PBT Modification with EVA/EVOH Copolymers: A Morphological Study

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Summary: Blends of PBT with different copolymers (EVA, EVOH and EVAVOH) were prepared in a Brabender mixer and their morphology was studied by SEM. VOH groups were found to be much more reactive than VA groups and the residual catalyst in PBT is able to promote grafting reactions at the interphase, and contrary to what was previously reported for PBT-EVA blends, a fine dispersion was obtained without the addition of fresh catalyst. Many variables such as viscosity ratio, VA content, hydrogen bonding formation and chemical reactions at the interphase were found to influence the final morphology. In particular, the effect of reactions at the interphase is an important factor for copolymers with low polarity.

Introduction

Polymeric materials prepared by melt blending of existing polymers have attracted a great interest both in industry and academia[1,2]. In fact, properties not available in any single polymeric material can be achieved with polymer blends. On the other hands, new materials can be developed avoiding the high cost and long development time needed by new chemicals (monomers). For thermodynamic reasons, most polymer pairs are immiscible and the development of new polymer blends is often a matter of controlling the morphology of the blends, because many properties are strongly dependent on the morphology, such as mechanical, rheological and barrier properties, to name a few. There are many factors which contribute to determine the morphology of a polymer blend: viscosity ratio between the matrix and the dispersed phase[3], interfacial tension[4] and also the process by which the blends are made can determine different morphologies. A special attention is deserved by blends in which the components have reactive groups along the chains or at the chain ends, so that reactive compatibilisation can be achieved during melt blending as a consequence of copolymer formation. Although they are difficult to identify and separate from the blend,

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these copolymers formed during reactive blending are supposed to be located at the interphase between the two (or more) immiscible components of the blend. In this way, they act as emulsifiers or surfactants, in the sense that they favour the dispersion of the second phase and stabilise the blend morphology obtained during the intensive mixing by preventing coalescence.

Poly(butylene terephthalate) (PBT) and ethylene-vinyl acetate copolymers (EVA) are immiscible and their blends can be compatibilised by copolymers formed as a consequence of transreactions between acetate groups in EVA and end-groups of PBT (hydroxyl and carboxyl) or the ester linkages themselves. The addition of exchange reaction catalysts may promote this reaction, making their kinetics compatible with the time scale of reactive processing. It was reported that graft copolymers formed either during the polymerisation of PBT in the presence of EVA[5,6)] or during melt mixing of PBT and EVA[7,8)] were able to reduce the average size of EVA dispersed phase particle and also to increase the adhesion between the matrix (PBT) and the dispersed phase. In the latter case[7,8)], a significant addition of fresh catalyst (up to 4 wt%) was required to obtain a fine dispersion of EVA in the PBT matrix.

In an attempt to contribute to a better understanding of the importance of transreactions for the control of the morphology of blends of PBT with EVA-based copolymers, we report here the results of a work in which we replaced EVA copolymers with ethylene-vinyl alcohol copolymers. This because we felt that the higher reactivity of the -OH groups compared to that of acetate groups could be exploited in order to reduce the amount of catalyst to be added and the reaction time required for reactive blending.

Experimental part

PBTs used in this work were commercial samples from General Electric Plastics with trade names Valox 195 and 315 (Mw 50000 and 120000, respectively). EVA copolymers with a different vinyl acetate (VA) content were obtained from Exxon: Escorene 00909 and 00728 with a VA content of 9 and 28 wt%, respectively and from Atochem: EVATANE 18500, 33400, 3345 and 4055, with a VA content of 18, 33, 33 and 40 wt%, respectively. Catalysts, Titanium tetrabutoxide (TBT) and Bu_2SnO and the inhibitor, di-n-octadecylphosphite (DNOP), were purchased from Aldrich and used as supplied.

The hydrolysis of vinylacetate groups in EVA copolymers to prepare ethylene-vinyl alcohol copolymer (EVOH) was carried out following two different procedures. The complete hydrolysis of VA groups was carried out by dissolving EVA copolymers in boiling toluene, then an excess of sodium methoxide was added dropwise and the reaction was monitored by taking small samples from the reactor and recording the infrared spectrum. When the carbonyl band of the vinyl acetate groups at 1720 cm^{-1} had completely disappeared, the reaction was stopped, the toluene solution was cooled and poured into an excess of methanol to precipitate the EVOH copolymers. After precipitation, EVOH copolymers were filtered, washed with fresh methanol and dried under vacuum.

A partial hydrolysis of EVA was carried out in the melt following a procedure adapted from that proposed by Lambla9). 40 g of EVA copolymer were loaded into the mixer of a Brabender Plasticorder heated at 190 °C, then 0.356 g of Bu_2SnO were added along with the amount of 1-octanol in order to have a molar ratio 1-octanol/VA groups of about 0.9:1.

After pre-mixing EVA with the catalyst for 2 min, 1-octanol was added and the reaction was carried out for 5 min at 190°C, then vacuum was applied to remove the excess of 1-octanol along with the reaction by-product (octyl acetate). After 15 min. under vacuum, the partially hydrolysed ethylene-vinyl acetate-vinyl alcohol copolymers (EVAVOH) were taken out from the mixer, cooled in water and then finely ground with a IKA M-20 laboratory grinder.

Table 1. Composition of the different copolymers used to prepare blends with PBT.

Copolymer	VA (mol%)	VOH (mol%)
EVA00909	3.1	0.0
EVA00728	11.2	0.0
EVA18500	6.7	0.0
EVA33400	13.8	0.0
EVA3345	13.8	0.0
EVA4055	17.8	0.0
EVOH009	0.0	3.1
EVAVOH28	7.2	4.0
EVAVOH4055	14.5	3.5

Blends of PBT with EVA, EVOH and EVAVOH copolymers were prepared in a Brabender mixer. The two polymers were dry-blended with the addition of Irganox 1098 (0.2 wt% respect to the copolymers) as stabiliser, the catalyst, when added before blending, or DNOP as catalyst inhibitor. The mixer temperature was set at 250 °C with a mixing speed of 60 rpm; dry nitrogen was fluxed in the mixer to prevent hydrolytic degradation. Samples for morphology study were taken at different mixing times and immediately quenched in ice-water.

Apparent shear viscosity were measured at 250 °C with a CEAST 1000 Rheoscope rheometer equipped with a capillary: 1.0 mm diameter, L/D equal to 40 and 90° entrance angle. The apparent viscosity values were taken at a shear rate of 200 s^{-1}, comparable with that applied to the polymer melt during the mixing at 60 rpm in the Brabender apparatus.

Blend morphologies were examined using a Philips XL-40 scanning electron microscope. The samples were fractured in liquid nitrogen and coated with gold. The apparent particle sizes were determined as the average of 20-30 particles.

DSC curves were recorded with a Perkin Elmer DSC7 at 20°/min. DMTA analysis was carried out using a Perkin Elmer DMTA7 on samples prepared by compression moulding; a three-point-bending geometry was used, with a frequency of 1 Hz in the temperature range -120 + 150 °C at 2°C/min.

Results and discussion

Melt mixing of PBT and EVOH with different catalysts

The reaction between PBT and EVOH copolymers that can take place during melt mixing are schematically reported in Figure 1. Hydroxyl groups in EVOH copolymer may react with the ester groups in PBT chains, leading to the formation of EVOH-g-PBT copolymers and PBT chains of lower molecular weight. These reactions can proceed further, leading eventually to the crosslinking of the EVOH phase by PBT segments. The extent and the rate of these reactions can be influenced by the amount of -OH groups and by the presence of transreaction catalysts, keeping temperature and the ratio between PBT and EVOH constant.

In the first part of the work, we used EVOH copolymers with low -OH content (3.1 mol%) in order to reduce the effect of crosslinking of the dispersed phase and therefore make easier the characterisation of the molecular structure of the resulting products. Several blends of this EVOH copolymer with PBT were prepared, with a PBT:EVOH ratio kept constant at 85:15 wt/wt; with the addition of DNOP or transesterification catalysts. Samples of each blends were taken at various times of mixing (5-20 min.).

In order to attain a quantitative indication of the extent of transreactions between PBT and EVOH, a selective fractionation was carried out according to the sequence of operations reported in Figure 2. In this way, each blend was first separated in two fractions, named Soluble I and Insoluble II and the latter was further separated, yielding the fractions named Soluble III and Insoluble IV. In Table 2, the characterisation data for the different fractions from PBT-EVOH blends are reported.

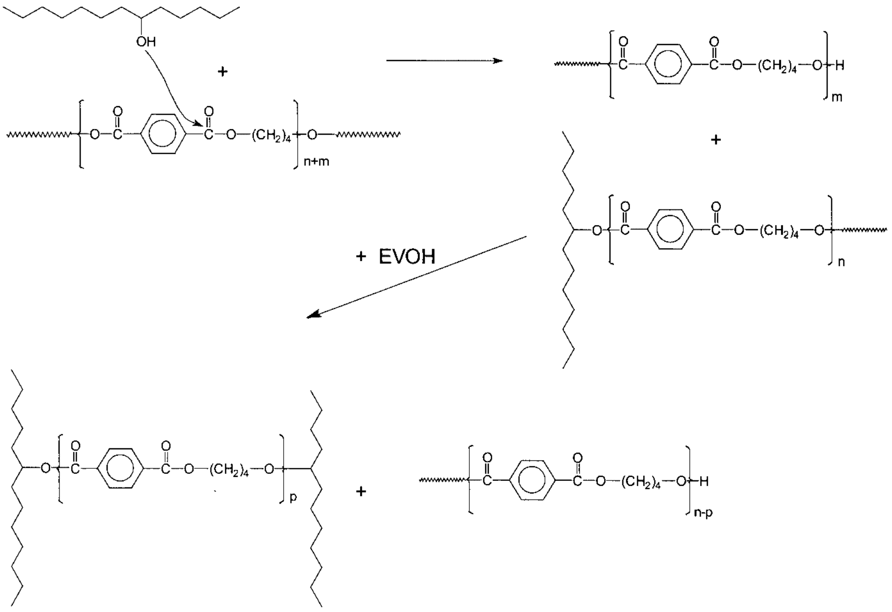

Figure 1. Scheme of the possible reactions taking place during the melt mixing of PBT with EVOH copolymers.

The selective fractionation procedure was checked with blend #1, to which DNOP, reported to be an efficient inhibitor of transreaction, was added$^{10)}$. As expected, no transreaction took place during melt mixing of PBT-EVOH; in fact, 85% by wt of the blend #1 was recovered as fraction Soluble I, while the remaining 15% was obtained as fraction Insoluble II and the IR spectrum did not present the carbonyl band at 1730 cm^{-1}. From the ratio of the absorbance of the C-H stretching band at 2975 cm^{-1} to the absorbance of the carbonyl band, it was also possible to infer that the fraction Soluble I contained only PBT. Therefore we can conclude that the selective fractionation procedure described in Figure 2 is able to separate quantitatively unreacted PBT and EVOH.

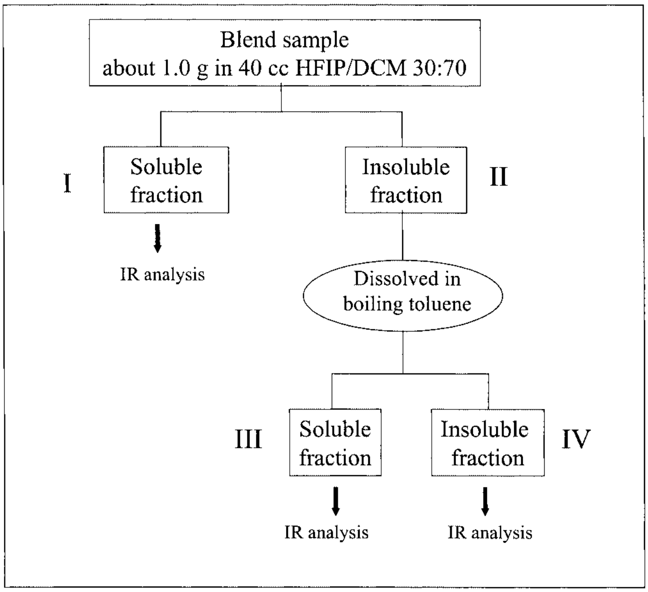

Figure 2. Selective fractionation scheme for PBT-EVOH blends.

Table 2. Characterisation by selective fractionation of PBT-EVOH blends: PBT/EVOH 85:15 by wt., 250 °C, 60 rpm, mixing time 20 minutes.

Blend	Additive (% by wt.)	Soluble I (wt%)	Insoluble II (wt%)	Soluble III (wt%)	Insoluble IV (wt%)
1	DNOP, (0.5)	85	15	-	-
2	none	76	24	1.5	22.5
3	Bu_2SnO, (0.21)	75	25	2.6	22.4
4	$Ti(OBu)_4$, (0.29)	79	21	1.7	19.3

For blends #2-4, the selective fractionation showed an increase of the fraction Insoluble II above 15% and a correspondent decrease of the amount of the fraction Soluble I. The former was further separated following the procedure already described. The data reported in Table 2 show that for all the blends without DNOP the further fractionation produced mostly fraction Insoluble IV. As we expect that any unreacted EVOH eventually left is present in fraction Soluble III, these results clearly indicate that after 20 min. of melt mixing, 85-90 % of the starting EVOH has reacted forming copolymers that are found in the fraction Insoluble IV due to their insolubility in boiling toluene. For all these blends, the IR analyses of the different fractions confirmed that the fraction Soluble I contained only PBT, while fractions

Insoluble II showed IR bands characteristic of both PBT and EVOH. After the further fractionation, IR analyses confirmed that fraction Insoluble IV contained EVOH-g-PBT copolymers, while for fraction Soluble III, the C=O band was very weak, supporting the conclusion that almost pure unreacted EVOH was contained in this fraction.

The results of the selective fractionation, along with those of the IR analysis, show a clear difference from the simple "unreacted" blend and the others; however, the differences among blends #2-4 are very limited, suggesting that the addition of a catalyst, being either TBT or Bu_2SnO, just before mixing, does not increase the transreaction rate with respect to the blend in which only the residues of the catalyst used for PBT polymerisation are active. These results are quite different from those reported in previous studies[7,8)] in which up to 4 wt% of catalyst had to be added to promote transreactions, but can be explained by considering that VOH groups have a higher reactivity compared to that of VA groups and that hydrogen bonding between –OH groups and PBT can lead to a thicker interphase where transreactions can take place more easily.

The morphology of PBT-EVOH blends #1-4 was studied SEM; typical pictures are reported in Figure 3a-d. Samples were etched with hot toluene vapours in order evidence the dispersed phase. Once again, blend #1 was taken as reference and the fracture surface shown in Figure 3a is a typical droplet morphology indicating a coarse dispersion of EVOH in the PBT matrix when no graft copolymers are formed during mixing. The average size of the dispersed phase particles is about 3-4 μm.

For the other PBT-EVOH blends (Figure 3b-d), a much finer and regular dispersion of the EVOH phase in the PBT matrix was obtained; the average dimension of the dispersed phase particles has been reduced to 0.2-0.4 μm with very little, if any, difference between the blends without and with added catalyst. A comparison between the morphology of samples taken after various times of mixing showed that the dimensions of the dispersed phase particles remained almost the same after 10 min. These results are in complete agreement with those obtained from the selective fractionation and IR analysis. They confirmed that there are almost no differences between PBT-EVOH blends prepared without added catalyst and with added TBT or Bu_2SnO and therefore that the residues of the catalyst used for PBT polymerisation are still active in transreactions to produce EVOH-g-PBT copolymers which are able to modify the morphology.

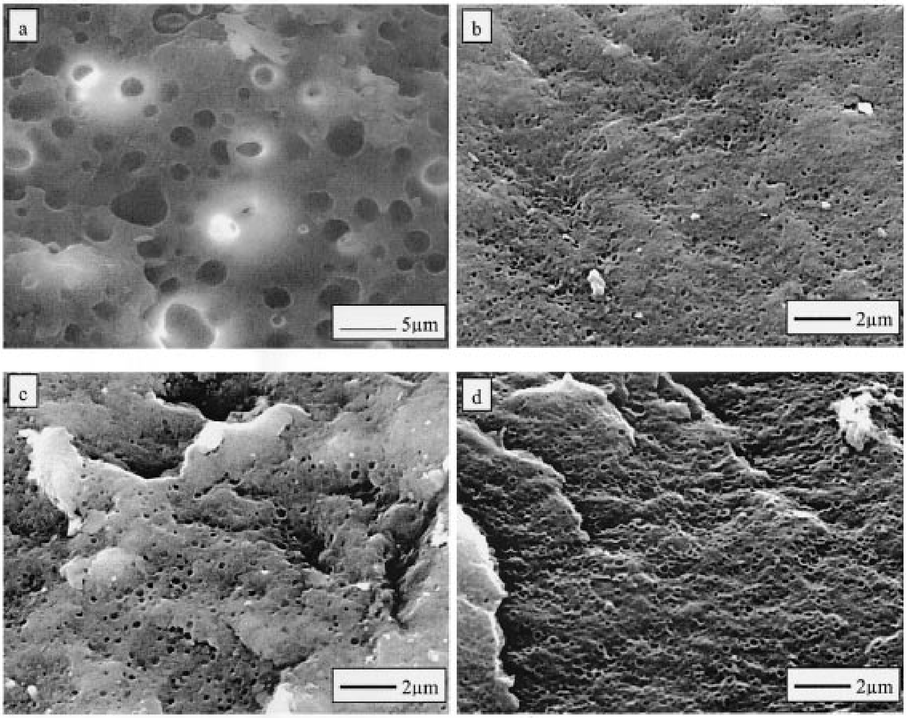

Figure 3. SEM pictures of the fracture surface of PBT-EVOH blends: a=#1; b=#2; c= #3 and d= #4.

Further investigations of these blends were carried out with DSC and DMTA. DSC curves showed only small changes for the melting of the dispersed phase (Tm_1 and ΔHm_1) for blend #1 with respect to blends #2-4 and no changes of the melting behaviour of the PBT matrix (Tm_2 and ΔHm_2).

Table 3. Thermal properties of PBT-EVOH blends prepared with different catalysts.

Sample	Tm_1 (°C)	ΔHm_1 (J g^{-1})	Tm_2 (°C)	ΔHm_2 (J g^{-1})
EVOH009	105	88	-	-
Blend #1	102	71	220	38
Blend #2	96	76	221	40
Blend #3	99	80	223	41
Blend #4	93	85	221	40
PBT	-	-	222	44

These results are in agreement with those obtained from the other characterisation techniques already discussed; from the point of view of thermal properties, changes induced by the formation of PBT-g-EVOH copolymers are comparable for blends in which the residues of PBT polymerisation catalyst are active and for blends to which Sn or Ti catalysts were added. The same conclusion can be drawn from the dynamic-mechanical behaviour of the four blends. DMTA spectra (not reported here due the limitation of the available space) did not reveal any significant shift in the tan δ peak associated with the glass transition of the EVOH dispersed phase which was observed at about 0 °C for the pure EVOH and for blends #1-4.

Blends of PBT with EVA, EVOH and EVAVOH copolymers

Many factors may influence the miscibility of polymers; it is well known that the viscosity ratio η_d/η_m has a relevant influence on the dimensions of the dispersed particles(3), but also copolymer composition and hydrogen bonding may affect the morphology of the resulting blends. As EVA copolymers are commercially available in a wide range of composition and melt viscosity, we considered different EVA copolymers and also copolymers in which a partial or complete hydrolysis of VA groups was carried out, in order to derive information about the effect of hydrogen bond interaction and of chemical reactions at the interphase.

The copolymers were blended at 250 °C in the Brabender mixer, with and without the addition of DNOP and examined by SEM. The average dimensions of the dispersed phase and the characteristics of the copolymers used in blends with PBT are reported in Table 4 and 5.

Table 4. Dimensions of the dispersed phase for PBT-EVA blends with different viscosity ratios: PBT/EVA 80:20 by wt., 250 °C, 60 rpm., mixing time 10 min.

Polymer code	η (Pa s)a)	VA (%wt)b)	η_d/η_m c)	η_d/η_m d)	d (μm) c)	d (μm) d)
PBT195	80	-	-	-	-	-
PBT315	700	-	-	-	-	-
EVA00728	200	28	2.50	0.29	1.5	1.6
EVA18500	5	18	0.06	0.01	4.4	2.2
EVA33400	5	33	0.06	0.01	3.3	2.6
EVA3345	45	33	0.56	0.06	2.3	1.3
EVA4055	45	40	0.56	0.06	2.0	1.0

a) at 250 °C and 200 s^{-1}; b) data from the producer; c) PBT195 was the matrix; d) PBT315 was the matrix.

By considering first PBT-EVA blends, we can derive information about the effect of viscosity ratio and VA content. With the commercial EVA samples available to us, the range of viscosity ratios studied was limited from 0.01 to 2.5. For the same copolymer, an increase of the viscosity ratio, obtained by changing the melt viscosity of the PBT matrix, led to an increase of the average size of the dispersed phase, as expected from the literature data[3)]. It is interesting to note that blends of EVA33400 with PBT195 has the same viscosity ratio of the blend EVA3345 with PBT315, nevertheless the dimensions of the dispersed phase in the second case are significantly lower than those of the blend EVA33400 with PBT195. Because the VA content is the same in both EVA copolymers, we can tentatively ascribe this difference to the nature and number of the terminal groups of PBT, which are almost exclusively –OH groups in PBT195 and almost exclusively –COOH groups in PBT315.

For other blends with comparable viscosity ratios, generally a finer morphology was observed for higher VA content, although the differences are small (see sample EVA3345 and EVA4055 in Table 4).

While VA groups are not able to undergo exchange reactions with PBT in the absence of freshly added catalyst[7,8)], it has been shown above that VOH groups are able to form graft copolymers; therefore for some EVA samples a fraction of VA groups was hydrolysed to VOH groups. The conversion of VA groups into VOH groups can lead to the formation of graft copolymers at the interphase, but also to an increase of physical interactions at the interphase due to possible hydrogen-bond formation. If we compare the data obtained for blends with and without addition of DNOP, the contribution of the chemical reactions can be separated from that due to hydrogen-bond formation. It is evident that a partial hydrolysis of VA groups leads to a significant decrease of the particle dimensions, also in the absence of transesterification reactions (when DNOP is added). In fact, by comparing blends #7 with #8 and blend #10 with #11, d_n decreased from 1.6 to 0.8 μm and from 1.0 to 0.6 μm, respectively. This decrease can be reasonably ascribed to hydrogen-bond formation.

The effect of the reactions occurring during blending may be inferred by comparison of the data obtained with and without DNOP added. Without DNOP, a further decrease of the dimensions of the dispersed phase was always observed, with particle size of about 0.2-0.4 μm. It is interesting to observe that the less polar is the copolymer added (higher ethylene content), the more pronounced is the decrease of d_n due to chemical reactions. This effect is more evident for EVOH009 which has 96.9 mol% of ethylene units where we may expect that the formation of graft copolymers during melt mixing has a dramatic effect on the interactions at the interphase. For the other copolymers containing both VA and VOH groups, EVAVOH28 and 40, the effect of transreactions is less marked because the higher concentration of polar groups favours stronger interactions at the interphase, reducing the effect of the graft copolymers.

Table 5. Blends of PBT315 with different copolymers: PBT/copolymer 80:20 by wt, 250 °C, 60 rpm, mixing time 20 min.

Blends #	Type of copolymer	VA (mol%)	VOH (mol%)	d_n (μm)
5	EVOH009 + DNOP	0.0	3.1	3.2
6	EVOH009	0.0	3.1	0.2
7	EVA00728 + DNOP	11.2	0.0	1.6
8	EVAVOH28 + DNOP	7.2	4.0	0.8
9	EVAVOH28	7.2	4.0	0.2
10	EVA4055 + DNOP	17.8	0.0	1.0
11	EVAVOH40 +DNOP	14.3	3.5	0.6
12	EVAVOH4055	14.3	3.5	0.4

From these results, we can conclude that morphology can be affected by the viscosity ratio and the copolymer composition, but hydrogen bonding and exchange reactions (leading to *in situ* formation of block copolymers) can also play an important role on its control.

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