Metal Catalysis to Improve Compatibility at PO/PET Blends Interfaces

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Summary: Reactive blending of 70/30 by weight PET/polyolefin (PO) mixtures was carried out in a discontinuous mixer using a polyolefin functionalized with dialkyl maleates and potential transesterification catalysts to improve the formation of graft PO-PET copolymers. The yield of this reaction was evaluated by the analysis of FT-IR spectra of blends residual fraction after selective extractions of unreacted polyester. The building of a calibration curve and the analysis of the spectra by deconvolution was performed to evaluate the percentage of grafted PET. The results are discussed in terms of influence of the different catalysts and of polyolefin structure on the blends morphology.

Keywords: blends; morphology; PET; polyolefins; transesterification catalyst

Introduction

Polyolefins (PO)/PET blends present a coarse morphology because of immiscibility of the two components. The presence of compatibilizing agents at the interface could produce a better morphology characterized by a low dispersed phase diameter and a lower interfacial tension. Only the blends that present this kind of morphology present good mechanical properties in terms of tensile and impact properties.[1]

Many papers report about the use of different compatibilizing agents. Chaudari et al.[2] studied the effect on morphology and mechanical properties of an Ethylene-acrylic acid copolymer on polyethylene-co-octene copolymer/PET blends observing an improvement of impact behaviour. Moreover the use of copolymers containing reactive units as Ethylene-glycidyl methacrylate copolymer (E-GMA)[3] or Ethylene-ethyl acrylate-glycidyl methacrylate copolymer (E-EA-GMA) [4] seems to be very efficient in forming comb PO-PET copolymers in high density polyethylene (HDPE)/PET blends because of the high reactivity of the epoxy ring towards hydroxyl and carboxyl PET terminal groups.

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Also functionalized polyolefins have been studied as possible compatibilizing agents. The polyolefins have been previously modified by radical grafting with different functionalizing monomers as maleic anhydride,[5] glycidyl methacrylate,[6] 2-idroxyethyl methacrylate-isoforone diisocyanate[7] or ricinolo oxazoline maleinate [8] that present respectively anhydride, epoxy, isocyanate and oxazoline reactive groups able to react with PET terminals to yield PO-PET copolymer.

The aim of this work is to study the reaction between a polyolefin functionalized with dialkyl succinate groups (PO-g-DAS) and PET during the melt blending process in the presence of different transesterification catalysts and its effect on the compatibility.

Some acetates of various metals have been studied and used as transesterification catalysts in PET synthesis. Tomita et al.[9] studied the transesterification between dimethyl terephthalate and diethylene glycol observing that Zn, Pb, Mn, Ce, Co, Cd and Mg acetates showed high activity. Fontana[10] hypothesized a mechanism that involved the formation of a metal alkoxyde to explain this catalytic process. This mechanism agrees with the inhibiting effect of carboxylic acids on the reactivity of zinc reported by Walkers[11] and Otton.[12] $Zn(CH_3COO)_2$ has also been added to blends of PET and poly(ethylene naphthalate 2,6-dicarboxylate) (PEN) to improve PET-PEN copolymer formation at the interface.[13] In fact kinetics studies on model molecules showed that the presence of this catalyst decreases the activation enthalpy of the direct ester-ester interchange transesterification.

$Zn(OOCCH_3)_2$ and $Mg(OOCCH_3)_2$ have been chosen as potential catalysts of transesterification at the interface because they are environmentally sustainable and easy to handle. Moreover Magnesium and Zinc stearate [$Mg(OOC(CH_2)_{16}CH_3)_2$ and $Zn(OOC(CH_2)_{16}CH_3)_2$] have been also tasted because their long aliphatic chain could enhance catalyst affinity towards the polyolefin phase containing DAS groups, involving them preferentially in the transesterification process with PET to produce the graft copolymer.

Experimental Part

Materials

Polyolefin material is a 85/15 by weight blend of Engage 8003 ethylene-octene copolymer (30% by weight of comonomer content, MFI = 1 dg/min at 190°C and 2.16 Kg, density of 0.886 g/cm^3)

and Riblene (Polimeri Europa) low density polyethylene. The blend has been functionalized in the melt with dimethyl maleate (DMM) and dibutyl maleate (DBM) in the presence of DCP as radical initiator. The two polyolefin materials present a functionalization degree of 0.7 and 0.8 % respectively by moles determined by an FT-IR method.[14]

PET is a post-consumer colourless material named SERI-L/AN from Se.Ri.Plast with intrinsic viscosity = 0.486 dl/g (1,1,1,3,3,3-hexafluoro-2-propanol at 25°C).

Reactive Blending

Blends have been prepared in a 50 ml discontinuous mixer at 250°C with a blades rate of 80 rpm and a reaction time of 10 minutes. After mixing the blends have been cooled to room temperature and characterized.

Characterization

A small quantity (0.6 g) of all the blends have been extracted with an 80/20 v/v solution of 1,1,1,3,3,3-hexafluoro-2-propanol(HFIP)/methane dichloride (DCM) for four hours. The obtained dispersions have been filtered and washed with fresh solvent on the filter. After the removing of solvent by vacuum the residual and extracted fraction have been characterized by FT-IR.

IR spectra were measured with a Perkin Elmer 1330 Fourier Transform infrared spectrometer on press moulded sample.

A Jeol JSM model T-300 was used for SEM and fractured surfaces at cryogenic temperature were examined.

Results and Discussion

The selected starting mixtures composition was 70 % by weight PET (with a molecular weight of 22500 determined by viscosimetric measurements) and 30% by weight of unmodified polyolefin (PO) or dimethyl maleate functionalized polyolefin (POG) or dibutyl maleate functionalized polyolefin (POF). The various catalysts have been added (Table 1) with an identical molar concentration corresponding to 5.4 moles per 100 PET macromolecules.

Table 1. Composition of 70/30 by weight PET/polyolefin blends.

Blends	polyolefin	Catalyst	Final torque (N*m)
POPET[a)]	PO	-	9.1
POGPET	POG	-	7.6
POGPETC1	POG	C1 = $Mg(OOC(CH_2)_{16}CH_3)_2$	7
POGPETC2	POG	C2 = $Mg(OOCCH_3)_2$	6.7
POGPETC3	POG	C3= $Zn(OOCCH_3)_2$	7.1
POGPETC4	POG	C4= $Zn(OOC(CH_2)_{16}CH_3)_2$	6.1
POFPET	POF	-	5.9
POFPETC3	POF	C3 = $Zn(OOCCH_3)_2$	5.3
POPETC1	PO	C1 = $Mg(OOC(CH_2)_{16}CH_3)_2$	6.1
POPETC4	PO	C4= $Zn(OOC(CH_2)_{16}CH_3)_2$	5.4

The blends final torques decrease when a potential catalyst is added. This is due to PET degradation during blending as confirmed by direct treatment of PET (Table 2 and Figure 1) in the presence of the potential catalysts under the same processing conditions.

Table 2. Final torque of PET blended in the presence of potential transesterification catalysts.

sample	Catalysts	Final torque (N*m)
PET	-	4.2
PETC1	C1 = $Mg(OOC(CH_2)_{16}CH_3)_2$	3.4
PETC2	C2 = $Mg(OOCCH_3)2$	2.3
PETC3	C3= $Zn(OOCCH_3)2$	1.9
PETC4	C4= $Zn(OOC(CH_2)16CH_3)2$	1.9

The lowest torque values are observed for PETC3 (zinc acetate) and PETC4 (zinc stearate) experiments. The values of torque reported for blends (Table 1) do not follow the same trend. In particular POGPETC3 presents the highest torque value (7.1 N*m).

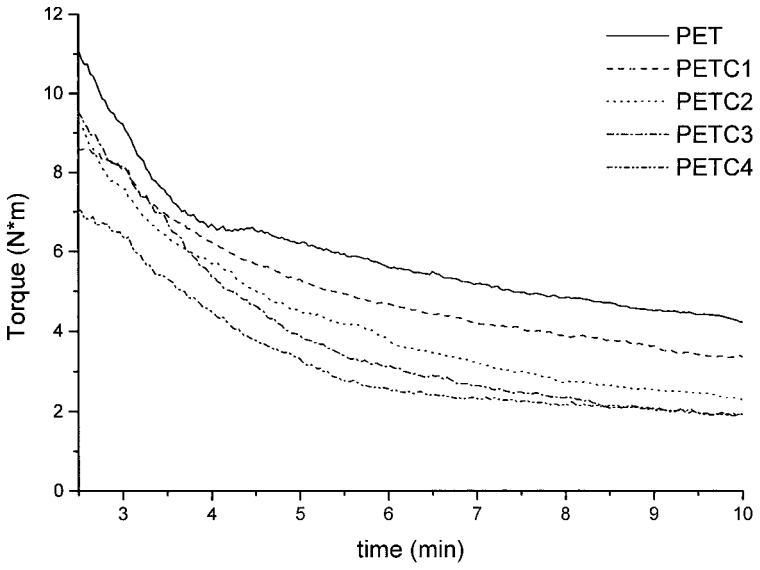

Fig. 1. Torque versus time curve obtained for PET in the presence of the potential catalysts.

A small quantity of all the blends reported in Table 1 has been extracted with a 80/20 v/v solution of 1,1,1,3,3,3-hexafluoro-2-propanol(HFIP)/methane dichloride (DCM) in which PET is soluble. Extraction results, in terms of percentage of extracted and residual fractions, can be affected by an high error. Then the more sensible FT-IR spectroscopy has been used to analyse the residual fractions films and the different spectra are compared (Figure 2). In the spectra, normalized at 1460 cm^{-1}, the PET bands at 1720 cm^{-1} show a different absorbance value comparing the different catalytic systems.

Some mechanical blends of not functionalized polyolefin and PET with known compositions (in the range 2-40% of PET) have been produced and moulded with a press. Three films for every mechanical blend have been analysed by FT-IR. For every blend the average ratio between C=O ester band of PET and CH_2 1460 cm^{-1} bending band (reference band) was determined and a calibration line (composition versus area ratio) has thus been traced (Figure 3).

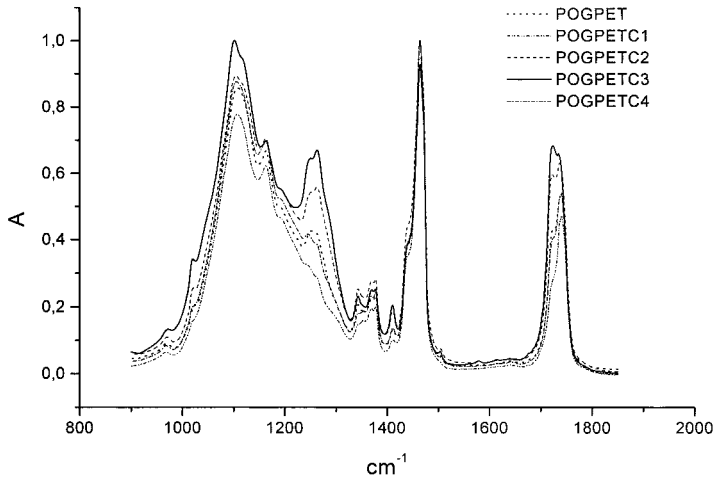

Fig. 2. FT-IR spectra of some blends residual fractions. The spectra are normalized with respect to 1460 cm^{-1} polyolefin band height.

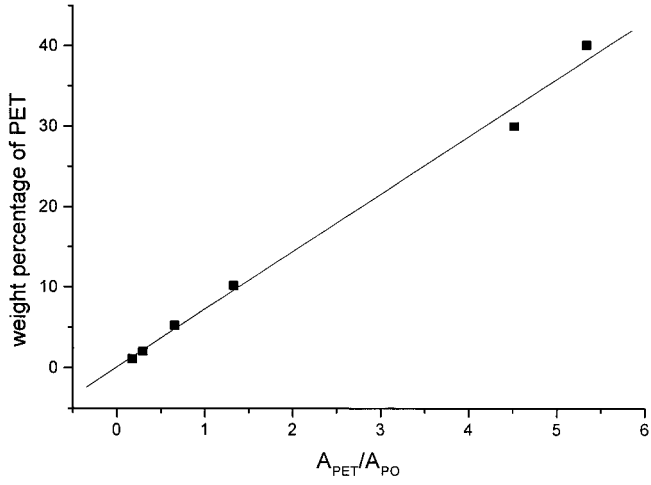

Fig. 3. Calibration line obtained analysing by FT-IR mechanical blends with known compositions.

The same average ratio has been calculated in three different spectra of residue to HFIP/DCM extraction. The area of PET band has been calculated correctly fitting the C=O ester band with three different bands (1710, 1720, 1730 cm^{-1}), as deduced carrying out preliminary fittings on calibration mechanical blends spectra. Then every residue spectrum in the 1680-1780 cm^{-1} range has been fitted with four different bands: three for PET and one (1742 cm^{-1}) for dimethyl succinate ester group (Figure 4). This latter band was obviously omitted in the calculus of the area ratio.

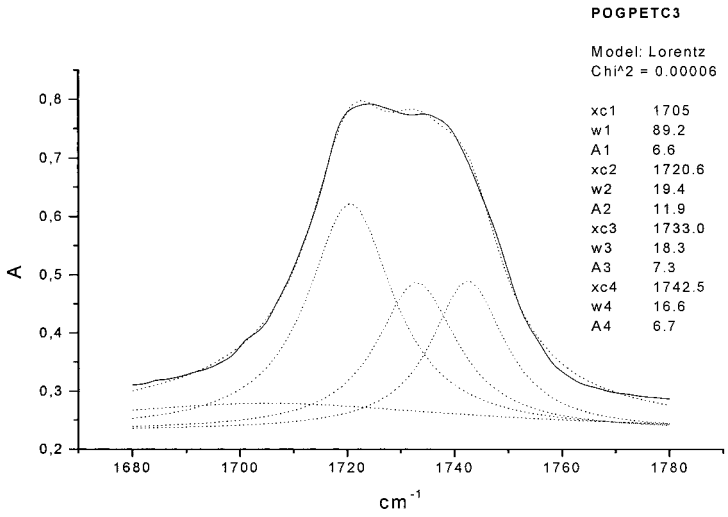

Fig. 4. Example of deconvolution of POGPETC3 residual fraction spectrum considering three bands for PET ester band and one for dimethyl succinate ester band.

The percentage of grafted PET in the residual fraction was thus determined by interpolation on the calibration line and the results are reported in Table 3.

The yield determination reveals low, but clearly evidenced, quantities of PET grafted in every blends. Furthermore some interesting differences among the catalytic systems can be evidenced. In particular PET in the residual fraction of POGPETC1 and POGPETC4 is similar to that of POGPET obtained in absence of a potential catalyst, whereas POGPETC3 shows an higher presence of grafted PET.

Table 3. percentage by weight of PET in the residual fraction of blends and grafting yield.

Blends	PET in the residual fraction (% by weight)	PET grafting yield[a]
POPET	2	0.9
POGPET	6	2.5
POGPETC1	4	1.5
POGPETC2	6	3.4
POGPETC3	9	3.8
POGPETC4	5	3.2
POFPET	5	1.4
POFPETC3	19	7.4

a) The grafting yield was calculated using extracted and residual fraction weight data.

Then on the whole stearates (C1 and C4) present lower catalytic activity than acetates (C2 and C3). The highest amount of grafted PET is obtained for POGPETC3, that is in the presence of zinc acetate.

The change of the functionalized polyolefin in POFPET leads to obtain the same amount of PET in the residual fraction than POGPET. Then dimethyl succinate and dibutyl succinate groups present the same reactivity in transesterification with PET. When Zinc acetate was used in the presence of POF a neat increasing of the PET percentage in the residual fraction was observed.

Morphological characteristics of blends (Figure 5) showed that the use of a functionalized polyolefin leads to obtain a better morphology in terms of interfacial adhesion with respect to a blend with an unmodified polyolefin as observed comparing POGPET and POFPET with POPET scanning electron microscopy (SEM) microphotographs.

The use of potential catalysts produces further changes in morphology. In particular a significant improvement of adhesion between the two phases is observed in all cases above all when acetates have been used. On the other hand when stearates are added the morphologic improvement could be due to their own compatibilizing effect. This is demonstrated comparing POPET morphology with those of POPETC1 and POPETC4, blends obtained with not functionalized polyolefin and equivalent amounts respectively of C1 and C4.

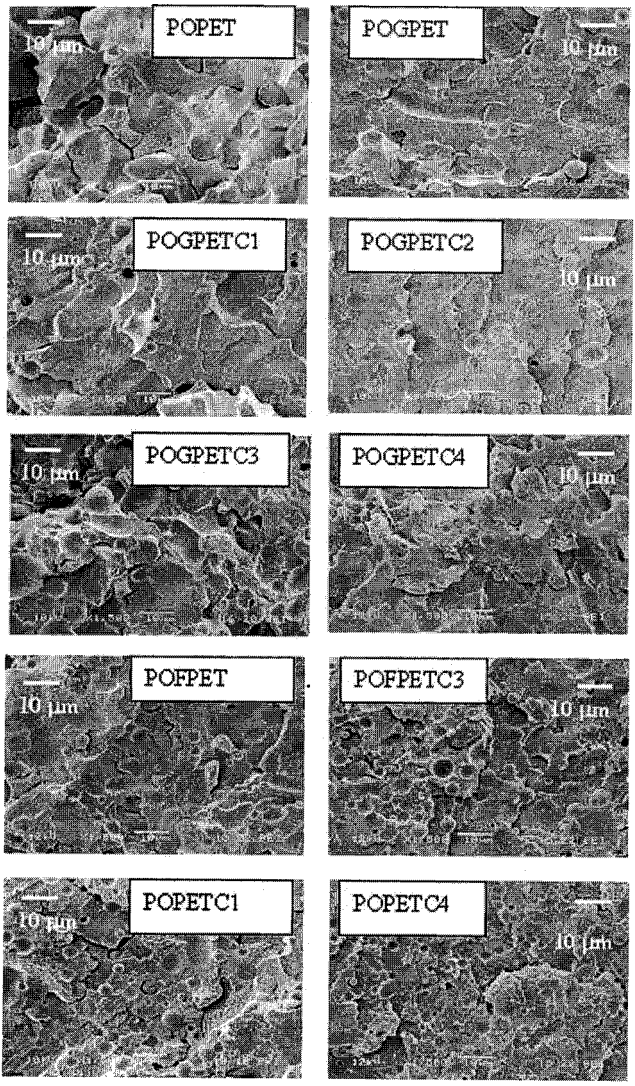

Fig. 5. SEM microphotographs of blends.

Very significant is the decreasing of dispersed phase diameter in POFPETC3 with respect to POFPET, in agreement with the above FT-IR results.

Conclusion

In this study a new method to evaluate the grafting yield of PET on a functionalized polyolefin has been applied. This method permits to compare the efficiency of different metal catalysts. A higher efficiency was observed for acetates than for stearates probably because of the higher reactivity of the former. Moreover zinc acetate seems to be the most efficient catalyst.

A neat increasing of grafting yield is observed when a dibutyl maleate functionalized polyolefin is used. Probably this is not the consequence of macromolecular structure but of rheological properties of the different functionalized polyolefins. In fact POF presents a lower melt viscosity of POG and this could produce a morphology characterized by an higher interfacial area, as confirmed by SEM results, that favour interphases processes.

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