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Morphology modification by interfacial chemical reaction in a polyester/ethylene vinyl acetate/polyethylene blend

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A morphological study of poly(butylene terephthalate) (PBT)/polyethylene (PE)/ethylene vinyl acetate (EVA) ternary blends is presented. Scanning electron microscopy analysis illustrates that, after the addition of a transesterification precursor (Bu_2SnO), the blend forms a composite droplet morphology where the PBT/EVA copolymer, synthesized *in situ* creates a boundary layer between the incompatible PBT matrix and PE dispersed phase. Electron microprobe analysis is used to localize Bu_2SnO in the PBT and EVA phases, where it would be expected to favour the formation of the copolymer at the interface. © 1997 Elsevier Science Ltd.

INTRODUCTION

Poly(butylene terephthalate) (PBT) is a high melting crystallizable polymer, with good processability and solvent resistance properties. Blends of PBT with PE are of significant practical interest largely due to the low cost of polyethylene. However, because of the high incompatibility between both polymers, simple melt blending leads to morphologically unstable and brittle products. An efficient method of compatibilizing is required.

One route often used to compatibilize polymer blends is to add copolymers which lower the interfacial tension, favour a fine dispersion and stabilize the morphology. An approach presented previously[1] consists of synthesizing such copolymers by interchain chemical reactions during processing operations. In that previous study, it has been shown that it is possible to synthesize polyester–polyethylene vinyl acetate copolymers by exchange reactions of ester groups in the presence of Bu_2SnO. The latter acts as a precursor of alkoxy, acyloxy distannoxanes, the true catalyst that makes the kinetics of the reactions achievable within the residence time of usual processing operations[2-4].

This paper presents a morphological study of ternary PBT/EVA/PE blends. The blends are compatibilized *in situ* during processing, by transesterification between ester groups of PBT and EVA, induced by the addition of Bu_2SnO. This reaction which occurs within the usual operating temperature range and residence time of twin screw extruders yields a copolymer which is particularly effective as an emulsifier of both PBT and EVA. Scanning electron microscopy and electron microprobe analysis were used to investigate the distribution of the blend components and the morphological changes.

EXPERIMENTAL

Materials

The materials investigated in this study are blends of a PBT, chosen as the main component, with both a high density polyethylene (HDPE) and an ethylene vinyl acetate copolymer (EVA), as the dispersed phase(s). The PBT, obtained from Hoechst Celanese (Celanex 2008), is a semi-crystalline polymer, having a melting temperature of 228°C and a specific gravity of $1.31\,g\,ml^{-1}$. The HDPE is a product of Dow Chemical with a melt index of $17\,g/10\,min$. Finally, the EVA copolymer (AT Plastics Inc., 2803M) contains 28% vinyl acetate by weight and has a melt index of $3\,g/10\,min$ (ASTM D1238).

Blend preparation

The binary and ternary blends were prepared in a Brabender Plasticorder at 40 rpm and 230°C for 15 min. Prior to blending, the PBT pellets were dried at 80°C for 12 h. In a second set of experiments, Bu_2SnO was added as the precursor of distannoxane to induce transesterification, at a total sample weight of 1.2-4%. For comparison, a twin screw extruder (Leistritz LSM 34 mm model, L/D = 33.5) was also used at 100 rpm and 250°C to prepare some blends.

Scanning electron microscopy

Morphological analyses were carried out on liquid nitrogen frozen and fractured samples. The corresponding

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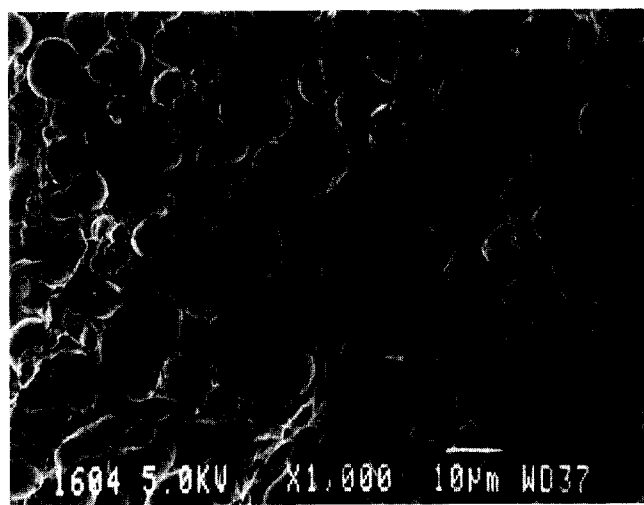
Figure 1 Scanning electron micrographs (×1000) of 70/30 binary blends: (a) PBT/PE; (b) PE/EVA 28%
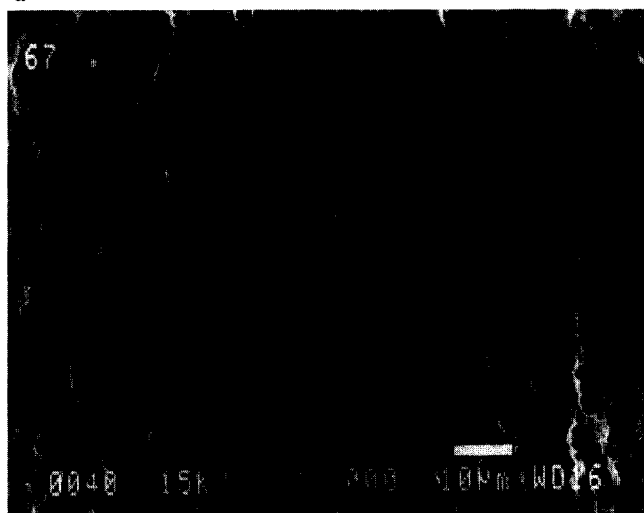
cross sections were examined by scanning electron microscopy, using a Jeol JSM-820. When specified, the observation was also made on chemically etched samples for which the EVA component was dissolved by immersion in toluene for 1 h at 50°C. Furthermore, electron microprobe analysis was performed to locate the Sn atoms present in the precursor Bu_2SnO. Note that the spatial resolution of the technique is about 1 μm and only the heavier elements can be detected at concentrations larger than 0.1% in weight.

## RESULTS AND DISCUSSION

Binary blends

From the three initial polymers, PBT, PE and EVA, the three different binary 70%/30% blends were prepared. Both the PBT/PE and PBT/EVA blends show a high level of immiscibility, leading to well separated phases and evidence of poor adhesion between components. *Figure 1a* illustrates the case of PBT/PE blend for which the components are clearly immiscible. The much finer morphology of the PE/EVA pair, shown in *Figure 1b*, suggests some interfacial interactions.

Ternary blends

Two ternary blends of PBT/PE/EVA at concentrations of 70/10/20 and 70/20/10 were prepared. As seen in
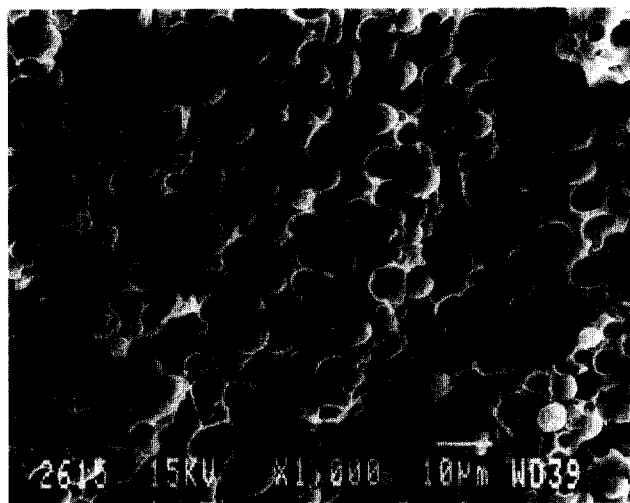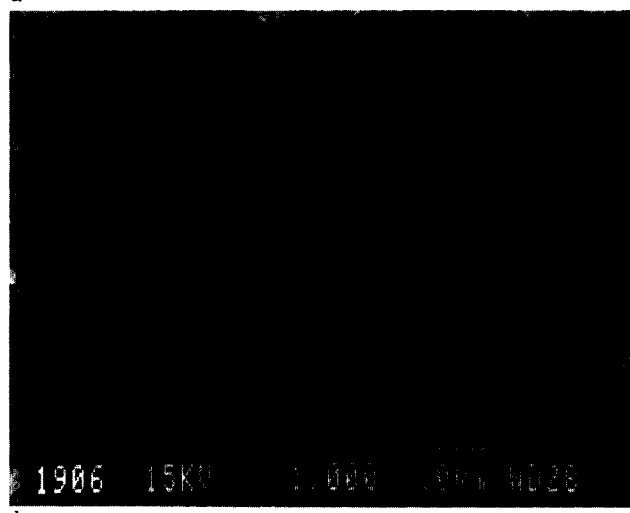
Figure 2 Scanning electron micrographs (×1000) of PBT/PE/EVA 70/10/20 blends: (a) without Bu_2SnO; (b) with 1.2 wt% Bu_2SnO

Figure 2a, the size of the dispersed phase is somewhat reduced in comparison with the previous PBT/PE blend (*Figure 1a*) but still there is indication of poor adhesion between the dispersed nodules and the PBT major phase. Upon addition of 1.2 wt% Bu_2SnO the morphology was modified as shown in *Figure 2b*. Rather than fracturing at the surface of the dispersed particle (*Figure 2a*), the fracture path in *Figure 2b* cuts right through the particles themselves. It will be shown later that this is due to the formation of sub-inclusions within the dispersed phase and this type of behaviour has been observed previously[5]. The morphology change is induced by a specific chemical reaction between PBT and EVA as illustrated in *Figure 3*. The ester exchange reaction between PBT chains and pendant acetate groups leads to the formation of a PBT/EVA copolymer[6] and the effective catalyst in this transesterification mechanism has proved to be a distannoxane structure derived from dibutyltin oxide $(Bu_2SnO)^3$. As discussed previously[1,3,4], Bu_2SnO acts as a precursor of distannoxane which increases the rate of transesterification to ensure compatibilization. The exchange reaction between pendant ester groups of EVA chains and ester groups of the PBT chain backbone yields the PBT/EVA copolymer and PBT chain scission with acetate terminal groups. It is important to maintain a low Bu_2SnO content to limit extensive polyester chain scissions involved in these transesterification reactions.

(PBT)— O — C —⬡—C — O— CH₂— (CH₂)₃—(PBT) +(EVA)— (CH₂)₂ — CH — (CH₂)₂ — (EVA)
          ‖   ‖ |
          O   O   O

Bu₂SnO

O=C — CH₃

(PBT)— O — C —⬡— C— CH —(CH₂)₂— (EVA)   +   CH₃ — C —O— CH₂ —(CH₂)₃— (PBT)
          ‖   ‖ | ‖
          O   O (CH₂)₂   O
                       (EVA)

Figure 3 Transesterification reaction between PBT and EVA

Figure 4 Scanning electron micrograph (×3000) of PBT/PE/EVA (70/10/20) blend containing 1.2 wt% Bu₂SnO

Figure 5 Scanning electron micrograph (×1000) of the EVA-extracted PBT/PE/EVA (70/20/10) blend containing 1.2 wt% Bu₂SnO blend

The micrograph of *Figure 4* obtained at higher magnification reveals the morphology for the ternary 70/10/20 system containing 1.2 wt% Bu₂SnO in more detail. The structure consists of three distinct phases with a high level of sub-inclusions within the dispersed phase. The PBT is the major component and PE is believed to be encapsulated in EVA shells. The composite droplet morphology was conserved when PE is the major component of the dispersed PE/EVA pair. This was verified by solvent extraction of the EVA using toluene. The micrograph of *Figure 5*, obtained after extraction, shows void spaces between the polyester matrix and the PE remaining particles, which were not soluble in toluene. This confirms that most of the PE nodules were embedded in the EVA. It is reasonable to assume that the copolymer formed by transesterification would be located at the PBT/EVA interface and could act as a compatibilizer. It is interesting to note that the composite droplet morphology could be barely observed for the uncompatibilized blend (see *Figure 2a*). The number and volume average diameters (D_n and D_v) changed from 4.3 and 6.0 μm, respectively, for the uncompatibilized blend (*Figure 2a*) to 3.8 and 5.0 μm for the compatibilized blend (*Figure 2b*). Despite the strong capacity of Bu₂SnO to catalyse the formation of PBT-EVA copolymer, the particle size changes little. This is likely due to the fact that the dispersed EVA particles now also contain PE sub-inclusions.

In previous studies[5,7], it was shown that a composite droplet morphology could be prepared reproducibly and

at various concentrations for a polycarbonate/polyolefin blend, as well as for a polyamide/polyolefin copolymer ionomer blend. In that study, the composite dispersed phase morphology was obtained by selectively imposing phase inversion and controlling the time of mixing. For the polycarbonate/polyolefin blend (a highly immiscible system), increasing the viscosity of the dispersed phase was found to improve the retention of the sub-inclusions with mixing time. In the case of the polyamide/polyethylene copolymer system, an interfacial reaction between sub-inclusions and the dispersed phase resulted in complete stabilization and high retention of the sub-inclusions, even for a relatively low dispersed phase viscosity and long mixing times.

The encapsulation can be explained by comparing the respective interfacial tensions of the various polymer pairs[8-11]. Recently, Hobbs and co-workers[12] showed that the encapsulation in a ternary polymer blend could be predicted via Harkin's equation:

$$\lambda_{31} = \nu_{12} - \nu_{32} - \nu_{13}$$

where λ_{31} is the spreading coefficient for a component 3 to encapsulate component 1, ν_{12}, ν_{32}, ν_{13} are the interfacial tensions between the respective polymer pairs in the blend. When λ_{31} is positive, encapsulation of component 3 about 1 will occur (where component 2 is the matrix material). In the case of Hobbs and co-workers, a three component system was studied with significantly different levels of interfacial interaction

Table 1 Surface tensions of PBT, PE and EVA

				Calculated at 180°C		
Polymer	ν (20°C)	Polarity	$-\mathrm{d}\nu/\mathrm{d}T$	ν	ν^{d}	ν^{P}
PBT	52.4	0.236	0.065	42	32.1	9.9
PEHD	35.7	0	0.057	26.5	26.5	0
EVA	31.3	0.09	0.037	25.4	23.1	2.3

73/27 weight ratio

inherently present in the system. The main distinction in this study is that the blend is compatibilized *in situ* by a transesterification reaction between PBT and EVA.

For the uncompatibilized blend, the respective interfacial tensions given below were estimated via the harmonic mean equation[13], which involves the dispersive and polar contributions ν^{d} and ν^{P}. The data used (surface tension ν at 20°C, polarity and $\mathrm{d}\nu/\mathrm{d}T$) are listed in *Table 1*. They were obtained from the literature[9,13]. Note that among the three polymers studied, PBT (component 2) has the highest surface tension, around $42\,\mathrm{mN\,m^{-1}}$ (estimated at 180°C) and is the major component. Both the PE and EVA (components 1 and 3, respectively) have similar values at 180°C, 26.5 and $25.4\,\mathrm{mN\,m^{-1}}$, respectively.

Hence

$$\nu_{12}(\mathrm{PE/PBT}) = 10.4\,\mathrm{mN\,m^{-1}}$$

$$\nu_{32}(\mathrm{EVA/PBT}) = 6.2\,\mathrm{mN\,m^{-1}}$$

$$\nu_{13}(\mathrm{PE/EVA}) = 2.5\,\mathrm{mN\,m^{-1}}$$

It is important to note that for the uncompatibilized PBT/EVA/PE blend, the spreading coefficient yields a low positive value, $\lambda_{31} = 1.7\,\mathrm{mN\,m^{-1}}$. In that case, *Figure 2a* reveals very little composite droplet formation. Upon addition of $\mathrm{Bu_2SnO}$, the PBT/EVA copolymer formed at the PBT/EVA interface would significantly reduce the interfacial tension ν_{32} as observed by adding interfacial modifiers in other types of blends[14-16]. Since the estimated interfacial tension between EVA and PE is low and interfacial tension ν_{12} remains large, the spreading coefficient after compatibilization should become much more positive, explaining the encapsulation observed in *Figure 4*. The composite droplet morphology reported in *Figure 4* may not be fully representative of the molten blend morphology, especially for crystalline materials. The crystallization temperatures of the three components of the ternary blends studied here are quite different and crystallization could also affect the morphology of the solid samples.

In parallel, some blends were prepared using a twin screw extruder (Leistritz LSM 34 mm model, L/D = 33.5). The micrograph of the uncompatibilized PBT/PE/EVA (70/10/20) blend (*Figure 6a*) shows much larger nodules ($D_{\mathrm{n}} = 7.8\,\mu\mathrm{m}$ and $D_{\mathrm{v}} = 14.2\,\mu\mathrm{m}$) compared to the same blend prepared by using the internal mixer ($D_{\mathrm{n}} = 4.3\,\mu\mathrm{m}$ and $D_{\mathrm{v}} = 6.0\,\mu\mathrm{m}$, *Figure 2a*). By adding $\mathrm{Bu_2SnO}$, a finer morphology of the extruded blend ($D_{\mathrm{n}} = 4.6\,\mu\mathrm{m}$ and $D_{\mathrm{v}} = 7.2\,\mu\mathrm{m}$) and better adhesion are obtained as shown in *Figure 6b*. This is evidence that the PBT/EVA copolymer can be formed within a typical residence time of a few minutes encountered in a twin screw extruder. A comparable morphology stabilization by $\mathrm{Bu_2SnO}$ catalysed interfacial reactions was demonstrated in a previous work for polyester/vinyl acetate copolymer blends prepared in an internal mixer followed by compression moulding[1].
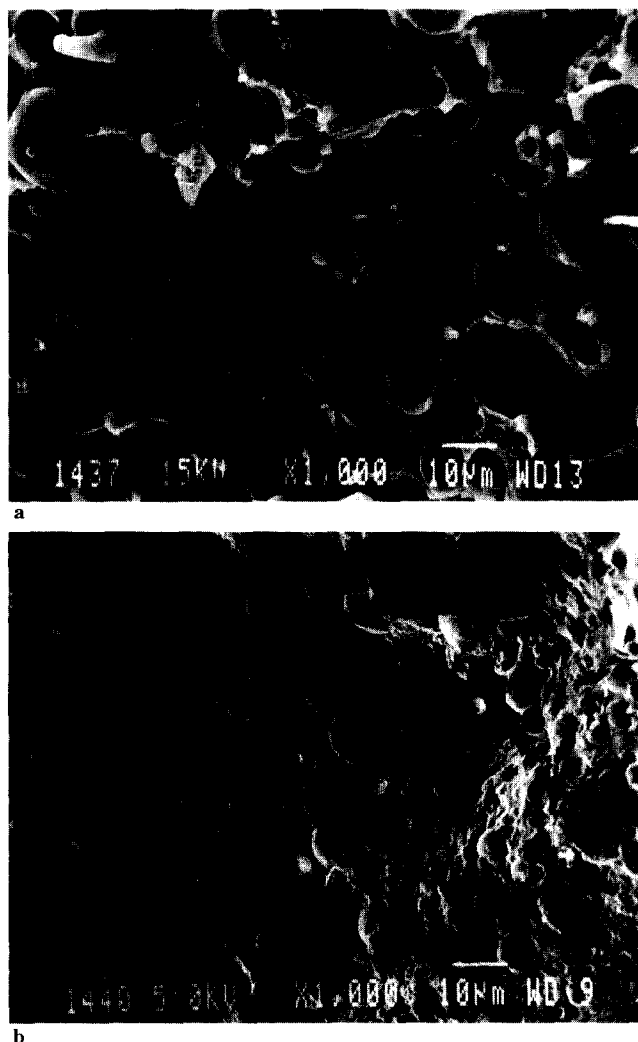

a

b

Figure 6 Scanning electron micrographs ($\times 1000$) of the PBT/PE/EVA (70/10/20) blend prepared using a twin screw extruder: (a) without and (b) with 4 wt% $\mathrm{Bu_2SnO}$

Electron microprobe

Electron microprobe analysis was used to determine the location of Sn in this multicomponent blend system and to confirm the reaction of the $\mathrm{Bu_2SnO}$ precursor with ester groups. For the actual conditions, the weight percentage of Sn atoms in the blends is estimated to be equal to 1.15% for a total content of 4% $\mathrm{Bu_2SnO}$. This value is above the sensitivity limit of the electron microprobe technique[17]. However, no quantitative determination by peak ratio measurements is possible, as only the Sn element related to $\mathrm{Bu_2SnO}$ is detected. All the other elements C, O and H are too light for accurate measurements.

Two samples were investigated, both of them mixed with 4% $\mathrm{Bu_2SnO}$, as described in the experimental section using the Brabender Plasticorder: the binary PBT/PE blend and the ternary PBT/PE/EVA for which EVA was extracted in toluene. For the 4% $\mathrm{Bu_2SnO}$ binary PBT/PE blend, the spectrum shown in *Figure 7a* focuses on a $10\,\mu\mathrm{m}$ PE particle, similar to that described previously in *Figure 1a*. No Sn peak is detected. The detection of Au and Pd is due to the alloy used for non-conductive sample metallization. On the other hand, the PBT matrix area in *Figure 7b* reveals two peaks attributed to the presence of Sn atoms. These results confirm that $\mathrm{Bu_2SnO}$ preferentially migrates to the PBT
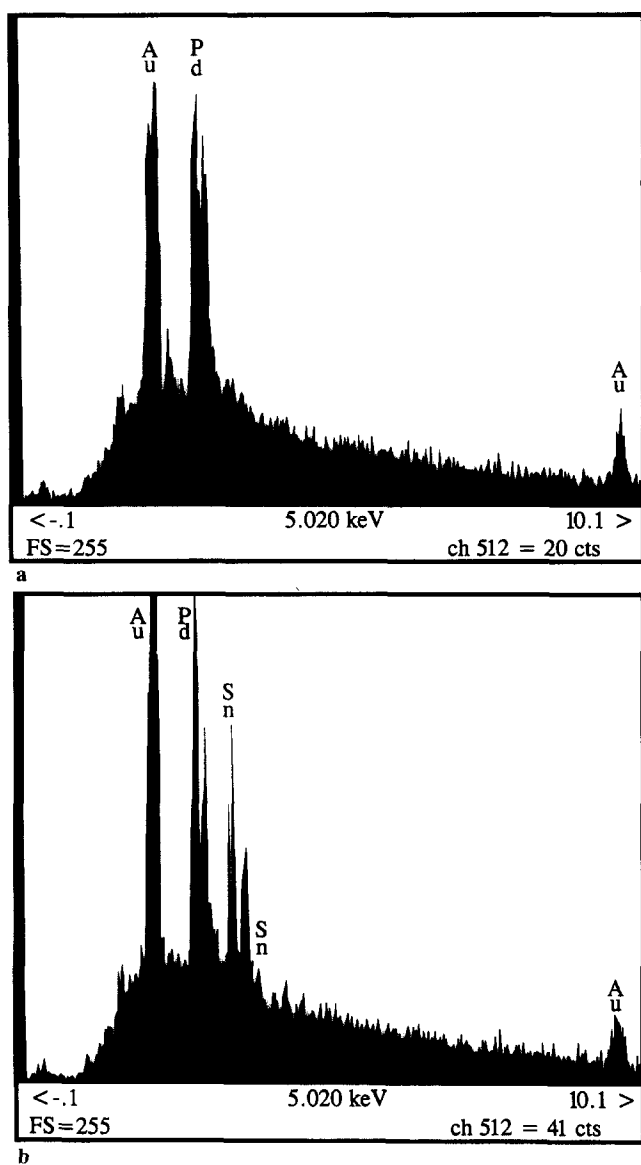
Figure 7 Electron microprobe analysis of the PBT/PE 70/30 blend mixed with 4 wt% Bu$_2$SnO. (a) PE particle of 10 µm; (b) PBT matrix area

phase, as virtually no evidence of Sn is present in the PE phase. In the case of the compatibilized PBT/PE/EVA blend from which the EVA was dissolved, the Sn peak was found to be very small in both the PBT matrix and in the remaining PE spheres. This indicates that the added Bu$_2$SnO was first present in the EVA phase and was then eliminated through the dissolution of EVA with toluene. These data illustrate that Bu$_2$SnO is preferentially present in the PBT and EVA phases, favouring the formation of a PBT/EVA copolymer at the interface.

CONCLUSION

Morphological changes induced by selective compatibilization have been studied in a PBT/EVA/PE ternary blend. The *in situ* formation of PBT–EVA copolymer induced by the addition of a distannoxane precursor (Bu$_2$SnO), which is the true catalyst of the transesterification reaction between PBT and EVA, leads to a finer dispersion of PE and EVA particles and stabilized interfaces by improved adhesion. The ternary blend system containing Bu$_2$SnO displayed three distinct phases with a high level of sub-inclusions within the dispersed phase. The PBT is the major component and PE is encapsulated in EVA shells. This morphology is tentatively explained in terms of interfacial tension modifications. The morphology obtained for reactive blends using the twin screw extruder was found to be comparable to that of the blends prepared via the Brabender internal mixer, although the residence time in the extruder was much shorter. Electron microprobe analysis demonstrated that the Bu$_2$SnO was preferentially located in the PBT and EVA phases.

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