

On the compatibilization of PET/HDPE blends through a new class of copolyesters

T.L. Dimitrova^{a,*}, F.P. La Mantia^a, F. Pilati^b, M. Toselli^c, A. Valenza^d, A. Visco^d

^aDipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy

^bDipartimento di Chimica, Università di Modena, Via G. Campi 183, 41100 Modena, Italy

^cDipartimento di Chimica Applicata e Scienza dei Materiali, Università di Bologna, Viale Risorgimento 2, 40136 Bologna, Italy

^dDipartimento di Chimica Industriale e Ingegneria Chimica, Università di Messina, Salita Sperone 31, 98166 S. Agata Messina, Italy

Received 16 April 1999; received in revised form 10 September 1999; accepted 24 September 1999

Abstract

Polyethyleneterephthalate (PET) and polyethylene are incompatible polymers and their blends show, in general, poor properties. Compatibilization is then a necessary step to obtain blends with good mechanical and barrier properties. In this work different compatibilizing agents were used, i.e. a maleic anhydride elastomer and some new products containing graft-copolymers having polyester segments grafted onto polyethylene backbone chains. Both the functionalized elastomer and the new products drastically improve the morphology and the ductility of the blend. In the case of the modified elastomer the compatibilizing action has been attributed to the formation of H-bonds whereas the copolymers contained in the new products act as compatibilizing agents as they contain polyester segments and polyethylene segments with thermodynamic affinity with PET and polyethylene, respectively. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: PET/HDPE blends; Copolyesters; Compatibilization

1. Introduction

Polyethyleneterephthalate (PET) is widely used for packaging—mostly bottles—electronics and other applications. The blends of PET with other polymers, and in particular with polyolefins, may offer an attractive balance of mechanical and barrier properties and of processability. Moreover, these polymers are found easily in the post-consumer urban plastic waste. The possibility of recycling these mixtures without any previous separation of the components could be a good chance for the economic of the recycling. The incompatibility of these two classes of polymers, polyesters and polyolefins, gives rise to a “bad” morphology—gross phase separation, lack of adhesion between the phases—and then to poor mechanical and barrier properties. Compatibilization is then a necessary step to obtain blends of PET and polyolefins with good properties both from virgin and recycled materials.

On the basis of its structure, PET is capable both of chemical reactions with polar polymers and of specific polar interactions, like H-bonding. Some attempts have been done to form compatible blends of PET with non-polar polymers by using elastomers [1], EVA [2], EAA

and EMA [3], or a functionalized third component, in particular PP-*g*-MA [4], PE-*g*-MA [5,6], PE-*g*-AA [7], SEBS-*g*-MA [8,9] and vinyl acetate (EVA) based graft-copolymers [8,10] and organo-titanate coated CaO [8]. Both improved morphology and better mechanical properties have been observed by using some of these components.

In this work uncompatibilized blends of PET and high-density polyethylene (HDPE) have been prepared and their morphology, rheological and mechanical properties have been compared with those of the same blends compatibilized with new ad hoc synthesized EVA and EVOH based copolyesters. Blends compatibilized with commercial maleic anhydride functionalized elastomers have been prepared for comparison. All the compatibilized blends have shown a dramatic change of the morphology, an enhancement of the viscosity and a significant improvement of the mechanical properties with respect to the uncompatibilized binary blend.

2. Experimental

2.1. Materials and blends preparation

The materials used in this work were PET, $[\eta] =$

* Corresponding author.

Table 1
Polymerisation conditions for the three copolyesters

Sample code	Reagents				Catalyst (wt%)	Time of addition of the EC (min) ^a	Reaction time, after addition of EC (min)
	DMT (mol)	DMI (mol)	EG (mol)	Ethylene copolymer, EC (g)			
TVA	3.6	–	7.94	EVA (175)	Ti(OBu) ₄ 0.1	33	75
TIVA	1.8	1.8	7.94	EVA (175)	CaAc ₂ /Sb ₂ O ₃ 0.1/0.05	0	170
TIVOH	1.45	1.45	6.4	EVOH (141)	CaAc ₂ /Sb ₂ O ₃ 0.1/0.05	120	30

^a After starting the second stage of polymerization.

0.81 dl/g and HDPE, MFI \approx 6.5 kindly supplied by Sinco and Polimeri Europa, Italy, respectively. The compatibilizers were three ad hoc synthesized copolyesters; a maleic anhydride functionalized elastomer was used for comparison. This thermoplastic rubber, Kraton FG 1901X (KF), manufactured and kindly supplied by Shell, is a triblock copolymer consisting of polystyrene end blocks and partly hydrogenated polybutadiene midblocks, onto which maleic anhydride was grafted. This rubber has been successfully used for compatibilizing different types of blends [8–12].

The other compatibilizers (named TVA, TIVA and TIVOH) are three copolyesters synthesized by polymerizing dimethyl terephthalate (DMT) and ethylene glycol (EG), in the presence of poly(ethylene-*co*-vinyl acetate) (EVA) for TVA and by reacting DMT, dimethyl isophthalate (DMI), and EG, in the presence of poly(ethylene-*co*-vinyl acetate) (EVA) for TIVA or of poly(ethylene-*co*-vinyl alcohol) (EVOH) for TIVOH. The polymerization reaction was carried out by the usual two-stage process for the polymerization of polyesters, at 150–210°C and atmospheric pressure in the first stage and at 210–275°C at reduced pressure in the second stage.

EVA was added on starting the second stage or after 33 min of reaction in the second stage, and was allowed to react for 170 and 75 min, for TIVA and TVA, respectively. For the preparation of TIVOH, EVOH was added after 120 min of reaction in the second stage and allowed to react for 30 min in the polymerization medium.

In Table 1 the composition, the catalysts and the reaction conditions for the synthesis of the three copolyesters are reported. The weight fraction of EVA in TVA and in TIVA and of EVOH in TIVOH was 0.25. Under the reaction conditions employed, transesterification reactions can take place leading to the formation of graft copolymers (copolyester grafted onto EVA or EVOH).

From selective solubility tests, carried out with chloroform (for TVA and TIVA) and hexafluoroisopropanol/methylene chloride mixtures (for TIVOH), combined with FTIR and ¹H-NMR analysis it was estimated that the fraction of polyester chemically linked with EVA or EVOH is small (about 1–3% by wt). Extraction with hot toluene of unreacted EVA/EVOH from the fraction insoluble recovered after the above described treatment leads to conclude that most of EVA is unreacted (about 97%) in TVA and

TIVA, while about 52% of EVOH is reacted in TIVOH sample.

The blends were prepared in a twin screw Brabender compounder model 42/7 ($D = 42$ mm, $L/D \approx 7$) attached to a Brabender Plasticorder PLE 651. The twin screw compounder is an intermeshing counter-rotating twin-screw extruder that allows intensive high shearing and cross flow. The head temperature was 260°C and the average residence time in these processing conditions was in the range 60–90 s. The extruded rod was drawn through two cooled rollers in order to obtain a constant and reproducible cooling rate. The crystallization rate of PET, and then the mechanical properties, are, indeed, strongly dependent on the cooling rate. The investigated blend was 80% (wt/wt) of PET. 5% of compatibilizing agents was added in the compatibilized blends. A catalyst, Ti(BuO)₄, was used in the blends compatibilized with the three copolyesters.

2.2. Characterization

Mechanical properties were measured using an Instron machine mod. 1122, performing the tests on rectangular samples cut from the extruded ribbon.

The flow curves were measured with a rheometer Rheometrics RDA II with parallel plates. The samples were cut from the sheets obtained by compression moulding and the tests were performed at 270°C in the frequency range 0.5–400 s⁻¹.

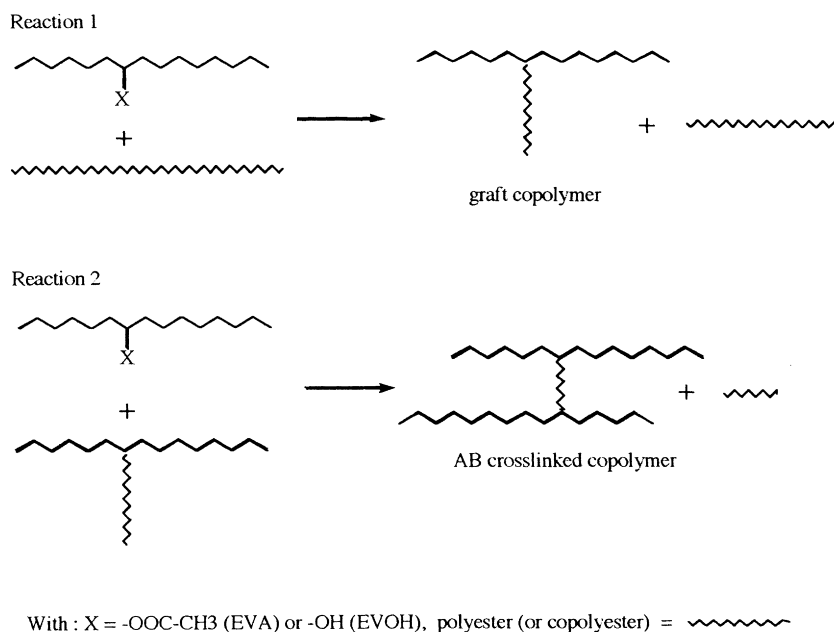
The morphology of the blends was studied by using a microscope Philips mod. 501 on samples broken in liquid nitrogen and gold coated.

3. Results and discussion

3.1. The new copolyesters

While Kraton FG 1901X is a commercial product, compatibilizers TVA, TIVA and TIVOH were prepared ad hoc for this study, and therefore they will be briefly described below.

They are the crude products resulting from the addition of ethylene-vinyl acetate copolymers (EVA, with 28 wt% of VA and MFI = 7 g/10 min and with 9 wt% of VA and MFI = 9 g/10 min, for TVA and TIVA, respectively) or



Scheme 1.

ethylene–vinyl alcohol copolymer (sample TIVOH, with EVOH obtained from the complete hydrolysis of EVA with 9 wt% of VA and MFI = 9 g/10 min) into the reactor during the polymerization of DMT and DMI with EG. Titanium tetrabutylate was used as catalyst for the preparation of TVA, whereas calcium acetate and Antimony trioxide were used for TIVA and TIVOH.

In the presence of these catalysts, the ester groups in EVA and the alcohol groups in EVOH can undergo exchange reactions with the ester groups of the polyesters. Both grafted and AB crosslinked molecular structures can result from these reactions, as described in Scheme 1 (exchange reactions between EVA (or EVOH) and polyester (or copolyester)).

Reaction 1 leads to the formation of graft copolymers, with copolyester chains grafted onto polyethylene backbone chains; the polyester segments of these graft copolymers can undergo further reaction (Reaction 2) with other acetate or alcohol groups (in EVA and EVOH, respectively) with the formation of AB crosslinked molecular structures. Unreacted EVA or EVOH and copolyester can also be present in the crude products resulting after polymerization.

Graft copolymers and AB crosslinked structures are potential compatibilizers for HDPE/PET blends having polyethylene segments and copolyester segments with thermodynamic affinity for HDPE and PET, respectively.

The relative amount of graft copolymers and AB crosslinked structures in the crude products can be important for the overall compatibilization effect.

The formation of graft copolymer and AB crosslinked structures is expected to be strongly dependent on reaction conditions, such as: the different reactivity of the functional groups (OH in EVOH is expected to be more reactive than

acetate groups in EVA); the catalyst employed; the miscibility of the polyester with EVA or EVOH (which depends on the VA-group content in EVA and decreases as the molecular weight of the copolyester increases during polymerization; the reaction time (as reactions 1 and 2 are consecutive reactions, the amount of graft copolymers goes through a maximum).

It is very difficult to separate and to estimate the concentration of the various components in the crude products (unreacted EVA or EVOH and copolyester, graft copolymer, AB crosslinked structures), and therefore, in order to have different amounts of molecular structures potentially useful as compatibilizers, we prepared crude products using different EVAs and different reaction conditions, as described in Table 1.

Even though many factors may affect the molecular characteristics of the final products, the process resulted quite reproducible with respect to the molecular structure (as suggested by the possible techniques of characterization, selective extractions combined with spectroscopic analysis) when the same reaction conditions were used.

Titanium tetrabutoxide was added before blending the copolyesters with PET and HDPE to favour further exchange reactions between PET and the polyesters segments present in the compatibilizers.

3.2. Rheological and morphological characterization of the blends

The flow curve of the uncompatibilized blend is reported in Fig. 1 together with the viscosity curves of the parent polymers. The viscosity curve of the blend is below those of the two components and this is a clear evidence of the

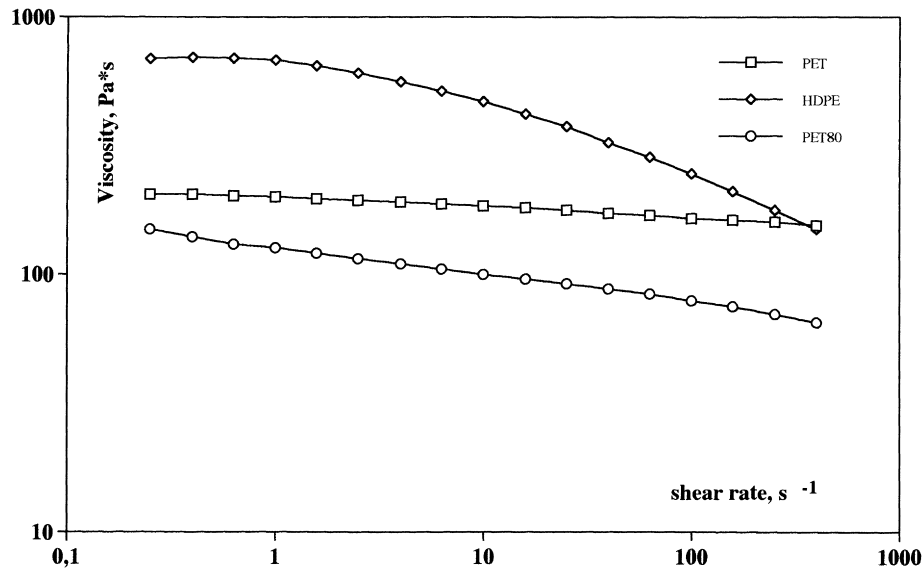


Fig. 1. Flow curve of the uncompatibilized blend and of the polymer parents.



Fig. 2. SEM micrographs of PET80 sample at different magnification.

lack of adhesion between the two phases for this blend. The SEM micrograph of this blend (Fig. 2a) confirms the strong incompatibility evidenced by the rheological tests. The dispersed particles are large, have very different dimensions, from few microns to about 10 μm , and do not show any adhesion with the matrix as better evidenced in Fig. 2b where the same micrograph is reported at a higher magnification. Some HDPE particles are slightly elongated because of the drawing undergone after the extrusion.

The flow curves of the blends compatibilized by adding 5% of the compatibilizing agents are plotted in Fig. 3. In the same figure the viscosity curve of the binary blend is also plotted. The flow curves of all the ternary compatibilized blends are similar and higher than that of the binary blend. This increase can be both due to the addition of a high viscosity third component or to some compatibilizing action of the same third component.

The increase of melt viscosity when the functionalized elastomer was added to the blend can be derived by both the above contributions; in fact, as plotted in Fig. 4, the viscosity of the maleic anhydride grafted elastomer is higher, at least in the low shear rate region, than that of the two components and than that of the binary blend. On the contrary, the flow curves of the three copolyesters are lower in the whole shear rate region, suggesting that the increase of the viscosity for the blends compatibilized with the copolyesters has to be attributed only to the compatibilizing action of these polymers.

In its turn, the increase of the viscosity of the blend compatibilized with KF cannot be attributed only to the high viscosity of the elastomer because if the third component had no compatibilizing effect, the viscosity of the ternary blend could not exceed the additive figure calculated through a linear equation and reported in the previous Fig. 3. The theoretical values are below the experimental curve

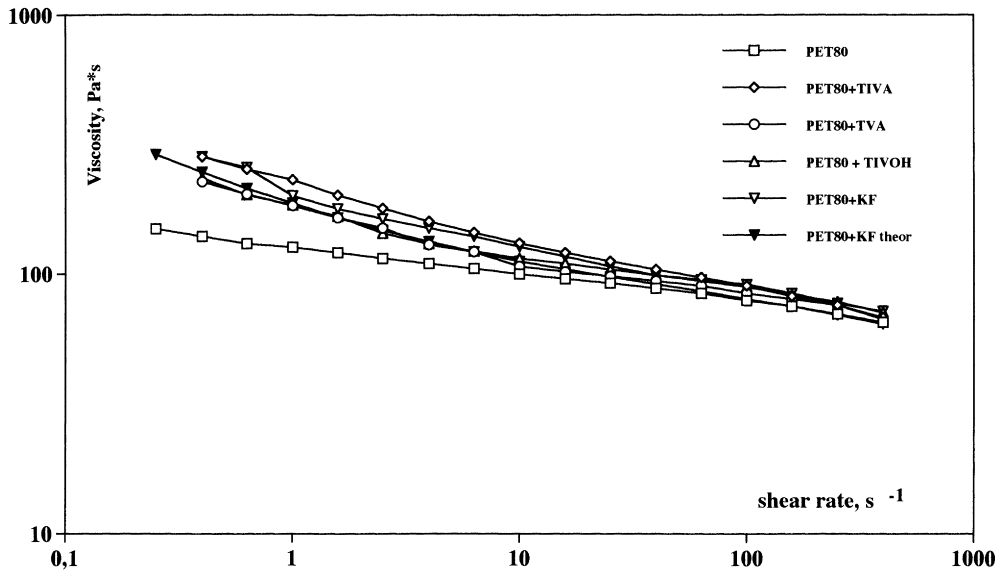


Fig. 3. Flow curves of compatibilized and uncompatibilized PET80 blends.

confirming the compatibilizing action of the functionalized elastomer. Moreover, it is worth to remember that in the high shear rate region the viscosity of KF is below that of the two pure components.

The SEM micrographs of the ternary blends confirm the hypothesis of the occurrence of some compatibilization. With respect to the binary blend, in Fig. 2, the micrographs of the ternary blends reported in Fig. 5 show more uniform dispersed particles of smaller dimensions, only a few microns, and with a better adhesion.

All these features clearly indicate the occurrence of a significant compatibilization between the two phases

induced by both the functionalized elastomer and the copolyesters.

3.3. Mechanical properties

Typical stress–strain curves of binary and ternary blends are plotted in Fig. 6. The binary blend shows a low value of the elongation at break near to the yield strain. The tensile properties of the polymer parents and of the blend are reported in Table 2. Like the rheological curves, the blend shows at least one mechanical characteristic, the elongation at break, below those of the two components. The coarse

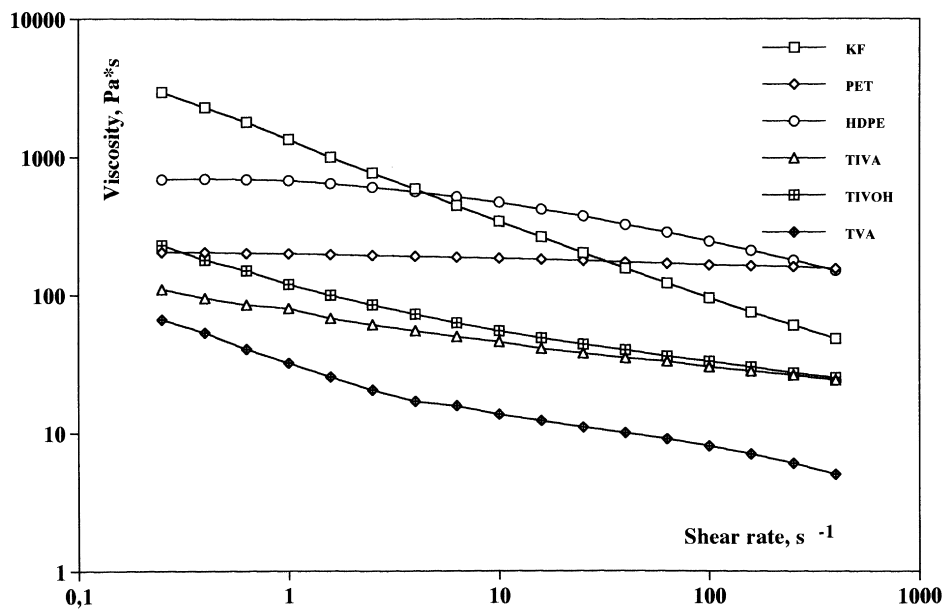


Fig. 4. Flow curves of the compatibilizing agents and of the pure components.

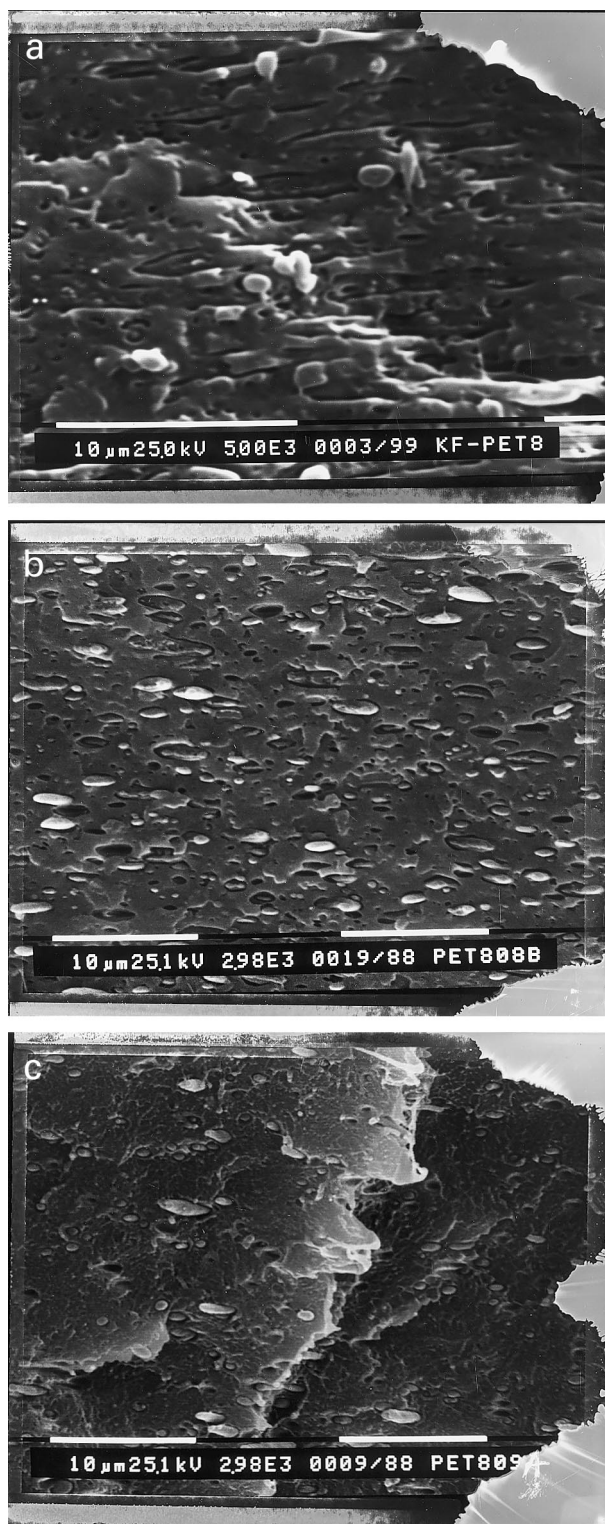


Fig. 5. SEM micrographs of the PET80 blend compatibilized with: (a) KF; (b) TIVA; and (c) TIVOH.

morphology and the lack of adhesion between the two phases are, of course, responsible for the fragile behaviour of the binary blend.

The stress–strain curves of the blend change drastically

Table 2
Tensile properties of the blend and of the polymer parents

Sample	E (GPa)	TS (MPa)	EB (%)
PET80	1.45	35.7	9
PET	1.52	40.8	260
HDPE	0.81	25.1	640

Table 3
Tensile properties of compatibilized and uncompatibilized blends

Sample	E (GPa)	TS (MPa)	EB (%)
PET80	1.45	35.7	9
PET80/KF	1.37	35.6	210
PET80/TVA	1.45	37.2	48
PET80/TIVA	1.54	35.2	55
PET80/TIVOH	1.45	38.7	33

Table 4
Tensile properties of the compatibilizing agents

Sample	E (GPa)	TS (MPa)	EB (%)
TVA ^a	–	–	–
TIVA	1.31	35.1	4.1
TIVOH	1.30	35.6	4.2
KF	0.057	9.3	670

^a Too brittle.

by adding the third component. All the compatibilized blends become ductile and in particular the ternary blend with KF shows a very high value of the elongation at break.

The fragile–ductile transition can be easily attributed to the more uniform morphology and by the better adhesion shown by the ternary blends with respect to that of the binary blend.

The tensile properties, elastic modulus, E , tensile stress, TS, and elongation at break (EB) of all the investigated blends are reported in Table 3.

The presence of the elastomers causes, as expected, a small reduction of the value of the elastic modulus while the copolyesters give rise to a small enhancement to a different extent. TIVA is only efficiently compatibilized as for the elastic modulus while TVA and TVOH do not give any improvement of the modulus. Also the tensile stress is slightly modified by the third component, however, TVA and TIVOH provoke a small rise of TS. Finally, all the copolymers strongly improve the elongation at break of the blend, in particular the elastomer.

The three copolyesters give rise to similar values of the elongation at break (35–55% versus about 9% of the binary blend) while the elongation at break of the blend with the elastomer is larger, about 210%.

As already discussed for the viscosity, the improvement of the elongation at break can be attributed to the compatibilization raised by the presence of the third component or

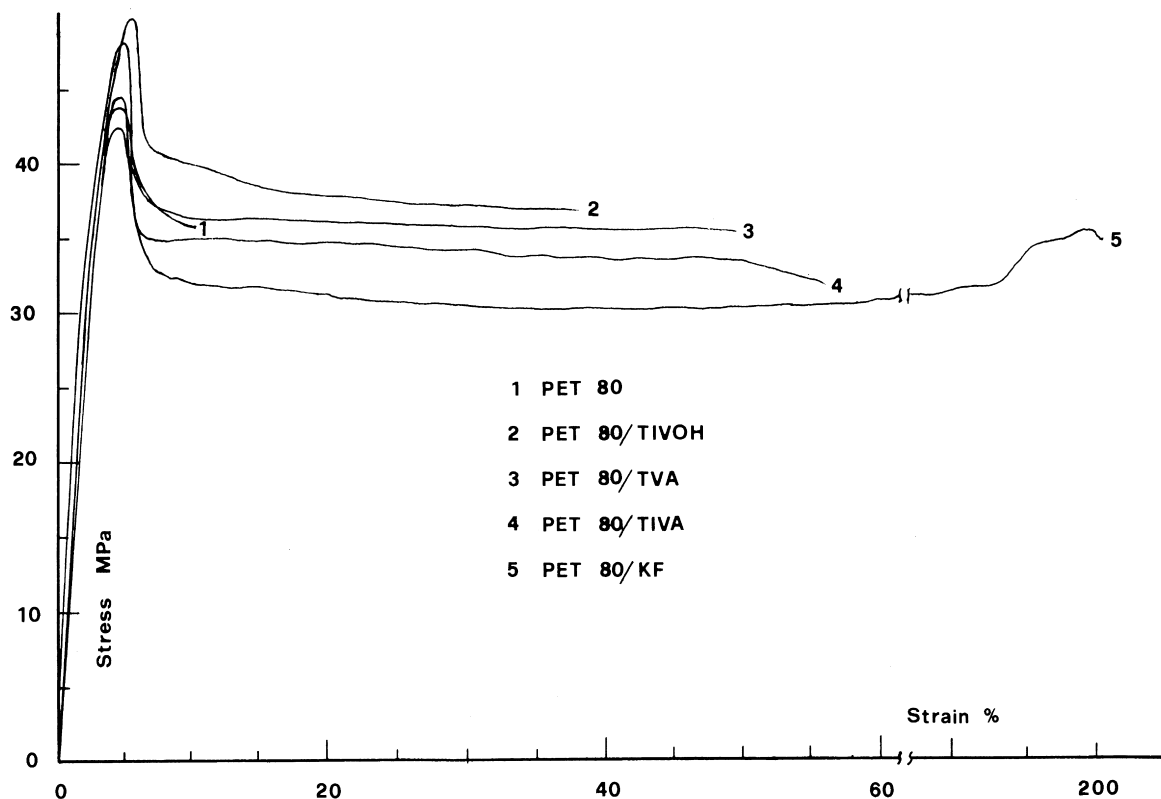


Fig. 6. Stress–strain curves of the uncompatibilized and compatibilized PET80 blends.

by the intrinsic high value of the elongation at break of the compatibilizer. As for the ternary blends with the copolyesters, this last hypothesis cannot hold because of the fragile behaviour of the three copolyesters. The elongation at break of these copolymers, in Table 4, is indeed very low and lower than that measured for the blend. The enhancement of the elongation at break and the fragile–ductile transition must be attributed to the better adhesion of the two phases. As for the blend with the functionalized elastomer, the maximum increase of the elongation at break due to the presence of a ductile elastomer, evaluated by means of an additive rule, should be about 60% and then well below the experimental value found for the ternary blend. The beneficial effect of the compatibilization is also evident for the mechanical properties.

4. Conclusions

PET/HDPE blends are fragile materials because of the incompatibility between the two phases. A significant improvement of the morphology and of the mechanical properties, and in particular of the elongation at break, can be achieved by using a third component acting as compatibilizing agent. The compatibilizing capability of the functionalized elastomer and of the copolyester used in this work is confirmed both by the viscosity curves and by the SEM micrographs. The compatibilizing action of the functionalized

elastomer employed in this work can be attributed to the formation of H-bonding with the polar component, as shown for the compatibilization of an other MA grafted copolymer [6,12–14].

The copolyesters synthesized in the frame of this research work can be usefully employed as compatibilizing agents probably because their blocks are partly compatible with the two phases. Although at present a correlation between the molecular structure of copolyesters and the compatibilizing effect is not possible, the results observed for TVA, TIVA and TIVOH, suggest that both graft copolymers and AB crosslinked structures, presumably contained in different amounts in the three samples, have a compatibilizing effect for HDPE–PET blends, even if present in small amount.

Acknowledgements

This work has been financially supported by CNR “PF MSTa II”. T. Loultcheva Dimitrova has received a financial support by RICAS, Palermo.

References

- [1] Traugott TD, Barlow JW, Paul DR. *J Appl Polym Sci* 1983;28:2947.
- [2] Wissler GE. *Proceedings of SPE ANTEC'90*, p. 1434.
- [3] Kalfoglou NK, Skafidas DS, Kallitsis JK, Lambert J-C, Van der Stappen L. *Polymer* 1995;36:4453.

- [4] Bataille P, Boissé S, Schreiber HP. *Polym Engng Sci* 1987;27:622.
- [5] Curry J, Kiani A. *Proceedings of SPE ANTEC'90*, p. 1452.
- [6] Xanthos M, Young MW, Biesenberger JA. *Polym Eng Sci* 1990;30:355.
- [7] Carté TL, Moet A. *J Appl Polym Sci* 1993;48:611.
- [8] La Mantia FP, Vinci M, Pilati F. *Polym Recycling* 1994;1:33.
- [9] Ballauri B, Trabuio M, La Mantia FP. In: La Mantia FP, editor. *Recycling of PVC and mixed plastics*, Toronto: ChemTec Publishing, 1996.
- [10] Dimitrova TL, La Mantia FP, Pilati F. *First ESAFORM Conference on Material Forming Sophia-Antipolis Francia, 17–20 Marzo, 1998*.
- [11] Holsti-Miettinen RM, Seppala JV, Ikkala OT, Reima IT. *Polym Eng Sci* 1994;34:395.
- [12] La Mantia FP, Scaffaro R, Plado G, Magagnini PL, Paci M. *Polym Networks Blends* 1996;6:171.
- [13] Miller MM, Cowie JMG, Tait JG, Brydon DL, Mather RR. *Polymer* 1995;36:3107.
- [14] Kozlowski M, La Mantia FP. *J Appl Polym Sci* 1997;66:969.