

In Situ Compatibilization of HDPE/PET Blends

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ABSTRACT: The reactive compatibilization of immiscible polymers such as high-density polyethylene (HDPE) and poly(ethylene terephthalate) (PET) by interfacial grafting of maleic anhydride (MA) without initiator in the molten state was investigated in this study. Grafting reaction of MA onto HDPE was carried out in a Rheocord HAAKE mixer varying reaction parameters such as the temperature, the shear rate, and the time of reaction. Then, the purified copolymers were characterized by infrared spectrometry and the MA content of HDPE-*g*-MA copolymers was determined by volumetric titration. It has been shown that thermomechanical initiation is sufficient to reach grafting yield of 0.3 to 2.5 wt % of MA. We studied then the compatibilization of HDPE/PET blends by interfacial grafting of MA. The *in situ* interfacial reaction leads to the formation of HDPE-*g*-MA copolymer which acts as a compatibilizer in the blends. The foremost interest of this work is that it provides a simple way of compatibilization of immiscible blends of polyolefin and polyester in one transformation step without using free-radical initiators. The mechanical properties of the blends are strongly improved by the addition of small quantities of MA. The SEM observations of the compatibilized blends show a deep modification of the structure (i.e., enhanced regularity in the nodule dispersion and better interfacial adhesion). © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 874–880, 2001

Key words: high-density polyethylene; poly(ethylene terephthalate); maleic anhydride; grafting; compatibilization

INTRODUCTION

Improvement in mechanical properties of immiscible polymers blends can be achieved by different techniques. Xanthos^{1,2} reviewed many compatibilization methods, giving detailed examples and explanations concerning this subject. High-density polyethylene (HDPE) and poly(ethylene terephthalate) (PET) are immiscible polymers in the molten state and their blends led to large interfacial tension, poor interfacial adhesion, and

mediocre mechanical properties. To enhance these properties, it is necessary to limit formation of segregated phases in the blend during the mixing step by adding or formation *in situ* of a third component which acts as a compatibilizer at the interface of the two polymers. This way has been largely studied in many publications related to number of polymer blends and compatibilization methodologies. Various copolymers were used to compatibilize the HDPE/PET blends. For example, the mechanical properties of these materials are improved when 10–20 wt % of hydrogenated styrene/butadiene/styrene copolymer (SEBS) or ethylene-propylene-diene monomer (EPDM) are introduced^{3–9} in the blends. Reactive copolymers

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were also tested successfully. Thus, the transesterification of PET with ethylene vinyl acetate copolymer (EVA) gives a graft copolymer which can act as compatibilizer.¹⁰ Most works concern the use of commercial copolymers such as polyolefin-grafted acrylic acid (PE-*g*-AA),¹¹ ethylene-co-glycidyl methacrylate copolymer (E/GMA),^{12–14} hydrogenated styrene/butadiene/styrene copolymer grafted with maleic anhydride (SEBS-*g*-MA),^{15,16} hydrogenated styrene/butadiene/styrene copolymer grafted with glycidyl methacrylate (SEBS-*g*-MAGLY),¹⁶ ethylene-propylene copolymer (EPR-*g*-MA)¹⁷ or ionomer resins.^{18–21} In each case, it is necessary to introduce 5–10 wt % of additives. Taking account of the price of these copolymers, they are not applied in this field of industrial applications.

In a previous publication,²² we showed that the mechanical properties of HDPE/PET blends are improved by adding graft copolymers which are synthesized by ozonization of HDPE followed by grafting of vinylic or acrylic monomers. The introduction of a third component which has affinities for both polymers induces a reduction of interfacial tension between phases and increases the interfacial adhesion. In this study, we looked for a simple and inexpensive way to compatibilize HDPE/PET blends in one step of processing. To synthesize a compatibilizer during the mixing step, we added a coupling molecule to the blend. The coupling molecule must react with both of the polymers so that a graft copolymer containing parts of each polymer is generated during the processing. This approach was used by Seadan²³ to compatibilize polypropylene/polyamide blends. The authors showed that interfacial grafting of maleic anhydride (MA) onto polyolefins by using free-radical initiators improves the mechanical properties and the morphology of blends. The originality of our work consists of grafting MA onto HDPE backbone in the molten state without initiator. The double bond of MA would react with macroradicals of HDPE and the hydroxyl end groups of PET would react with the anhydride functions. The use of a free-radical initiator, which is costly and environmentally hazardous, is avoided. We aimed to demonstrate that thermomechanical treatment is sufficient to initiate the grafting reaction of MA onto HDPE. Our goal was also to show the possibility of enhancing mechanical properties of HDPE/PET blends by adding a coupling agent (MA) to the blends in the molten state. The grafting reaction of MA onto polyolefins in a solvent or in the molten state with free-radical initiator has been largely studied by many authors such as Gaylor,^{24–26} Gabara and Parejko,^{27,28} Ganzeveld and

Janssen,²⁹ or Flat,³⁰ but the mechanism of the reaction has not yet been clearly elucidated. We describe hereafter the *in situ* grafting of MA onto HDPE in the molten state without using any initiator.

EXPERIMENTAL

Materials

HDPE (Stamylan 6621) supplied by DSM (France) had a weight-average molecular mass (M_w) of 111,000 g/mol, a number-average molecular mass (M_n) of 9000 g/mol, and a melt-flow index of 0.16 g/10 min (190°C, 2.16 kg). PET (Arnite A), supplied by Akzo Nobel (Belgium), had an intrinsic viscosity of 0.70 dL/g. MA of purity 99% was purchased from Aldrich.

Grafting Procedure

Grafting reaction in the molten state was carried out in a Rheocord HAAKE mixer (50 cm³). The HDPE (45 g) was introduced in the preheated batch mixer and was mechanically mixed, varying the roller speed and the time of reaction. When temperature was stabilized, 4.5 g of maleic anhydride was added. After reaction, samples were taken off the batch mixer and quenched into liquid nitrogen to stop further reactions. Then, the copolymers were purified by dissolution in anhydrous refluxing toluene and precipitation into anhydrous acetone at room temperature. This solvent permits the precipitation of the modified HDPE, the dissolution of the excess of monomer which did not react, and the elimination of homopolymer. The purified copolymers were dried under vacuum at 60°C for 8 h.

Analysis of Graft Copolymers

To determine the MA content of HDPE-*g*-MA copolymers, we used a volumetric titration. Purified copolymer (5 g) were dissolved in 200 mL of anhydrous refluxing toluene. When the copolymer was completely dissolved, the temperature was decreased to 90°C. The solution is then titrated with a 0.05M KOH solution in isopropanol with phenolphthalein as indicator. The color had to persist for 30 s to evaluate the end point.

To confirm the presence of MA grafted onto HDPE, we also used infrared spectrometry. This analysis was performed with a Fourier transform infrared (FTIR) spectrophotometer (NICOLET

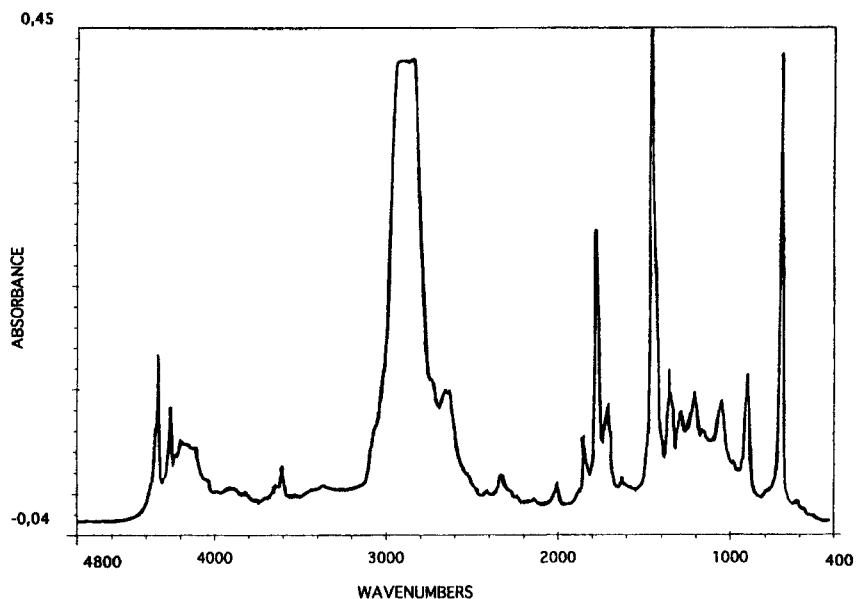


Figure 1 Infrared spectrum of HDPE-g-MA copolymer.

510 P). Thirty-two scans were recorded with a 4-cm^{-1} resolution.

Melt Processing

Before blending, pellets of PET were dried 12 h at 120°C . HDPE/PET blends at composition 60/40 (wt %) were prepared in a Rheocord HAAKE mixer (50 cm^3). HDPE and PET were introduced into the cell preheated to 270°C and mixed at 64 rpm for 5 min. The blends were then compression molded at 270°C under 100 bars. The sheets ($10 \times 10 \times 2\text{ mm}$) were cut into ISO 1/2 test bars. After molding and prior to testing, specimens were conditioned in a laboratory atmosphere for a minimum of 3 days.

Characterization

To study the morphology of the blends, the samples were fractured in liquid nitrogen. The fractured surfaces were examined by scanning electron microscopy (SEM, Cambridge Stereoscan 260) after being coated with a thin conductive layer of palladium alloy. The enlargements were specified in the legends.

The performances of the specimens were evaluated by the mechanical properties in terms of strength at break and elongation at break. The specimens were tested on a 1195 model INSTRON. A crosshead speed of 2 mm/min was used to evaluate the strength at break (confidence limit: $\pm 0.7\text{ MPa}$) and elongation at break (confidence

Table I Experimental Domain

	Lower Limit	Upper Limit
Temperature ($^\circ\text{C}$) (X_1)	170	230
Roller speed (rpm) (X_2)	50	150
Time (min) (X_3)	2	10

limit: $\pm 1\%$ in our experimental range). The values reported for the properties were the average of at least 10 determinations.

RESULTS AND DISCUSSION

Synthesis of Grafted Copolymers

The grafting reaction onto HDPE in the molten state is carried out in a closed batch mixer HAAKE by using 10 wt % MA. The use of a closed batch mixer HAAKE avoided the volatilization of MA in the atmosphere. We studied the effect of the reaction time, the temperature, and the roller speed on the grafting yield of the copolymers. The evolution of the grafting reaction is followed by the variation of the torque because this reaction induces an increase in the melt viscosity which becomes stable at the end of the reaction. The modified polymers are uncrosslinked because they are totally soluble in refluxing toluene. The relation between the increase in melt viscosity and the applied conditions was not investigated in this study. After purifica-

Table II Matrix of Experiment

Experiment Number	X_1 (Temperature)	X_2 (Roller Speed)	X_3 (Time)
1	-1	-1	-1
2	-1	1	-1
3	1	-1	-1
4	1	1	-1
5	-1	-1	1
6	-1	1	1
7	1	-1	1
8	1	1	1
9	0	0	0
10	1	1	0

tion (dissolution in refluxing anhydrous toluene and precipitation in anhydrous acetone), the copolymers were characterized by volumetric titration of MA functions and by infrared spectroscopy. The infrared spectra of purified copolymers (Fig. 1) showed a peak located at 1778 cm^{-1} corresponding to the characteristic absorption band of MA and two peaks located at 719 and 1464 cm^{-1} , corresponding to the characteristic absorption bands of polyethylene. That confirms that the grafting of MA onto HDPE in the molten state without free-radical initiator has occurred.

Influence of Reaction Parameters on the Grafting Yield

The effect of the temperature, the roller speed, and the reaction time on the grafting yield were studied by using the well-known experimental method.³¹ With these parameters, we have to operate 2^3 reactions with different experimental conditions. We consider only the lower and upper limit for each parameter (Table I). So, the matrix of experiment can be summed up in Table II. We defined Y_{th} as the theoretical answer for each reaction, in other words, the grafting yield determined by titration method. Y_{th} can be expressed as a function of X_1 , X_2 , and X_3 . All parameters exert an influence on the grafting yield which can be estimated by b_j coefficients. So, the theoretical

Table IV B_j Coefficients

b_0	1.34
b_1	0.24
b_2	0.36
b_3	0.46
b_{12}	-0.04
b_{13}	0.11
b_{23}	-0.01
b_{123}	0.04

answer Y_{th} as a function of these conditions can be expressed as:

$$Y_{th} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3$$

To check the mathematical model, we made two additional experiments (number 9 and 10) that we submitted to the model. The experimental grafting yields (Table III) obtained varying experimental conditions allowed us to calculate the b_j coefficients (Table IV) defined as¹²:

$$b_0 = \frac{\sum_i Y_{\text{exp}_i}}{8}$$

$$b_j = \frac{\sum_i Y_{\text{exp}_i} \times X_{ij}}{8}$$

Each coefficient represents the weight of parameter X_i on the grafting yield obtained. The theoretical response in function of parameters is

$$Y_{th} = 1.34 + 0.24X_1 + 0.36X_2 + 0.46X_3 - 0.04X_1X_2 + 0.11X_1X_3 - 0.01X_2X_3 + 0.04X_1X_2X_3$$

Table III MA Content (wt %) of Graft Copolymers

	Experiment									
	1	2	3	4	5	6	7	8	9	10
MA (wt %)	0.3	1.2	0.7	1.3	1.1	1.8	1.8	2.5	1.4	1.7

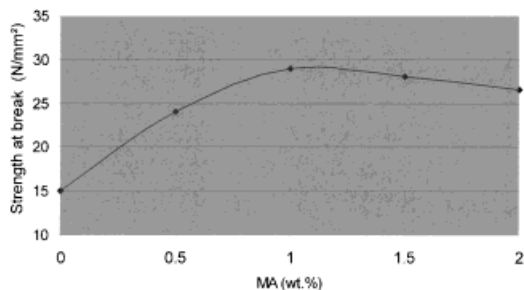


Figure 2 Strength at break of HDPE/PET (60/40 wt %) blends versus MA content.

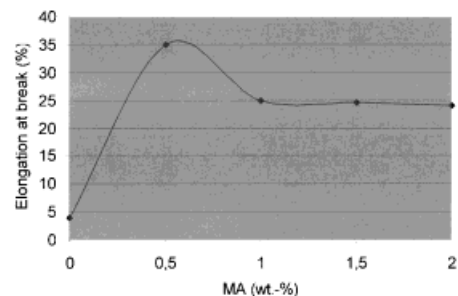


Figure 3 Elongation at break of HDPE/PET (60/40 wt %) blends versus MA content.

Table IV shows that the reaction time has a greater effect than the roller speed or the temperature on the grafting yield because $b_3 > b_2 > b_1$.

The control of the validity of our model was done by verifying the response of the model for experiments 9 and 10. The following results have been obtained

$$Y_{th}(9) = 1.34; \quad Y_{exp}(9) = 1.4$$

$$Y_{th}(10) = 1.9; \quad Y_{exp}(10) = 1.7$$

So, we observe good agreement between theoretical and experimental grafting yields. We conclude that the model gives us a good representation of the experiment under the applied conditions. We have also shown that it is possible to graft MA onto HDPE in the molten state without free-radical initiator.

Compatibilization of HDPE/PET Blends

The HDPE/PET blends without compatibilizer possess poor mechanical properties, particularly at the composition 60/40 (wt %).²² It is therefore necessary to compatibilize these blends. Previous works have shown that compatibility and adhesion can be improved by the addition of suitable block or graft copolymers, which act as compatibilizers located at the interface between immiscible phases. Another possibility investigated in this study consists of generating a copolymer *in situ* during the processing. We also studied the compatibilization of HDPE/PET blends by interfacial grafting of MA. Several tests were carried out in a closed batch mixer HAAKE by using different quantities of MA (0–2 wt %). Mechanical behavior (strength at break and elongation at break) of the blends are reported in Figures 2 and 3. Low MA quantities improve the strength at break and the elongation at break of HDPE/PET (60/40 wt %) blends with regard to the

uncompatibilized blends. For example, the introduction of 0.5 wt % of MA to the blend increases the strength at break of 15–25 N/mm² and the elongation at break of 4–35%. The fractured surfaces of the HDPE/PET blends with and without MA are observed by SEM to study the effect of the compatibilizer on the morphology. The HDPE/PET (60/40 wt %) blends without MA possess a coarse morphology (Fig. 4) with larger domain size in comparison to compatibilized blends. The larger particle size, with no evidence of adhesion between the matrix and dispersed phase, confirmed the incompatibility of the two components. In comparison, compatibilized blends with 0.5 wt % of MA (Fig. 5 and 6) show a more regular dispersion of PET nodules inside of HDPE matrix, a smaller nodule size, and an improvement in interfacial adhesion. The introduction MA directly to the blends is more effective than adding a graft copolymer to the blends (see results in ref. 3). We assume that the *in situ* grafting of MA at the interface of HDPE/PET blends leads to the formation of a compatibilizer. The following scheme illustrates the possible mechanism of the reaction:

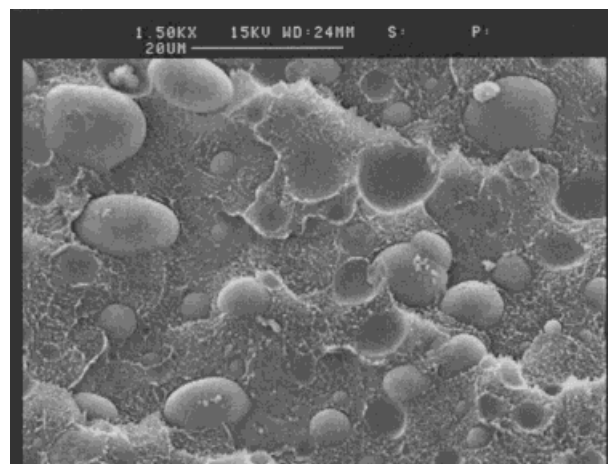
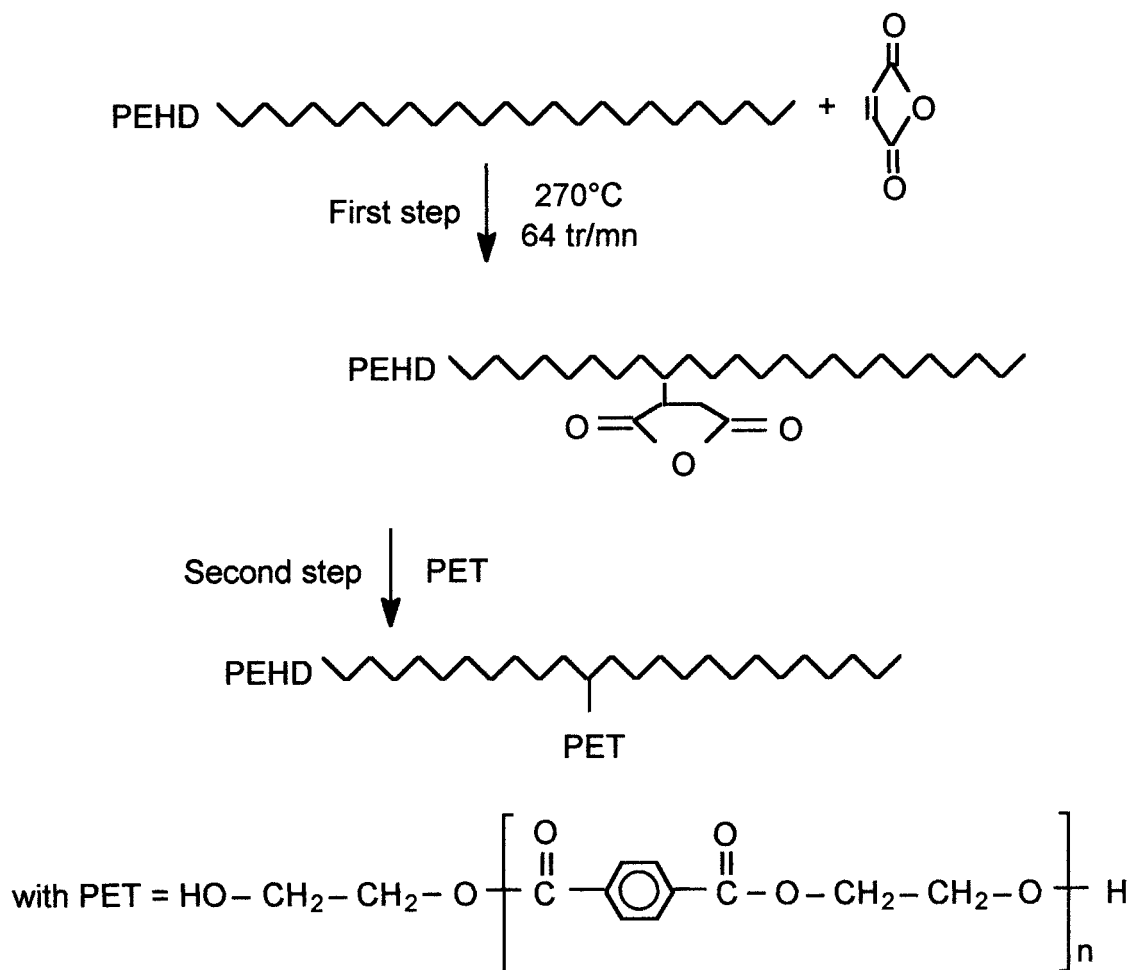


Figure 4 Microscopic observation of HDPE/PET (60/40 wt %) blend (magnification, $\times 1500$).



We could also assume a reversed scenario where anhydride functions would react first with the end groups of PET and after with the macroradicals of HDPE. The two competitive reactions should occur and further work is necessary to highlight the right hypothesis.

CONCLUSION

This study gives an original approach to compatibilize immiscible polymers such as HDPE and PET by adding small quantities of coupling agent (MA). In a first step, a reactive copolymer is prepared *in situ* by grafting MA onto HDPE. In a second step, succinic anhydride will react with functional end groups of PET. This work shows that interesting grafting yields of 0.3–2.5 wt % are obtained when the grafting of MA onto HDPE in the molten state happens without any free-radical initiator and only with thermomechanical

initiation. Moreover, there are no crosslinking reactions because we do not use an initiator. Contrary to the classic method of compatibilization,

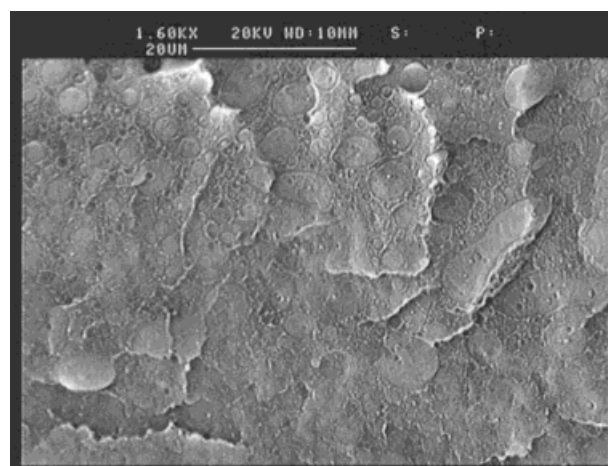


Figure 5 Microscopic observation of HDPE/PET (60/40 wt %) blend with 0.5 wt % of MA (magnification, $\times 1600$).

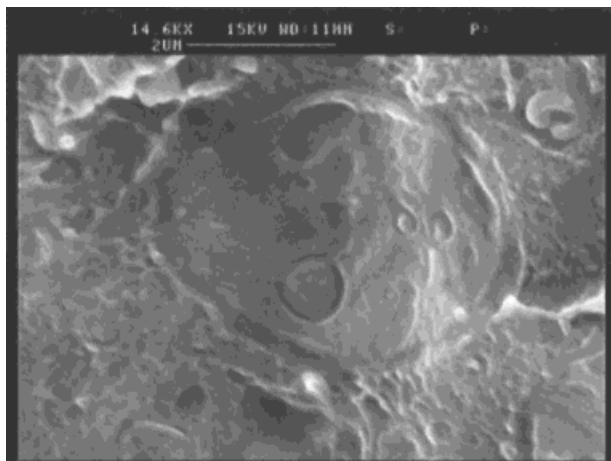


Figure 6 Microscopic observation of HDPE/PET (60/40 wt %) blend with 0.5 wt % of MA (magnification, $\times 14,600$).

which consists of adding a third component (reactive or no reactive copolymers) to the HDPE/PET blends during the processing, we prepared a reactive copolymer *in situ* by grafting MA onto HDPE without using free-radical initiator. Adding MA directly to HDPE/PET blends improves mechanical properties such as strength at break and elongation at break and morphology. Compatibilized blends possess better interfacial adhesion, smaller nodules size, and more regular dispersion of nodules inside of HDPE matrix with regard to uncompatibilized blends.

The compatibilization of blends with adding small quantities of MA in one step of processing is an interesting way particularly for recycled blends because it does not require prior expensive synthesis and leads to better results compared to those obtained by adding of graft copolymers to the blends.² Moreover, it makes the step of processing more environmentally friendly considering the high toxicity of peroxides and other free-radical initiators. This type of approach should be successful for virgin or recycled polymer blends such as polyolefin/polyester or polyolefin/polyamide.

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