, and 235°C. These results suggest fraction I consists of unreacted PBT.

But other resonances are observed on the $^1\text{H-NMR}$ spectrum: *D* ($\delta = 1.310 + 1.610$) and a badly resolved resonance *E* ($\delta = 2.205$). *D* resonances correspond to methylenic protons of unexpected polyethylene structure and *E* to methylic protons of CH_3CO — groups. In fact, when the reaction of transesterification is conducted between EVA and PBT, two products are theoretically obtained: the

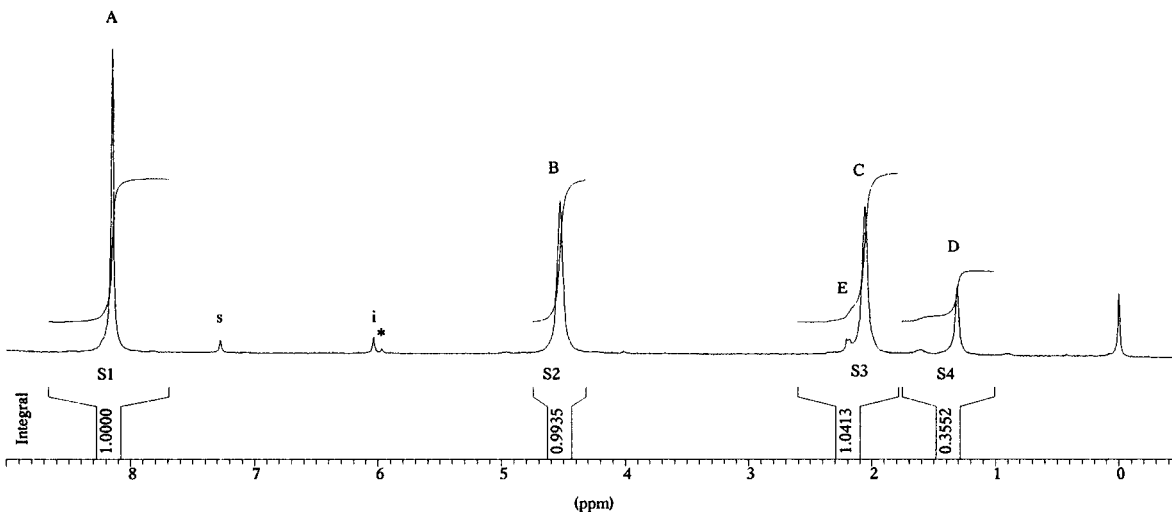
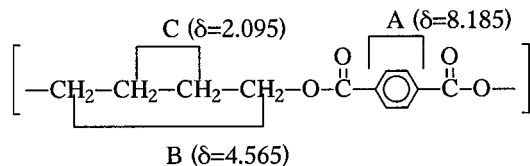


Figure 1 $^1\text{H-NMR}$ spectrum (250 MHz) of fraction I in $\text{CF}_3\text{COOD} + \text{CDCl}_3$ (1/1 by volume) at ambient temperature. i: impurity already observed in the spectrum of initial PBT, *: residual DCAA from the extraction, s: CHCl_3 .



Scheme 6 Chemical structure and $^1\text{H-NMR}$ chemical shift values of pure PBT in $\text{CF}_3\text{COOD} + \text{CDCl}_3$.

PBT grafted on the polyethylene backbone at ester pendant sites—which is not expected to be soluble in DCAA—and soluble-shortened PBT chains ended by an acetate group coming from the acyl interchange reaction with EVA polymer (Scheme 5). This last product ought to be soluble in DCAA, as pure PBT is, whereas pure EVA is not. However resonances *D* indicates that some EVA is present in fraction I. The integral ratio $\frac{2 \times S_4}{S_1 + S_2} = 2.80$, which corresponds to the molar ratio BT/E (butylene terephthalate/ethylene) in fraction I, is 16 times higher than in the initial PBT/EVA blend. Because resonance *E* corresponding to the CH_3CO — groups is included in the S_3 area ($E + C$) but badly resolved, its contribution has to be calculated. As $C = (A + B)/(2) = (S_1 + S_2)/(2)$, then the contribution of CH_3CO — is equal to $[S_3 - (S_1 + S_2)/(2)] = E$. The molar ratio $\text{CH}_3\text{CO}/\text{ethylene}$ ($4E/3D$) is then found to be four times that in initial EVA. These results show that fraction I is mostly constituted of ungrafted PBT with some chains bearing a terminal acetyl group and a small quantity of EVA drawn.

Fraction II

This fraction was insoluble in DCAA, but soluble in hot toluene. IR spectrum of this fraction is the same that of pure EVA. DSC analysis shows one melting peak at 75°C . It corresponds to the melting temperature of EVA. $^1\text{H-NMR}$ spectrum of the soluble part of this fraction was realized in TCE/ C_6D_6 (Fig. 2). All the peaks corresponding to EVA are present: $\text{CH}\alpha$ at $\delta = 4.890$, CH_3CO at 1.870, and all methylenic protons at higher field. But a lot of insoluble impurities cannot be analyzed by NMR spectroscopy. They can result from degradation during extraction three days in boiling toluene.

Fraction III

This fraction is composed by products insoluble in toluene and DCAA but soluble in hot TCE.

In a view to evidence the presence of PBT seg-

ments grafted on the polyethylene backbone, a model compound obtained by reaction between EVA and methyl benzoate has been analyzed and compared with EVA in a first step. The two resonances, which are sensitive to transesterification reaction are $\text{CH}\alpha$ and $\text{CH}_2\beta$, as indicated on Scheme 7. A deshielding effect is observed on the $\text{CH}\alpha$, which is nearly the same in tetrachloroethylene ($\delta' - \delta = 0.275$) and tetrachloroethane ($\delta' - \delta = 0.270$), which are solvents of both EVA and EVA substituted by methyl benzoate. A much lower deshielding effect is observed on the $\text{CH}_2\beta$, which is solvent dependent ($\Delta\delta = 0.05$ in tetrachloroethylene and $\Delta\delta = 0.125$ in tetrachloroethane).

In a second step, fraction III, soluble in $\text{CF}_3\text{COOD} + \text{CDCl}_3$ (Fig. 3) and in tetrachloroethane, is compared with EVA partially substituted by methyl benzoate. This allows us to assign both $\text{CH}\alpha$ (S_2) from initial EVA and $\text{CH}\alpha'$ (S_1) from substituted pendant groups. In spite of the fact that chemical shift values are strongly solvent dependent, the difference between them ($\delta' - \delta = 0.270$) remains constant. Similarly, $\text{CH}_2\beta$ from EVA and EVA substituted are assigned to $\delta = 1.570$ and 1.715, respectively ($\Delta\delta = 0.145$ is not so different from $\Delta\delta = 0.125$ already observed in tetrachloroethane). Of course, the other characteristic features of EVA are present in the spectrum: CH_3CO at $\delta = 2.155$ and $[\text{CH}_2]_n$ at $\delta = 1.270$.

Besides the $\text{CH}\alpha'$ and $\text{CH}_2\beta'$ resonances typical of the transesterification on acetyl pendant groups of EVA by PBT chain segments, the presence of PBT in this fraction is attested by the three main resonances $\delta = 8.115$, 4.500, and 2.025 corresponding, respectively, to A, B, and C protons (Scheme 6). The resonance at $\delta = 3.915$ (S_3) is assigned to F protons (Scheme 8) because these protons in butyl acetate have a chemical shift that is strongly solvent dependent ($\delta = 3.970$ in TCE/ C_6D_6 and 4.195 in $\text{CF}_3\text{COOD} + \text{CDCl}_3$). Resonances related to methylenic protons in the β and γ position to the acetyl group are also strongly solvent dependent and are expected to overlap with other polyolefinic $[\text{CH}_2]_n$ resonances in the range 1.9–1.2 ppm.

The CH_3CO resonances at $\delta = 2.155$ are expected to come from both the unreacted pendant acetyl group from the EVA backbone and the acetyl end groups borne by PBT segments grafted on the EVA. The following relation between resonance areas is verified: $S_4 = 3S_2 + (3/2)S_3$.

The presence of the grafted PBT chains ended by an acetate group can be explained by the fact

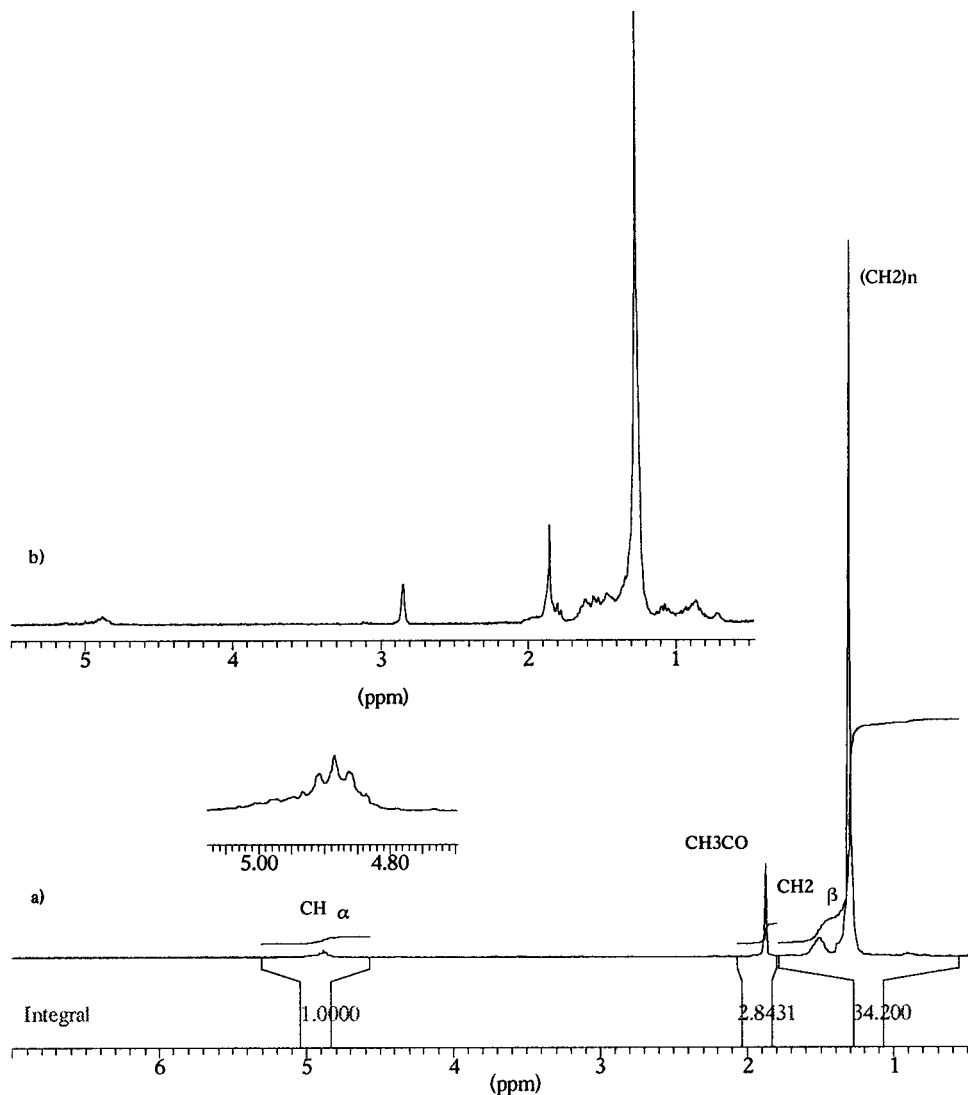
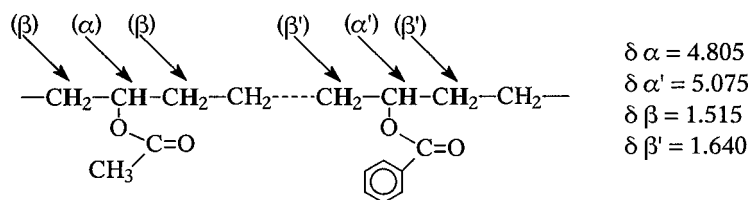


Figure 2 $^1\text{H-NMR}$ spectrum (250 MHz) in tetrachloroethylene/ C_6D_6 (2/1 by volume) of (a) initial EVA, (b) fraction II.

that a PBT segment of the copolymer reacts a second time. This explains the presence of fraction IV, which is completely insoluble in all the solvents. When the copolymer reacts a second time, two products can be formed: 1) in one case, a net-

work is obtained; 2) in the second case, a copolymer with a PBT segment ended by an acetate group is produced (see Scheme 9).

The existence of the copolymer PBT-*g*-EVA is also attested to by the presence of typical EVA



Scheme 7 Chemical structure of EVA substituted by methyl benzoate and $^1\text{H-NMR}$ chemical shifts in tetrachloroethane (common solvent for EVA, EVA substituted by methyl benzoate, and PBT-*g*-EVA, only at elevated temperature for the last one).

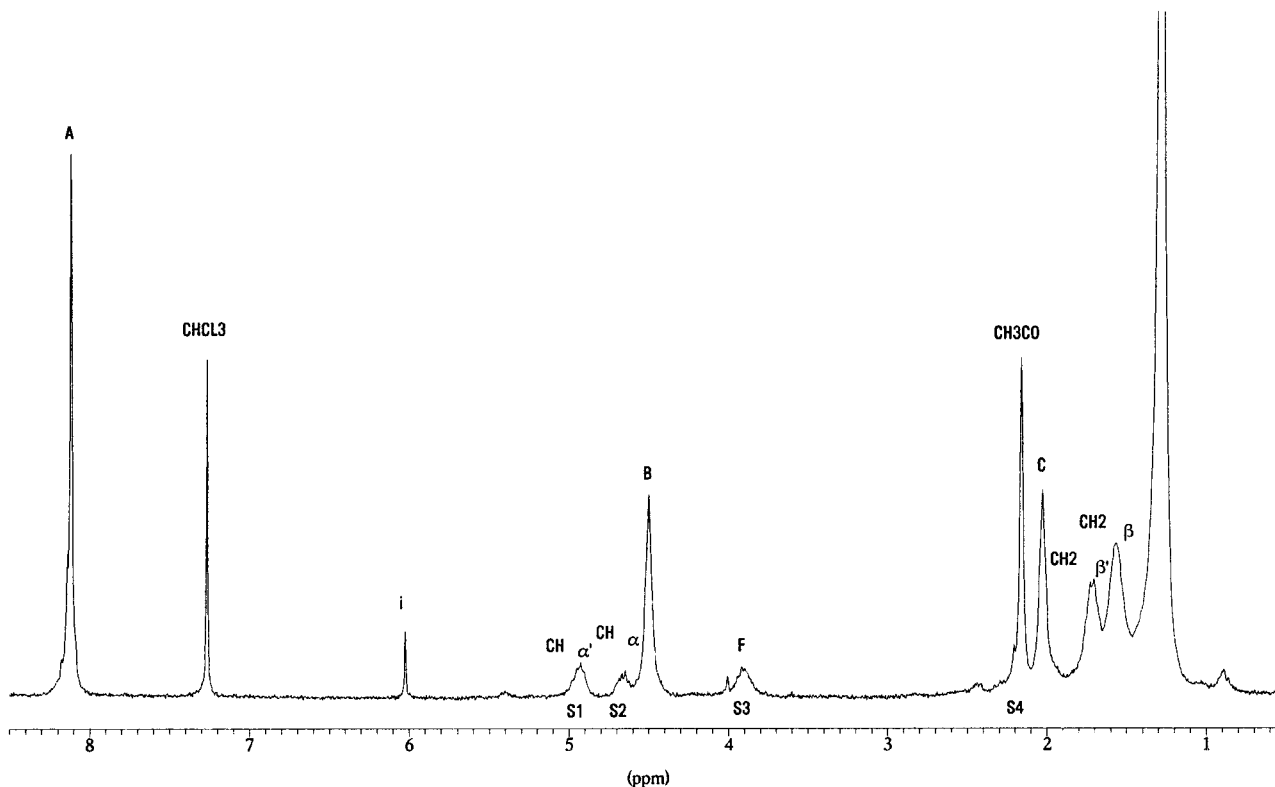


Figure 3 $^1\text{H-NMR}$ spectrum (250 MHz) in $\text{CF}_3\text{COOD} + \text{CDCl}_3$ (1/1 by volume) of fraction III.

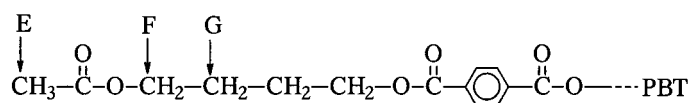
resonances in the spectrum of fraction III realized in $\text{CF}_3\text{COOD} + \text{CDCl}_3$, because pure EVA is insoluble in this solvent. The solubility is well explained by the fact that PBT chains grafted on EVA draw it in solution.

Moreover, IR spectrum of this fraction is similar to that of EVA substituted by benzoate groups (model reaction). It shows two bands due to carbonyl group at 1733 and 1715 cm^{-1} and two others due to C-O at 1245 and 1274 cm^{-1} . Two ester groups are present in this fraction. Comparison with spectra of EVA and PBT shows that they correspond to ester groups of this two polymers (EVA: 1738 and 1241 cm^{-1} ; PBT: 1716 and 1269 cm^{-1}). DSC analysis of this fraction presents three melting peaks at 68 , 190 , and 240°C . This study shows that a copolymer PBT-*g*-EVA can be obtained by transesterification at the interface between two polymers PBT and EVA in the

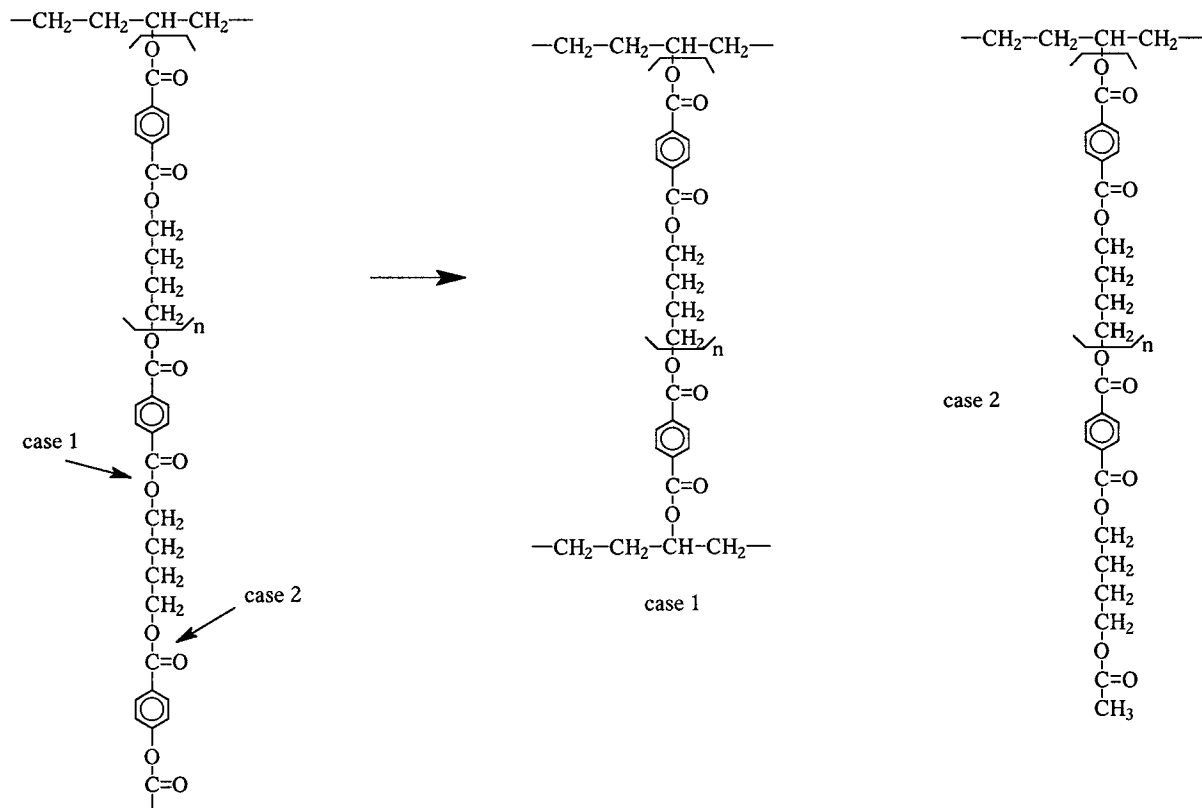
presence of DBTO. In a second part, the synthesis of this copolymer has been realized *in situ* during processing of a blend of PE/PBT/EVA/DBTO. Influence of this copolymer on the morphology of the blend has been studied.

Study of Morphology of the Blends PE/PBT/EVA/DBTO

The properties of multicomponent systems of polymers are not single-valued functions of the composition, but may vary broadly with the morphology of the system. This implies that the degree of component dispersion attained during mixing and the nature of the interface between components as generated affect the mechanical and rheological behavior of blends. The interfacial tension between polymer phases plays an important role in the way the phases break up and



Scheme 8 PBT chain ended by an acetate group.



Scheme 9 Reaction of the copolymer.

disperse during processing. In immiscible blends, adhesion is often nearly nonexistent. The addition of a copolymer containing segments miscible with the blend components changes the morphology. It tends to concentrate at the interface and acts as an emulsifier.

In a previous work, Legros et al.¹⁷ have studied PETG/EVA/DBTO blends. PETG is an amorphous copolyester synthesized from a mixture of terephthalic acid, ethylene glycol, and 1-4-cyclohexanedimethanol. Properties of such blends have been explained by the synthesis of the PETG-EVA copolymer. Change in morphology and improvement of the elongational properties suggest that the copolymer ensures a good stress transfer across the interface.

In the blends studied, PE is the matrix and PBT the dispersed phase. The formation of the PBT-*g*-EVA copolymer is performed *in situ* during the processing of the blend. The copolymer EVA is incompatible with PBT, but presents a slight miscibility with PE.¹⁴ This miscibility depends on the content of VA comonomer incorporated: it decreases with increasing content of vinyl acetate units. To optimize miscibility of EVA and PE, the EVA used in these blends contains 9% in weight

VA units. The PBT segment of the copolymer is expected to promote adhesion with the PBT phase, as the PETG segment did in a blend studied by Legros.

EVA and DBTO are added to PE and PBT. The blends in which copolymer is formed are composed by PE, PBT, EVA, and DBTO. Morphology of such blends has been compared to morphology of PE/PBT and PE/PBT/EVA blends. Influence of the concentration of PBT and EVA, of the presence of DBTO and of the synthesis of copolymer on particle size has been analyzed.

The weight composition of different blends containing 10% of PBT is given in Table II. Other

Table II Weight Composition of Blends with 10% of PBT

| PE | PBT | EVA | DBTO |
|----|-----|-----|------|
| 90 | 10 | 0 | 0 |
| 89 | 10 | 0 | 1 |
| 85 | 10 | 5 | 0 |
| 84 | 10 | 5 | 1 |
| 80 | 10 | 10 | 0 |

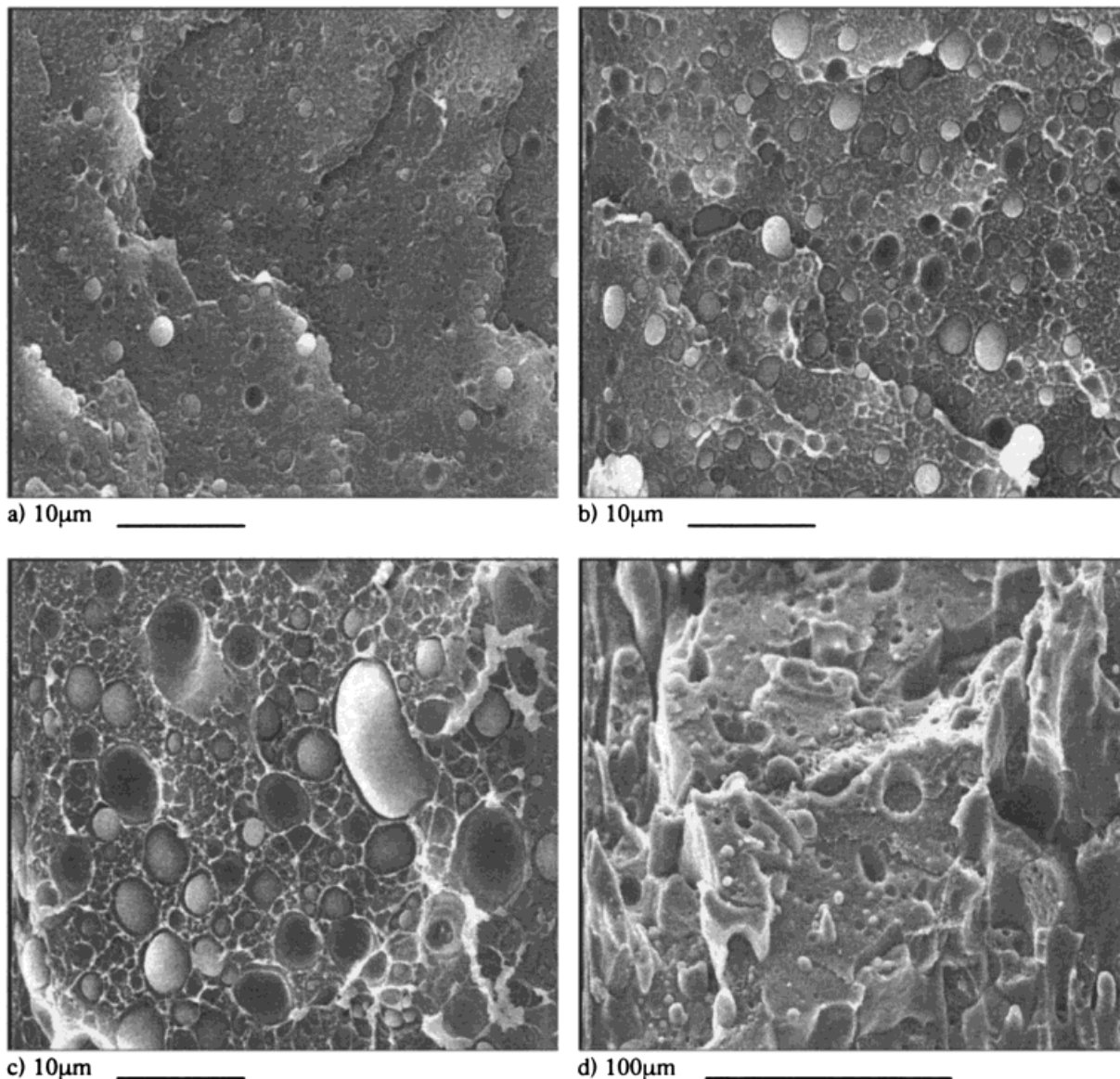


Figure 4 SEM micrographs of blends of PE/PBT: (a) 90/10, $\times 2000$; (b) 80/20, $\times 2000$; (c) 70/30, $\times 2000$; (d) 60/40, $\times 400$.

series of blends have been realized with the same weight fraction of EVA and DBTO, increasing weight amount of PBT (20, 30, and 40%) and correlated decrease of PE.

Influence of PBT Content

Under identical processing conditions, the relative proportions of the components and their differences in melt viscosity play a significant role in determining the morphology. In our case, the minor component (PBT) is of lower viscosity compared to the major one (PE). It will be finely dis-

persed in the matrix of PE. Figure 4 shows the morphology of PE/PBT blends with 10, 20, 30, and 40% PBT. As PBT content increases, the size of particles increases. The average number particle size for these blends has been determined with a computer program on, in each case, at least 100 particles. The results obtained are shown in Figure 5. At 40% PBT, the two phases are nearly cocontinuous and it becomes very difficult to determine the size of the PBT domains. Small particles of PBT dispersed in the PE matrix are present as larger ones. In all cases, there is no evidence of adhesion between the minor phase and the matrix

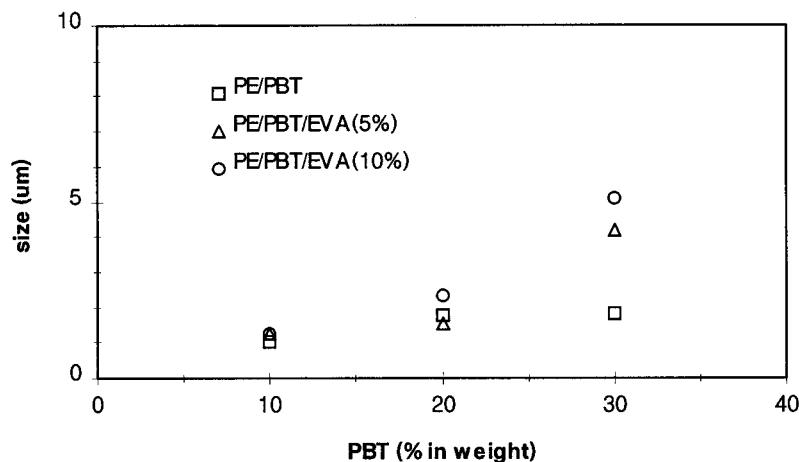


Figure 5 influence of EVA on the size of dispersed phase.

because the surface of PBT particles is perfectly clean. Moreover, some microvoids can be observed around PBT nodules.

Influence of EVA

Two concentrations of EVA have been studied: 5 and 10% in weight. Addition of EVA in the PE/PBT blends does not really change morphology. At 10, 20, and 30% PBT is always dispersed as spherical nodules in the matrix. Adhesion between PE and PBT is not improved. SEM micrographs for these blends are similar to those previously shown for blends of PE/PBT. Only at 30% PBT a slight increase in particle size is observed (see Fig. 5).

Influence of DBTO

Addition of 1% in weight of DBTO in PE/PBT/EVA blends enables synthesis of the PBT-*g*-EVA copolymer. Without DBTO, as previously observed, contrast between PE and PBT is very good: particles of the dispersed phase are easy to distinguish from the matrix, whether EVA is present or not. On the contrary, in the presence of DBTO it becomes very difficult to distinguish the two phases, as we can see on Figure 6(a) for a blend of PE/PBT/EVA/DBTO : 74/20/5/1. Similar observations can be done for blends with 10, 30, and 40% PBT. Micrographs of PE/PBT/DBTO do not show this morphology, as can be seen in Figure 6(b) for a blend of PE/PBT/DBTO : 79/

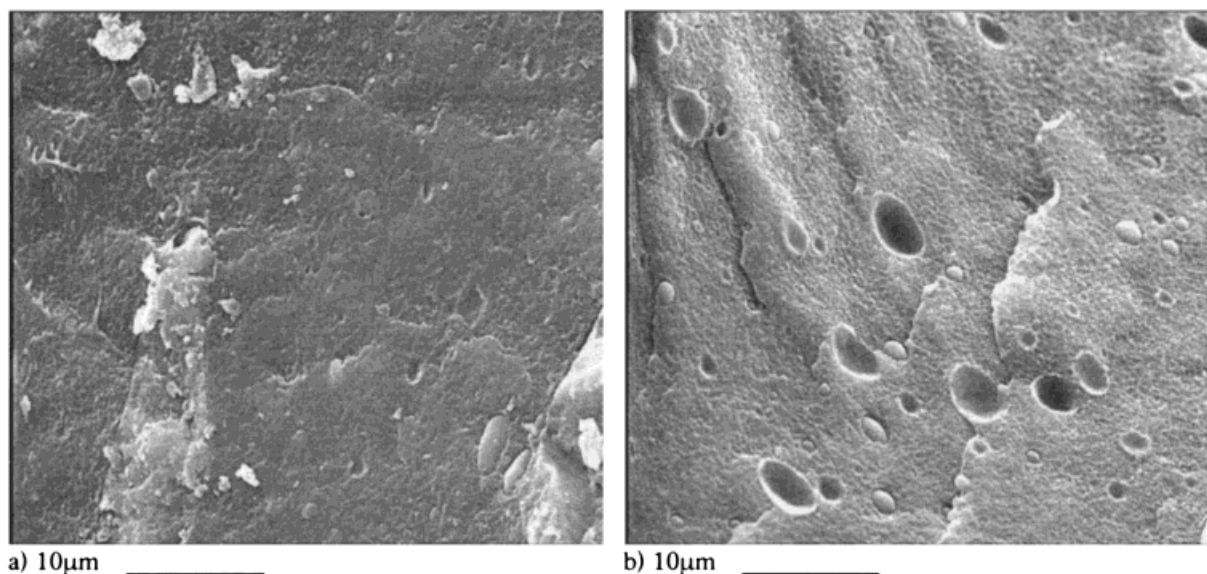


Figure 6 SEM micrographs of blends of (a) PE/PBT/EVA/DBTO: 74/20/5/1, $\times 2000$; (b) PE/PBT/DBTO: 79/20/1, $\times 2000$.

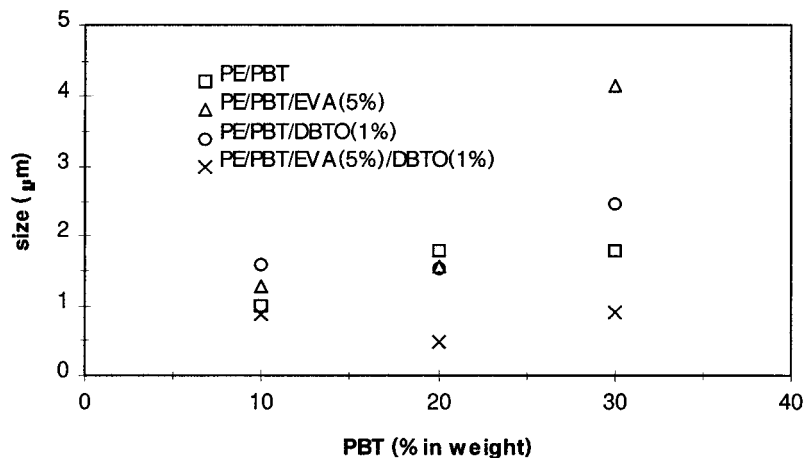


Figure 7 influence of DBTO on the size of the dispersed phase.

20/1. So loss of contrast is only observed when PBT, EVA, and DBTO are present, in other words, when synthesis of copolymer is possible.

Contrast of blends of PE/PBT/EVA/DBTO is too bad to directly determine the average size of PBT particles. So, for these blends, PBT has been extracted with a solution of phenol/1,1,2,2-tetrachloroethane. Micrographs realized on these samples show holes where PBT nodules were localized before extraction. The average sizes of these holes have been determined and compared to the sizes of PBT nodules in blends of PE/PBT, PE/PBT/EVA, and PE/PBT/DBTO (see Fig. 7). A slight decrease is observed.

In the presence of ester groups, DBTO reacts to give distannoxane structures, which are the true and effective catalyst for transesterification reactions through alkoxy acyloxy ligand exchange and tin atom complexation. Such structures have been evidenced with PBT and EVA. As this two polymers are incompatible, transesterification reactions can only occur at the interface. So, if the copolymer is obtained, it will be in the right place to act as a compatibilizer. The important changes in morphology that occur when EVA and DBTO are added to PE/PBT blends suggest that this reaction really takes place at the interface.

CONCLUSION

To compatibilize PE/PBT blends, a grafted copolymer PBT-EVA has been synthesized *in situ* during the processing operation, through ester exchange reaction. EVA is partially compatible with PE. So the EVA segment of this copolymer is expected to provide adhesion with the PE phase,

while the PBT graft should improve adhesion with the PBT phase.

In a first step, the synthesis of PBT-*g*-EVA copolymer has been carried out from the PBT/EVA/DBTO blend in the melt. It has been evidenced by an NMR study. As PBT and EVA are incompatible, the copolymer can only be synthesized at the interface, and so its amount is small. So it cannot be directly analyzed from the PBT/EVA/DBTO blend but must be first isolated by selective extractions. The copolymer presents all the resonances of PBT and EVA and two new ones, typical of the copolymer. These resonances have been analyzed with the help of a model reaction.

In a second step, the synthesis of the copolymer has been realized *in situ* during the processing of the blends with PE as the matrix (PE/PBT/EVA/DBTO). Morphologies of these blends have been compared to those of blends in which the copolymer cannot be obtained, in other words where PBT, EVA, and DBTO are not present together (PE/PBT/EVA or PE/PBT/DBTO blends). SEM analysis shows that when the synthesis of the copolymer is possible, important changes in the morphology of the blend take place. Contrast between PE and PBT is considerably reduced, and a decrease in PBT particle size is also observed.

PBT-*g*-EVA copolymer can only be synthesized at the interface PBT/EVA. The results obtained by SEM analysis show that adhesion between PE/PBT seems to be increased in blends where this copolymer can be obtained. Additional studies are in progress to evaluate the influence of this copolymer, located at the interface, on the mechanical and rheological properties for PE/PBT blends.

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