

# Compatibilization of hiPP/HDPE blends by a metallocene copolymer

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**ABSTRACT:** A high impact polypropylene / high density polyethylene 80/20 blend was compatibilized by incorporating 5wt% of different metallocene random copolymers ethylene- $\alpha$ -olefin (mPE). The comonomer (butene or octene) content is ranged from 8.3 to 19.2 wt%. In some cases, a great improvement of mechanical properties was obtained due to a better interfacial adhesion. For example, elongation at break could increase from 60 to 340%.

The comonomer content has a strong effect on these results. On the contrary, viscosity, comonomer type or molecular weight are not influent parameters. The presence of 22wt% of EPR in high impact polypropylene has also a great impact on performances. EPR and metallocene copolymer are miscible.

**Key words:** Compatibilization, polymer blend, polyolefin, metallocene copolymer

## 1 INTRODUCTION

Polyolefins are the most common plastics used in the world. In particular, polyethylene and polypropylene represent more than 40wt% of the total amount consumed in the world [1]. Due to their closed density, these two polymers, which are non miscible and incompatible, could not be fully separated. So compatibilization treatments have to be performed to allow the material recycling of polyolefins.

Different ways could be carried out according to this objective. The first is the addition of peroxides which react with macromolecules and allow the combination of macroradicals at the interface to create a covalent bondings between the phases [2,3]. Irradiation is an alternative, involving radicals too [4]. But in these two cases, the presence of radicals could enhance the scissoring of PP chains and so the degradation of mechanical properties. Polyfunctional coagent could be added to avoid these consequences. A second way is the reactive extrusion by adding a small amount of two fonctionnal polymers, each one compatibilized with one phase [5]. For example, amine and maleic anhydride functions could react and form covalent bondings at the interface if one function is taken by PP and the second by PE.

Nevertheless, the most useful possibility to compatibilize PP and HDPE is to add a copolymer

which is compatible with both phases [6]. This copolymer migrates at the interface and reduces interfacial tension. Morphology is finer and mechanical properties which are dependent on interfacial adhesion are improved, like elongation at break or impact strength. Generally, block copolymers are more satisfying.

During the last decade, new random copolymers ethylene- $\alpha$ -olefin (mPE) are obtained using metallocene catalyst. These copolymers have a narrower molecular weight distribution and a distribution of comonomers more uniform. Even if numerous studies have been performed about the miscibility or the mechanical properties of PP or PE with these copolymers ethylene- $\alpha$ -olefin [7-10], very few publications deal with the compatibilizing effect of these copolymers on PP/PE blends.

In this article, we show some results indicating the great compatibilizing potential of metallocene random copolymers ethylene- $\alpha$ -olefin for polyolefin blends. Some critical parameters have been identified.

## 2 EXPERIMENTALS

### 2.1 Materials

Two PP were used in this study. The first is PP108MF97 from Sabic and contains 22wt% of EPR

(50wt% ethylene and 50wt% propylene). The second is the homopolymer PPH7060 from Total Petrochemicals. HDPE was Lupolen 4261 AG Q 469 from Basell. Random metallocene copolymers ethylene- $\alpha$ -olefin (called from E7380 to E8842) were Engage<sup>®</sup> from Dow Chemical.

## 2.2 Processing

Blends were performed using a corotating extruder. PP108, HDPE and mPE were added in the same time. For compatibilized blends, PP108/HDPE ratio was fixed at 4 and 5wt% of mPE were incorporated. Standard specimens were injection-moulded at 220°C for mechanical tests.

We performed too binary blends PP/mPE and HDPE/mPE 50/50 using a Haake plasticorder to study the miscibility between the different polymers. Temperature was fixed too at 220°C.

## 2.3 Testing

Molecular weight of polymers was measured by size exclusion chromatography (SEC), using a high temperature Waters Alliance 2000 device. Comonomer content of mPE was determined using Bruker DRX400 spectrometer (400 MHz, <sup>1</sup>H spectrum). Values were given in Table 1.

Tensile tests were performed at 22°C on 2\*5\*30 mm standard samples on MTS apparatus according to ISO 527-1:1993. Young's modulus was measured at 1mm/min. Yield stress, elongation and stress at break were measured at 50 mm/min.

Impact tests at -22°C ( $\pm 2^\circ\text{C}$ ) were performed using a Charpy impact testing machine with 4J pendulus according to ISO 179. Notched samples (2mm notching) were stored in a freezer during 12h.

Two DSC experiments were performed using DSC Q10 apparatus from TA Instruments.

The first was a serie of heating and cooling ramps at 10°C/min between 0 and 220°C for PP/mPE blends or 180°C for mPE and HDPE/mPE blends, to measure melting enthalpy, melting peak temperature and crystallisation peak temperature.

The second experiment was an isothermal crystallization of PP and HDPE to study the crystallization kinetics according to Avrami equation:

$$\ln(-\ln(1-X_t/X_\infty)) = \ln K + n \ln t$$

with  $n$  Avrami exponent,  $K$  crystallization rate coefficient,  $X_t$  the crystallinity index at  $t$  time and  $X_\infty$  the final crystallinity index

This procedure was applied by Li and al. for studying melt miscibility of PP/LLDPE blends [9, 11] and HDPE/LLDPE [12]. The sample was melted at 180 or 220°C and cooled very quickly to crystallization temperature. All of the DSC measurements were performed under a nitrogen purge.

SEM observations were carried out using a FEG SEM S800 Hitachi on standard specimen broken at cryogenic temperature. The fracture surfaces were etched in heptane to remove only mPE.

Table1. Molecular weight and MFI of polymers and comonomer content and type of mPE

Polymers	Mw (kg/mol)	MFI <sup>1</sup> (dg/min)	Comonomer content (mol%)	Comonomer type
PP108	150	100	/	/
HDPE	126	3.5	/	/
E7380	108	<0.5	15.9	butene
E7447	79	5	17.9	butene
E7467	87	1.2	19.2	butene
E8003	135	1	8.3	octene
E8100	90	1	12.3	octene
E8200	70.5	5	13.6	octene
E8407	70	30	12.4	octene
E8842	196	1	14.8	octene

<sup>1</sup> Conditions of MFI measurement : PP108, 230°C, 2.16kg - HDPE, 190°C, 5kg - mPE, 190°C, 2.16kg

## 3 RESULTS

### 3.1 Mechanical properties

Mechanical properties of PP108/HDPE are measured for different PP108/HDPE ratios. Adding a small content of HDPE entails a drastic drop of tensile properties, especially elongation at break (given in Figure 1). This property is particularly dependent on interfacial adhesion and decreases from more than 700% for PP108 to 60% for PP108/HDPE 80/20.

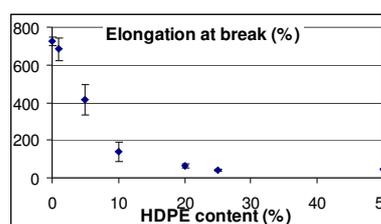


Figure1. Elongation at break of PP108/HDPE blends

So we could conclude that PP and HDPE are not compatible in these blends, despite the presence of EPR. So compatibilizing treatment is necessary.

Mechanical properties of compatibilized PP108/HDPE/mPE 76/19/5 blends were compared to those of PP108/HDPE 80/20 blends (Table 2). Great improvement of impact strength (50-100%) is obtained adding all mPE, due to the high ductility of these copolymers. In return, we could observe a decrease of yield stress and Young's modulus. Elongation at break increases weakly for all mPE, except E7467 and E8842. For these two copolymers, a great improvement is noticed : elongation at break increases from 64 to 339 and 253% respectively. Even if standard deviations are high (not shown here), we assume that it could be related to better interfacial adhesion.

Table2. Mechanical properties of reference blend PP108/HDPE 80/20 and compatibilized blends PP108/HDPE/mPE 76/19/5

Polymers	Young's modulus (MPa)	Yield stress (MPa)	Elongation at break (%)	Impact strength (kJ/m <sup>2</sup> )
reference blend PP108/HDPE	381	17.5	64	8.5
Ref. blend +				
E7380	364	15.9	96	13.3
E7447	355	16.0	87	14.1
E7467	337	16.7	339	14.3
E8003	366	15.2	72	19.2
E8100	364	14.6	95	12.7
E8200	372	14.5	92	16.6
E8407	379	14.2	88	14.4
E8842	335	15.7	253	18.5

We could notice that these two copolymers contain the highest content of comonomer (butene or octene). On the contrary, neither viscosity nor comonomer content of mPE are correlated to mechanical properties of compatibilized blends.

### 3.2 SEM observations

Figure 2 shows broken cross-sections of compatibilized blends with E7467 and E8200. No differences are observed between the both blends. We could notice that HDPE nodules are surrounded by voids in both cases. Voids correspond to mPE removed by heptane etching. No significant morphological difference could explain the best results obtained with E7467 and E8842.

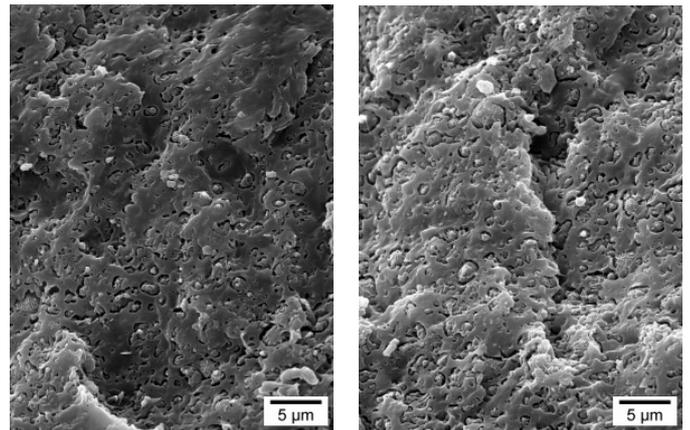


Figure2. SEM observations of compatibilized blends PP108/HDPE/mPE (E7467 and E8200) 76/19/5

### 3.3 Miscibility between polymers

To understand the best results obtained with E7467 and E8842, we carried out DSC analysis on binary blends 50/50.

#### 3.3.a HDPE/mPE and PP/mPE

Isothermal crystallization was performed on HDPE/mPE and PP108/mPE blends. Isotherm temperatures were fixed at 120 and 148°C respectively. Avrami parameters are  $n$  and  $K$ .  $n$  is related to the mechanism of nucleation and the crystal morphology.  $K$  depends on the crystallization rate. Small changes of these parameters could be noticed according to mPE (not shown here). Crystallization rate of PP is higher in blending with E8842 than E8003, due to the lowest content of comonomer for this last copolymer. Inverse influence is observed for the crystallization rate of HDPE.

Nevertheless, no great change of the PP or HDPE crystallization is observed. We could assume that none of mPE modifies the crystallization of the two main phases of the blends. This result is in agreement with literature and could not explain differences between the mechanical results obtained with E7467 or E8842 and with another mPE.

#### 3.3.b EPR and mPE

No interaction between PP, HDPE and mPE was observed. Nevertheless, there is a fourth polymer present in the blends : EPR copolymer at 22wt% in PP108. A part of EPR is probably formed by PE chains, as indicated by a melting peak at 117°C in PP108.

DSC scans of PP108/mPE 50/50 blends show that

EPR and mPE co-crystallizes partially. Two additional crystallization peaks could be pointed out in Figure 3 for the PP108/E7467 blend. In the same time, the crystallization peak corresponding to PE chains present in EPR disappears. The two additional peaks, at 46 and 72°C are observed for all PP108/mPE blends but their intensity could be weakly stronger for E7467 and E8842. This good compatibility between mPE and EPR could lead to the great mechanical performances observed previously.

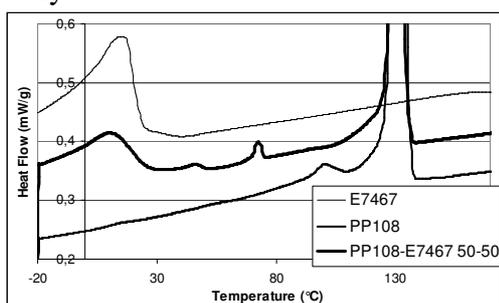


Figure 3. DSC scans of E7467, PP108 and PP108/E7467 50/50 during cooling ramp. Arrows indicate the two additional peak

To verify this last hypothesis, a blend PP/HDPE/E7467 76/19/5 was performed with a PP homopolymer which does not contain EPR (called PPH7060). The results are presented in Figure 4 and compared with those of PP108/HDPE/E7467 76/19/5.

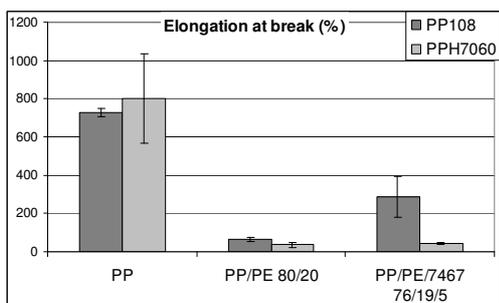


Figure 4. Elongation at break of PP, PP/HDPE 80/20 and PP/HDPE/E7467 76/19/5 with two PP

No significant improvement of elongation at break is observed with PPH7060. So, we could consider that the presence of EPR has a great impact on the compatibilization of PP and HDPE by mPE copolymer.

#### 4 CONCLUSIONS

This work deals with the possibility to compatibilize polyolefin blends adding a small content of metallocene copolymer ethylene- $\alpha$ -olefin. Great improvement of interfacial adhesion was performed

using some mPE. The best results were obtained with mPE containing the highest content of comonomer. On the contrary, viscosity or comonomer type have not revealed any effect.

Moreover, the presence of EPR could explain the good properties ; the miscibility between EPR and mPE assures a good compatibility.

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