Reactive compatibilization of polyester/vinyl acetate copolymer blends: rheological, morphological and mechanical properties

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The '*in situ*' compatibilization of poly(ethylene terephthalate) (PET) copolymer (PETG) with ethylene vinyl acetate (EVA) copolymer via catalysed transesterification reactions was examined through rheological, morphological and mechanical studies. The addition of dibutyltin oxide catalyst was found to diminish the size of the dispersed phase, enhance its adhesion with the matrix and lead to an increase in the dynamic elastic modulus (G') with temperature. This improvement in adhesion also results in a considerable increase in the elongation at break, from 20 to 140% when 2.4 wt% of catalyst is added to a 70/30 PETG/EVA blend. The comparative behaviour of blends with and without catalyst is explained via copolymer formation at the interface and co-crosslinking of EVA and PETG chains.

(Keywords: polymer blends; transesterification; compatibilization)

INTRODUCTION

Transesterification or ester exchange reactions are well established in polyesters and the like, at melt processing temperatures above 230°C. They are reported in the literature[1–4] to explain the partial miscibility observed in certain blends such as poly(ethylene terephthalate) (PET)/polycarbonate (PC), polyester/phenoxy or polyester/polyarylate. These reactions, which are assumed to be induced by residual catalyst remaining from the polyester polymerization, have been studied by infra-red spectroscopy (i.r.), nuclear magnetic resonance (n.m.r.) and differential scanning calorimetry (d.s.c.). They lead to the formation of a copolymer, primarily located at the interface, whose role in interfacial tension reduction and miscibility enhancement is broadly recognized experimentally and theoretically in reactive processing[5–7]. Furthermore, the production of such a compatibilizing agent during melt compounding presents a major economic advantage.

The previously quoted studies concern transesterification involving ester groups present in the main polymer chains. Less work is devoted to transesterification involving polymers containing pendant ester groups[8–10]. One example is given by Pilati[9] who prepared blends by adding ethylene vinyl acetate (EVA) copolymer during the polymerization of poly(butylene terephthalate) (PBT), using $Ti(OBu)_4$ catalyst. In the final product, PBT-*g*-EVA copolymer, formed by transesterification, and crosslinked EVA were found, in addition to linear PBT and non-reacted EVA.

In the present study, blends based on an amorphous polyester (PETG) and EVA copolymers (containing 28 wt% vinyl acetate) have been investigated. This system was chosen with the aim of studying the compatibilization of polyester/polyethylene (PE) blends via the addition of EVA, and of trying to improve the impact toughness of the polyester, as EVA is already used to achieve better low-temperature impact resistance for polypropylene[11]. In polyester/EVA/PE ternary blends, EVA is expected to create a boundary layer between both incompatible polyester and PE polymers. For blends based on PETG and EVA, however, the rate of transesterification is very slow at temperatures below 200°C. The use of a catalyst is required to ensure compatibilization reaction within realistic extruder residence times. An organometallic compound, dibutyltin oxide (Bu_2SnO), was chosen as it has proved to be efficient in the transesterification between acrylic ester/propylene copolymer and EVA copolymer[10,12].

Owing to chemical structure similarities, EVA displays some miscibility with PE. In addition, acetate groups borne by alternate carbon atoms laterally to the main chain can react readily with the polyester macromolecules and form either a grafted EVA/polyester copolymer or crosslinked EVA/PETG. This is illustrated in *Figure 1*. Ester exchange reactions between EVA and polyester as shown in *Figure 1a* can occur with one or several acetate

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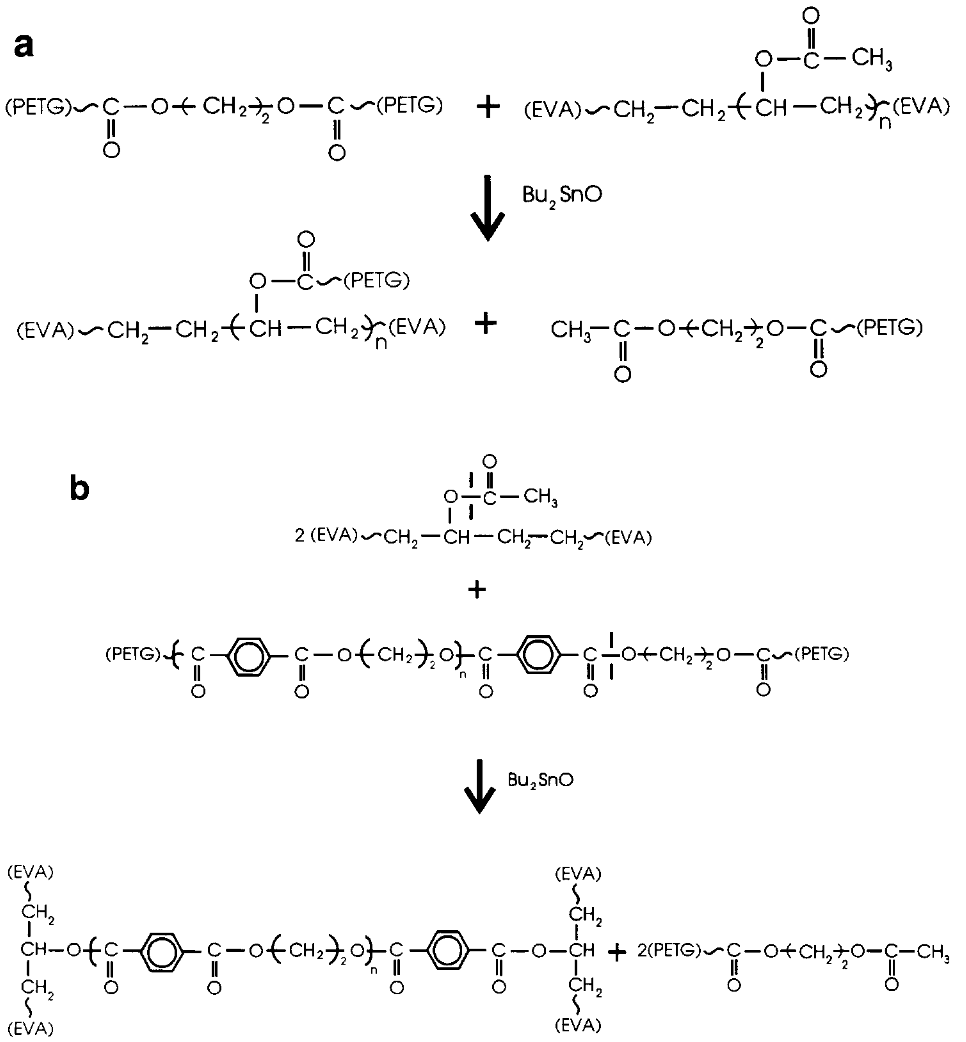


Figure 1 Schemes for transesterification between terephthalic-type polyester and acetate groups from EVA: (a) copolymer formation; (b) co-crosslinking of EVA and polyester chains

groups borne by the same EVA molecule and result in either single or several grafted polyester chains. This does not lead to the crosslinking of the polyester, as opposed to the case of simultaneous exchange reactions between two pendant acetate groups, which form co-crosslinked EVA/PETG (see *Figure 1b*).

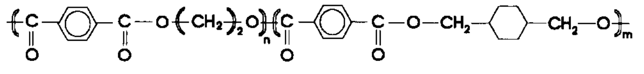
It is seen from both reaction pathways described in *Figure 1* that transesterification taking place in the studied blends leads necessarily to polyester chain scission. A compromise has to be achieved in order to produce sufficient copolymer at the interfaces, without extensive decrease in the polyester molecular weight.

In this article, we report results of a preliminary investigation on the reactivity of molten PETG/EVA blends in the presence of Bu_2SnO catalyst, using a rheological method. The effect of chemical modification during melt mixing was investigated in terms of the minor phase dispersion quality and stability, as well as the mechanical properties.

EXPERIMENTAL

Materials

The blends investigated in this study are based on an EVA copolymer with a copolyester (PETG) synthesized from a mixture of terephthalic acid, ethylene glycol and 1,4-cyclohexanedimethanol. PETG was chosen, since it can be processed at temperatures less than the reaction threshold temperature. It is a product from Eastman Kodak (PETG 6763) having the following chemical structure:



Because of the introduction of the cyclic diol moiety, the crystallizability of PETG is hampered compared to that of PET. The latter is obtained simply from terephthalic acid and ethylene glycol polycondensation and has a more regular chemical structure. While PET is semicrystalline, PETG is essentially amorphous and has a glass transition temperature around 80°C. The PETG 6763 used has a molecular weight of $26\,000\,\mathrm{g\,mol^{-1}}$.

EVA was kindly supplied by AT Plastics Inc. (AT 2803M). It contains 28% vinyl acetate by weight and has a melt index of 3 g per 10 min (ASTM D1238). The approximate molecular weight, as given by the supplier, is $M_n = 30\,000\,\mathrm{g\,mol^{-1}}$.

Blend preparation

The copolyester was dried under vacuum at 80°C for at least 12 h to minimize possible hydrolysis during melt processing. Blending of 25 g samples was performed using a Brabender Plasticorder at 40 rev min^{-1} and under a continuous flow of nitrogen. Two sets of time–temperature conditions were adopted: 5 min at 180°C and 10 min at 210°C. As an indication of the melt viscosity ratio, the torque ratio of PETG and EVA was found to be equal to 2.5 at 180°C and 1.5 at 210°C, for which condition, mixing was easier.

After the blending step, a portion of each sample was quenched in liquid nitrogen and fractured for morphology analysis. The rest of the blend was compression moulded into a specimen 1.5 mm thick, and used for rheological and mechanical measurements. Moulding conditions in the heating press were 7 min at 180°C, using a progressive pressure starting from 0.75 to 4 tons. The moulded sheets were finally cooled down to room temperature under pressure.

The different compositions of the PETG/EVA blends were 70/30, 50/50 and 30/70 (weight percentages). Bu_2SnO was added to the blends as an ester exchange reaction catalyst, with contents ranging from 1.2 to 4 wt% of the total sample weight.

Scanning electron microscopy

The morphology of the freeze–fractured cross-sections was examined using a scanning electron microscope, Jeol JSM-820. Observations were made both on the original and chemically etched samples. For that purpose, the EVA component was dissolved by immersion in toluene for 1 h at 50°C. Morphological stability was assessed by comparing Brabender mixed and quenched samples to those obtained after mixing and compression moulding.

Differential scanning calorimetry

D.s.c. experiments were performed on a Perkin-Elmer DSC-2 instrument, over the temperature range 250°C to room temperature, at a cooling rate of 10°C min^{-1}.

Rheology

Dynamic rheological measurements were carried out on a Bohlin CSM rheometer using a parallel-plate geometry ($R = 1.25 \times 10^{-2}$ m) and a gap of approximatively 1.5 mm. Most experiments were performed at a fixed angular frequency ($\omega = 6.28$ rad s^{-1}), all under nitrogen atmosphere. The oscillatory shear–strain response never exceeded 0.02, in order to be in the domain of linear viscoelasticity.

Mechanical properties

Tensile stress–strain properties were obtained at room temperature with an Instron tensiometer, Model 4201. As for the rheological experiments, samples were cut with a standard die from a compression moulded specimen. At least four specimens of each sample were tested using a cross-head rate of 5 mm min^{-1}.

RESULTS AND DISCUSSION

Differential scanning calorimetry

In this system, it was not possible to evaluate the extent of miscibility by glass transition temperature determination[6]. Indeed, the glass transition region for PETG is masked by the melting peak of EVA, situated at about 80°C for a 28% vinyl acetate content. On the other hand, the crystallization behaviour of EVA chains may be studied in order to evaluate the influence of the addition of both amorphous polyester and reactive tin compound.

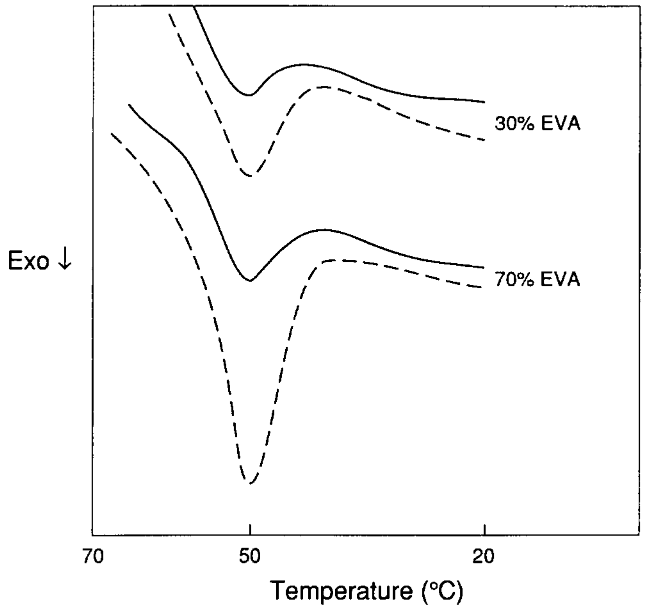


Figure 2 D.s.c. cooling traces of different PETG/EVA blends: (– – –) without; and (——) with 4 wt% Bu_2SnO. The traces are normalized for the same weight of sample

Specimens of equal weight were maintained for 5 min at 250°C and cooled at a rate of 10°C min^{-1}. Thermograms of PETG/EVA blends are illustrated in *Figure 2*, for the compositions 70/30 and 30/70, containing 0 or 4 wt% Bu_2SnO. A comparison between crystallization peaks obtained for the blends without Bu_2SnO shows a decrease in the specific area, when the amount of ethylene copolymer is reduced. This phenomenon is not surprising, considering that these peaks situated at 48 ± 2°C correspond to the crystallization ability of ethylene sequences only, present in EVA. Consequently, the degree of crystallinity of the total blend decreases with the percentage of ethylene copolymer. It also appears that the position of the crystallization peaks is only slightly affected for the blends, relative to pure EVA, for which the minimum was measured at 48°C. In order to understand the influence of polyester chains, a cooling scan was performed on PETG alone. No detectable crystallization peak was observed under the experimental conditions (cooling from 250°C to room temperature).

An additional reduction of the crystallization peak is observed when the blends are mixed with the tin compound. This effect may be explained by transesterification reactions and particularly the crosslinking of EVA chains according to *Figure 1b*, which is favoured when the number of EVA chains increases. Such reactions produce bridging between ethylene copolymer macromolecules, which modify or hinder their crystallization ability[13].

Rheology

For a more detailed study of the influence of the tin catalyst on copolyester/vinyl acetate copolymer blend reactivity, the viscoelastic properties were measured by small amplitude oscillatory shear in the molten state. Changes in G' and G'', the storage and loss modulus respectively, were computed under non-isothermal

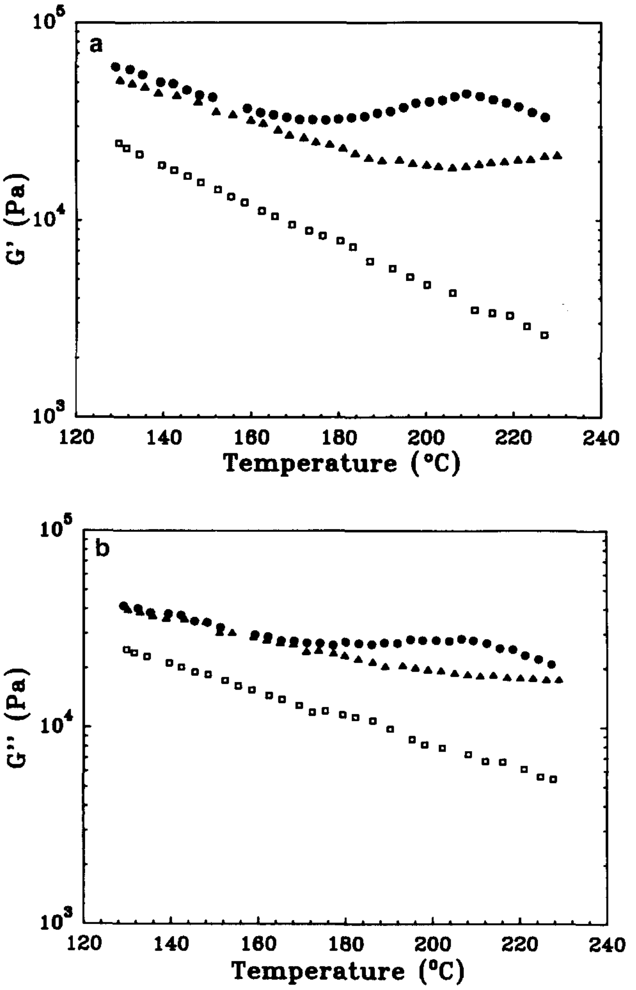


Figure 3 Temperature dependence of (a) storage modulus G'; and (b) loss modulus G'': EVA alone (□); EVA with 1.2 (▲) or 4 wt% (●) Bu_2SnO

conditions. Temperature sweeps were carried out from 130 to 230°C, to determine the most favourable conditions for Bu_2SnO catalysed reactions, in either EVA copolymer or PETG/EVA blends.

Figures 3a and *3b* represent the temperature dependence of G' and G'' for the original EVA and EVA containing 1.2 or 4% Bu_2SnO. As usually observed for polymers, both the storage and loss moduli of EVA decrease as the temperature increases and as the viscosity is expected to drop. Variations are more important for the storage modulus, G', than for the loss modulus, G''. For the highest Bu_2SnO content, G' reaches a minimum as the polymer becomes fluid and then begins to increase as the temperature goes beyond 170°C. This effect is explained by the formation of chemical crosslinking between EVA copolymer chains through an acetoxy alkoxy distannoxane structure[12], which leads to an increase in the elastic modulus. Crosslinking modifications prevent molecular mobility and the evolving network confers an increasing stiffness on the copolymer. For a Bu_2SnO content of 1.2%, the variation of G' with temperature is intermediate between both cases described above. The elastic modulus first decreases and then starts to increase at temperatures above 190°C. At the end of the experiment (230°C), the viscous behaviour dominates for the EVA without catalyst ($G'' > G'$), while elastic behaviour is a characteristic of the final stage of the reaction between EVA and Bu_2SnO, due to the network formation ($G'' < G'$). It is necessary to underline that the initial moduli on *Figures 3a* and *3b* are not the same for EVA and catalysed EVA. This may be due to a simple filler effect having strong interactions with the EVA matrix.

The effect of heat treatment on EVA–tin oxide reactivity has been confirmed by measuring viscoelastic properties before and after the temperature scan. *Figure 4* shows corresponding variations in G' as a function of frequency (from 6.3×10^{-2} to 188 rad s^{-1}) for EVA containing 4% Bu_2SnO. After chemical reaction, the elastic modulus is higher relative to the first measurement and G' tends to reach a plateau value at very low frequencies, which is a characteristic of a crosslinked polymer. A dissolution test was also performed on the same reacted sample to prove that reaction occurred in the melt. It has been found that 25 wt% of the EVA–Bu_2SnO sample is insoluble in toluene at 50°C; the crosslinked moiety remains as a gel fraction in the solution[14].

Figure 5 reports data obtained for PETG/EVA blends prepared with different amounts of Bu_2SnO. The blend containing 30 wt% EVA and 1.2 wt% Bu_2SnO reveals

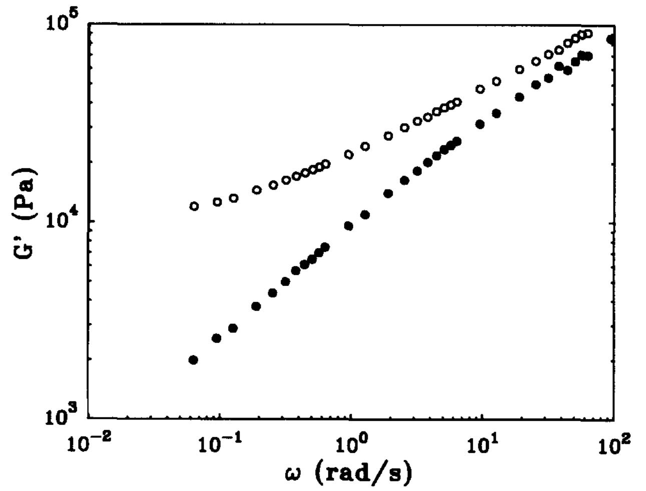


Figure 4 Frequency dependence of storage modulus G' for EVA + 4 wt% Bu_2SnO: (●) before; and (○) after reaction

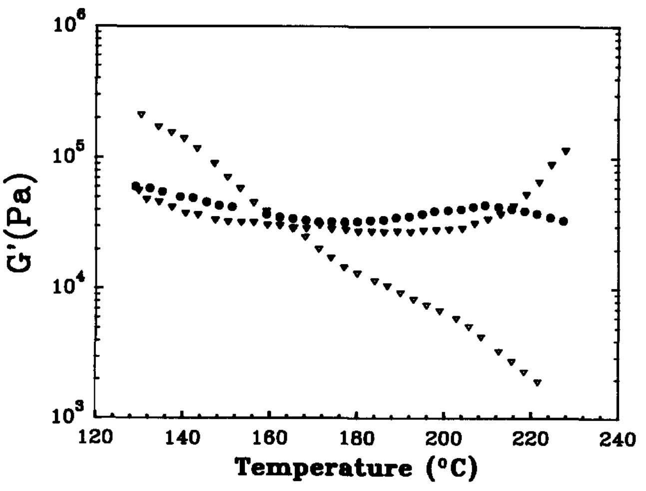


Figure 5 Temperature dependence of storage modulus G': EVA + 4 wt% Bu_2SnO (●); PETG/EVA 70/30 with 1.2 (▽); and 4 wt% Bu_2SnO (▼)

an elastic modulus which decreases over the entire temperature range studied. The storage modulus for the PETG/EVA 70/30 blend without catalyst is not shown here, but follows exactly the same trend. Under the above conditions, only the reaction scheme shown in *Figure 1a* should be taking place at the interface between both phases, but its extent is too small to be detected by rheological measurements. On the other hand, when a higher percentage of Bu_2SnO is used, a stable G' transition region is observed for the PETG/EVA blend, followed by a drastic increase at high temperature, due to the co-crosslinking of EVA and polyester (*Figure 1b*). Note that this reaction is shifted towards higher temperature in the case of the PETG/EVA blend when compared with the 100% EVA sample. *Figure 5* also shows that the initial modulus of the blends decreases when the amount of Bu_2SnO is increased from 1.2 to 4%. This indicates opening of ester bonds by the organometallic compound which leads to chain scission and molecular weight decrease, before any coupling can take place. This effect is a result of the previous thermal history in the Brabender.

Figure 1a gives an example of copolymer synthesis by ester exchange between one acetate group of EVA and one phthalic ester function from ethylene glycol. For the studied PETG copolyester, the same reaction can take place involving the phthalic ester sequences of 1,4-cyclohexanedimethanol which are less frequent in number. Comparable direct transesterification has been shown by Devaux *et al.*[15] to be the most likely mechanism of interchange reactions in blends of polycarbonate (PC) with PET or PBT. Similar studies were carried out by Godard *et al.*[1] on melt processing of PC/PET with and without organometallic catalyst. They arrived at the same conclusion that the main reaction occurring in molten PC/PET was transesterification between PC and PET, rather than degradation. A third example is given by Kimura and Porter[16], who demonstrated that transesterification dominates over molecular-weight reduction, when PC/PBT blends are held at 250°C for various periods.

Morphology

Electron microscopy was used to investigate morphological changes due to chemical reactions between the different components. *Figure 6* shows micrographs of fractured surfaces, obtained for the PETG/EVA 70/30 blends, which were prepared at 210°C with 0, 1.2 and 2.4 wt% Bu_2SnO respectively. A two-phase morphology is clearly seen for the non-reacted blends, suggesting immiscibility between PETG and EVA at this processing temperature. In this sample, the EVA dispersed phase appears as spheres which have a very low level of adhesion to the matrix. Indeed, the degree of adhesion is so low that many of the dispersed spheres have been flung from their respective cavities during the fracture. The rupture propagates preferentially along the interfaces, which are the weakest part of the material.

By the addition of 1.2% Bu_2SnO, adhesion between the matrix and the droplets is enhanced, leading now to the presence of some cross-sectioned spheres observed on the micrograph. This observation is a clear indication of the presence of the PETG/EVA copolymer, produced by transesterification as shown by *Figure 1a*. In the case of 2.4% catalyst content, EVA domains are not observed any more, suggesting that the fracture takes place in the matrix itself, which now constitutes the least resistant phase. The three micrographs of *Figure 6* clearly

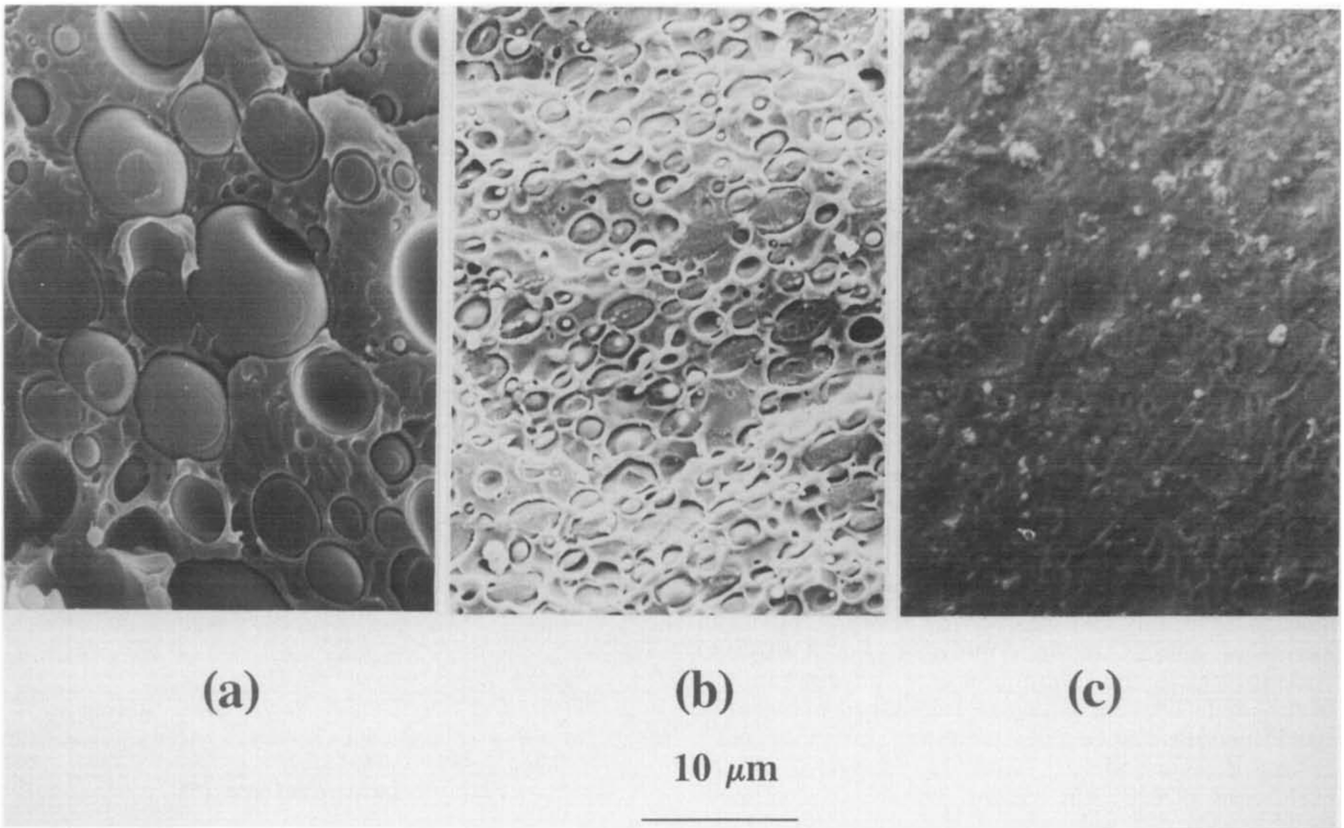


Figure 6 Scanning electron micrographs of PETG/EVA 70/30 blends: (a) without; (b) with 1.2; and (c) with 2.4 wt% Bu_2SnO

demonstrate the rupture-type changes as adhesion between phases is enhanced. The adhesion improvement is attributed to newly created interfacial chemical bonds between both phases. For even higher quantities of catalyst, it becomes necessary to extract the minor phase by selective dissolution in order to observe a dispersed domain size. Micrographs in *Figure 7* show the morphology of the extracted blends, prepared either with or without 4 wt% Bu_2SnO. Comparing *Figures 7a* and *7b*, we note a significant decrease in EVA particle dimensions caused by compatibilization. The number-average diameter d_n was measured using a semi-automatic method of image analysis. The diameter decreases from 3.9 μm for the non-compatibilized blend to 1.9 μm for PETG/EVA containing only 1.2% Bu_2SnO.

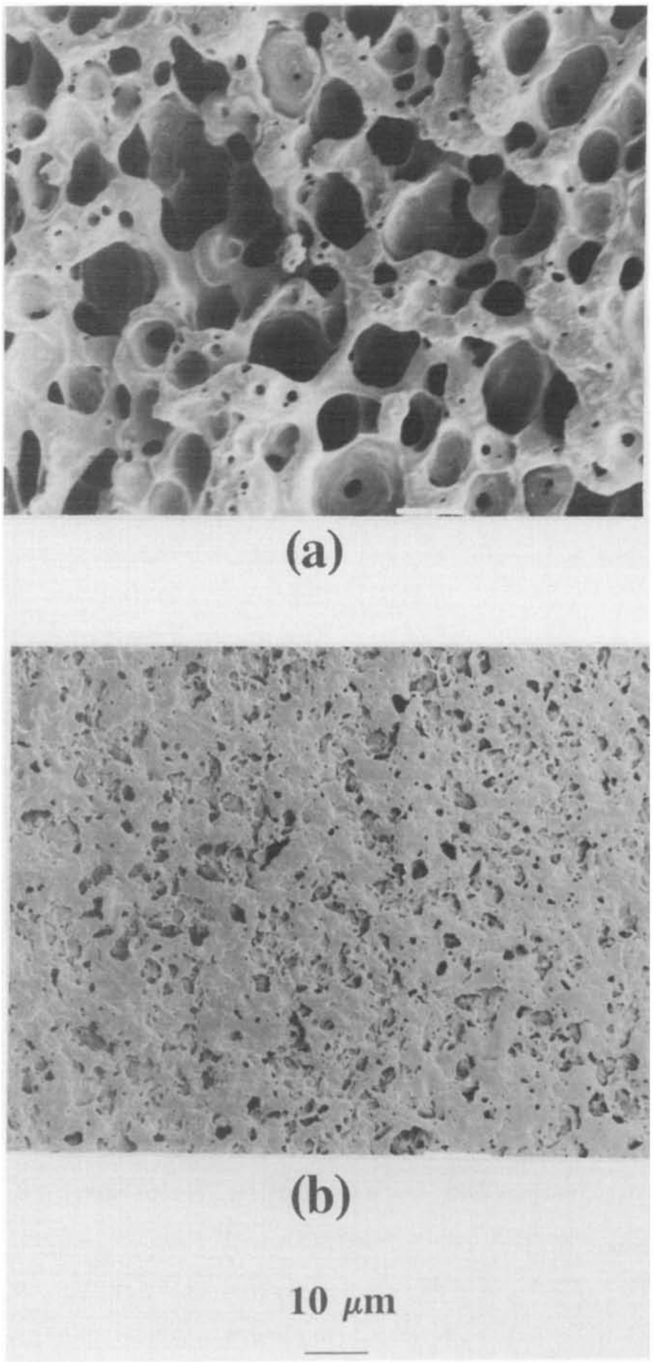


Figure 7 Scanning electron micrographs of extracted PETG/EVA 70/30 blends: (a) without; and (b) with 4 wt% Bu_2SnO

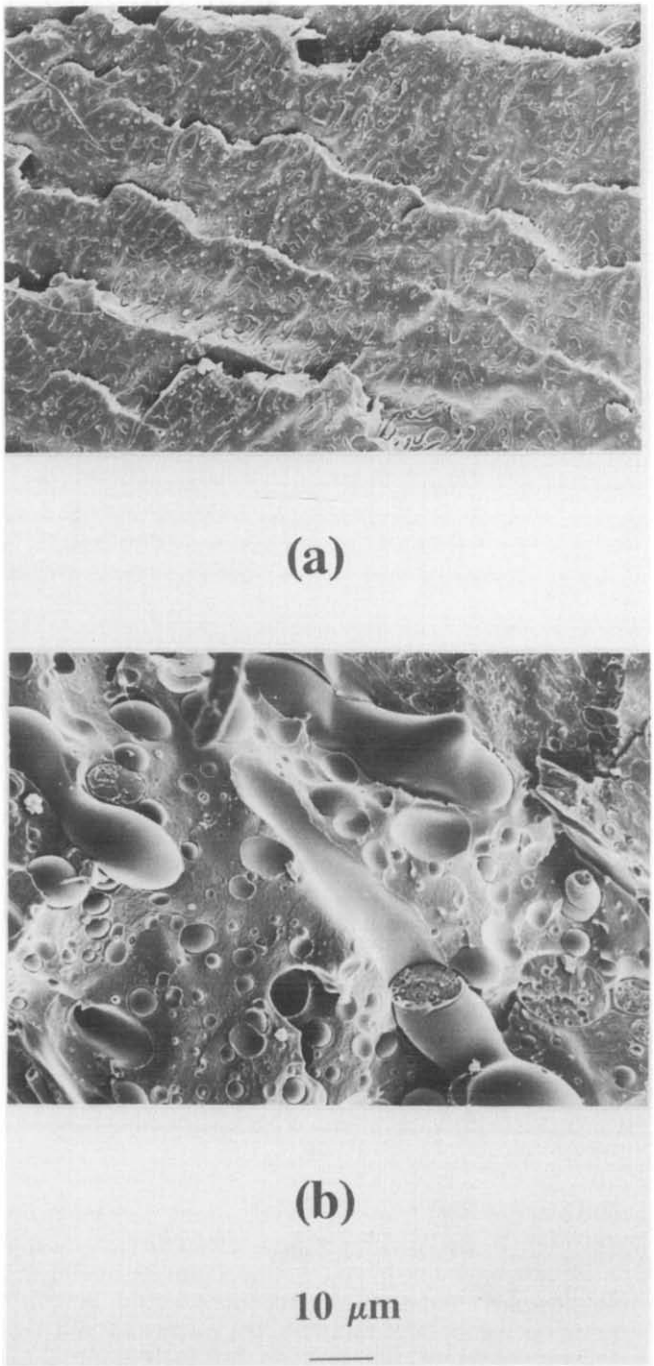


Figure 8 Scanning electron micrographs of PETG/EVA 50/50 blends without Bu_2SnO: (a) quenched sample after blending; (b) moulded sample at 180°C

Morphological stability of the blends has been examined in terms of coalescence as a function of moulding conditions and of Bu_2SnO concentration. Samples of the same composition were observed after mixing and quenching only, from the Brabender Plasticorder, and compared to samples obtained after both mixing and moulding in a press at 180°C. *Figure 8* shows SEM micrographs of 50/50 blends containing no Bu_2SnO. The observed morphology is typical of the co-continuous type, which tends to be particularly sensitive to any composition variations. The quenched-mixed-only sample, which is perfectly homogeneous, shows the typical morphology of two interpenetrating phases. On the contrary, the moulded sample is very

Table 1 Tensile properties of PETG/EVA 70/30 blends

Bu_2SnO (%)	Modulus (MPa)	σ_{max} (MPa)	$\Delta L/L_0$ (%)
0	585	15.4±0.2	20
1.2	557	20.1±0.6	98
2.4	555	18.3±0.6	141
4.0	905	18.5±0.4	115

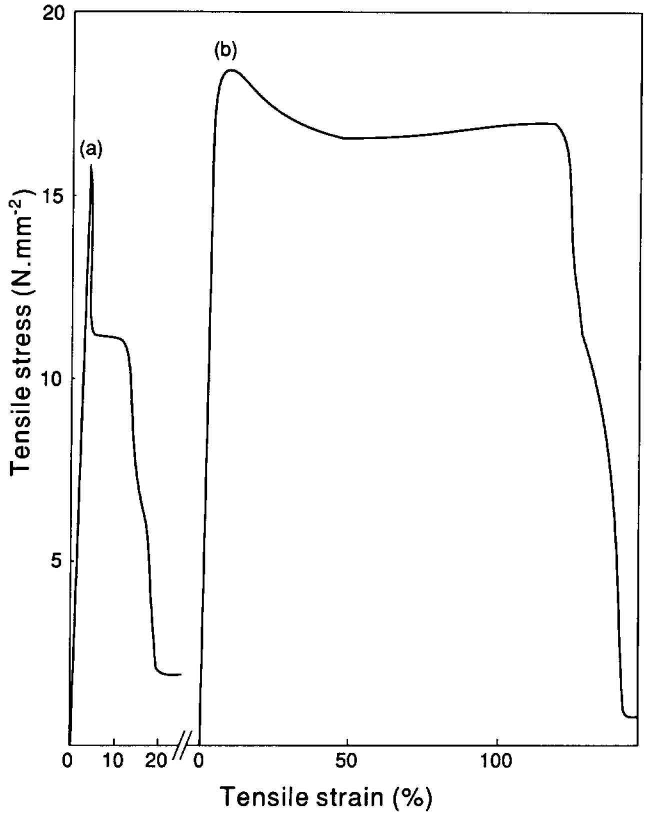


Figure 9 Stress–strain tensile curve of PETG/EVA 70/30 blends: (a) without; and (b) with 1.2 wt% Bu_2SnO

heterogeneous and contains some elongated particles larger than 10 μm, which are apparently formed during compression moulding by coalescence. Parallel experiments have demonstrated that the morphology of Bu_2SnO containing blends is similar for the quenched and the moulded specimens. To sum up the principal results arising from the morphology study, it appears that catalysed interfacial reactions in PETG/EVA blends lead to a finer dispersion of EVA droplets as well as a more stable morphology[17].

Mechanical properties

It is well known that the elongation at break is very sensitive to the state of the interface[18]. Results of tensile tests are given in *Table 1* for PETG/EVA 70/30 blends with Bu_2SnO contents ranging from 0 to 4 wt%. At values up to 2.4% of catalyst, the tensile modulus of the blends is not affected, while the elongation at break is considerably increased from 20 to 141%. This effect can also be seen in the stress–strain curves of *Figure 9*, which show a change from brittle to rubbery behaviour as the content of Bu_2SnO increases from 0 to 2.4 wt%. Note that the stress for the modified blend remains at a high level during the elongational test and drops only when the sample breaks.

For a 4 wt% Bu_2SnO content, the modulus increases indicating a more rigid material, but at the same time the ultimate elongation drops slightly. Apparently, there is a critical value for which the failure-type changes from ductile to brittle. For a large amount of tin compound, the co-crosslinking density of EVA and PETG chains may be too extensive in the interfacial region as suggested by the rheology experiments.

CONCLUSION

In this work, significant evidence has been found to support the *in situ* generation of a compatibilizer for PETG/EVA blends with tin oxide catalyst. First of all, the decrease of EVA dispersed-phase dimensions as well as the stabilization of morphology are explained by the presence of the newly formed interfacial modifier, which may be compared to an emulsifying agent. Furthermore, improvement of the elongational properties of the reactive blends suggest that the copolymer ensures a good stress transfer across the interface. However, at higher levels of Bu_2SnO, grafting or crosslinking density becomes very large and the blends become more rigid, with a lower elongation at break.

It is important to maintain a low catalyst content in order to produce sufficient transesterification at the interfaces, without extensive chain scissions of the polyester. In the present study, a Bu_2SnO content of 1.2 wt% appears to yield good results in terms of morphological stability and elongational properties. Blending EVA with Bu_2SnO in a first step and then adding this to PETG may also result in favourable transesterification at the interfaces.

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