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## Study Of Mechanical, Rheological And Morphological Properties Of Ternary Compatibilized Polyolefins/PA Blends



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### ABSTRACT

The effect of polyamide and reactive compatibilizer SEBS-MAH on morphology, melt rheological properties and impact strength was investigated for compatibilized polyolefin pre-blends. The blends were prepared by melt mixing using twin-screw extruder. PP/PE blends showed dispersed morphology. The addition of SEBS to the blends increased their viscosity and elasticity, and changed their morphology to a co-continuous structure. Morphology of compatibilized polyolefin/PA blends exhibited finer dispersion than that of the non-compatibilized blends, except for the composition 80%PA where a clear phase separation was observed. The impact strength presented a synergetic behavior with a maximum at 90%PA content. The predicted phase inversion composition according to Paul, Metelkin, and Utracki models for the compatibilized polyolefin/PA blends, was located at the 50%PA composition.

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### KEYWORDS

Blends;  
 Polyamide;  
 Polyolefins;  
 Compatibilizer;  
 Impact strength;  
 Rheology;  
 Morphology;  
 Phase inversion prediction.

### INTRODUCTION

Blend of polyolefins with polyamides (PA) are of high commercial interest. They are generally requested for their high thermal stability, good chemi-

cal resistance, excellent dimensional stability, and ease of processing. But polyamides are incompatible with polyolefins. Therefore, it is necessary to add a suitable reactive (compatibilizer) to ameliorate the interfacial properties, and to stabilize the

morphology against the coalescence<sup>[1-3]</sup>. To achieve a proper material design of multiphase polymer systems, such as blends and composites, the knowledge on their rheology and flow-induced structure development is indispensable. The efficacy of block copolymers in the compatibilization of immiscible polymer blends has been well established for several years, and has been proven through thermodynamic models and also experimentally. They are often known as interfacial agents, compatibilizers or emulsifying agents because of their tendency to locate at the blend interface, to prevent coalescence between minor phase particles, and to improve the adhesion between the phases<sup>[4]</sup>. The goal of compatibilization is to obtain a stable dispersion that leads to the desired morphologies and properties. Compatibilization can be achieved by many methods: addition of block copolymers (linear or star-shaped), or graft or random copolymers to the polymer blends, co-reaction within the blend to generate in-situ either copolymers or interacting polymers, cross linking of the blend ingredients, modification of homopolymers

a midblock of poly(ethylene-co-butylene) (EB) with a molecular weight of 37500 g/mol. Its density is 0.90 g/cm<sup>3</sup> and it is known to be a good compatibilizer for polyolefinic blends. Kraton FG 1901X, abbreviated as SEBS-g-MAH, is essentially a low molecular weight SEBS copolymer grafted with 2wt% maleic anhydride (MAH). Its density is 0.919 g/cm<sup>3</sup> and its polymeric styrene content is 28 wt%.

Before performing the processing and the rheological measurements, the polyamide, as well as the blends containing polyamide, was dried for a period of 16 hours at 65°C to remove absorbed water.

### Blend preparation

The polypropylene was mixed to polyethylene in equal amounts (50/50), with and without 10%SEBS. We have used the "b" symbol to indicate this particular composition. Thus b=PP/PE (50/50)+ 10% SEBS. The b/PA blend compositions based on weight percentage with 15%SEBS-MAH are presented in TABLE 1.

TABLE 1: Composition of b/PA+15% SEBS-MAH blends

Composition b/PA	100/0	90/10	80/20	60/40	50/50	40/60	20/80	10/90	0/100
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through incorporation of acid/base groups, hydrogen bonding groups and ionic groups, etc.<sup>[5]</sup>.

The aim of the present work is to determine the effect of compatibilizers on rheological, morphological, and mechanical properties of ternary polyolefins/PA blends.

## EXPERIMENTAL

### Materials

Polypropylene (PP) VESTOLEN P5000, high-density polyethylene (PE) LUPOLEN 6031M and the polyamide 66 (PA) DURETANE A30 were used in this study. The densities of PP, PE and PA were 0.902, 0.963 and 1.140 g/cm<sup>3</sup> respectively.

The compatibilizers used were two triblock thermoplastic elastomers from Shell: Kraton G1652 and Kraton FG 1901X. Kraton G1652 is a polystyrene-block-(poly(ethylene-stat-butylene))-block-polystyrene copolymer (SEBS), having polystyrene end blocks with a molecular weight of 7200 g/mol, and

### Processing

Test samples were prepared in the form of 100 mm long tensile bars (cross section of 6x4 mm) using an ARBURG 270S injection-molding machine. The melt and mold temperature were 270°C and 70°C, respectively, for the PA and the blends containing PA, and 250°C and 60°C for the polyolefins and their blends.

### Techniques

Melt rheological data were obtained through the use of an ARES rheometer in a parallel-plate geometry, in an oscillation mode, on properly dried pellets of melt-blended polymers. Frequency sweeps of 0.1—100 rad/s were performed at 270°C in a N<sub>2</sub> atmosphere. A strain of 5% was used, which was determined to be within the linear viscoelastic range.

The injection-molded specimens were broken cryogenically in liquid nitrogen, and the PA phase was extracted from the smooth surface of the blends by etching them with formic acid. After being sput-

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ter-coated with a thin film of gold, the specimens were examined in a LEO 435 VP Scanning Electron Microscopy (SEM).

The Izod impact resistance tests were performed using a CEAST apparatus, according to ASTM D 256-73 in notched samples at room temperature.

## RESULTS AND DISCUSSIONS

### Impact Resistance

The addition of 10% of the compatibilizer SEBS slightly improves the toughening of PP/PE binary blend, the impact strength value increasing from 6 to 9 kJ/m<sup>2</sup>. This improvement can be associated to the flexibility of the elastomeric middle block (ethylene-butylene) of the SEBS.

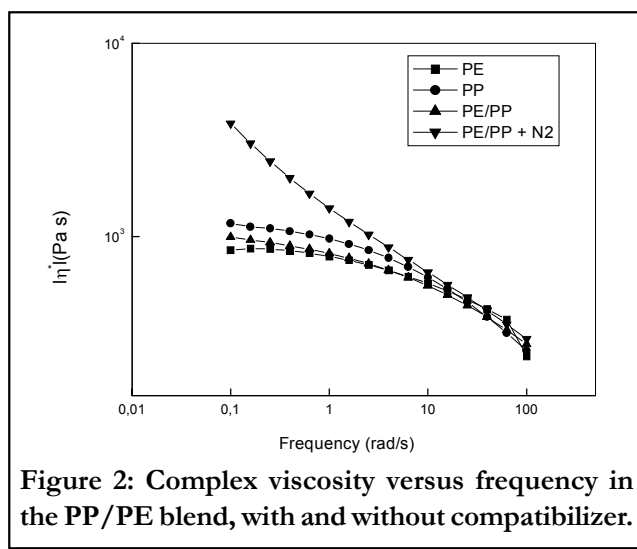
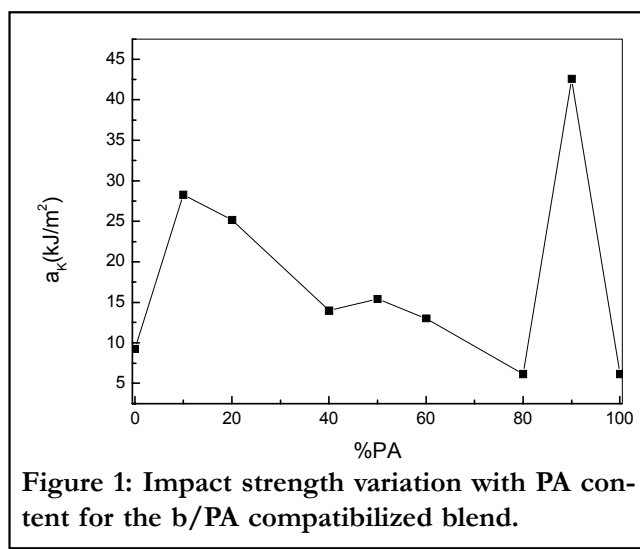
The impact strength value of the PA was found to be about 6 kJ/m<sup>2</sup>, similar to that of the b blend. The variation of the impact resistance with the PA content in the b/PA ternary compatibilized blend (Figure 1) presents a synergetic behavior, with a high maximum (43 kJ/m<sup>2</sup>) at the 90%PA composition and a minimum at 80%PA.

The SEBS-g-MAH seems to be a good impact modifier, through strong intermolecular interactions. The occurrence of chemical reactions between the carboxyl groups of the maleic anhydride and the amino end groups of the polyamide has been proposed for most of the blends, except for that containing 80%PA.

### Rheological study

Plots of the complex viscosity of the PP/PE (50/50) blends, with and without SEBS, versus frequency at 270°C (Figure 2), show that the viscosity of PE is lower than that of PP and both exhibit a Newtonian plateau. For a well "behaved" system, the viscosity of the blend should lie between those of homopolymers. This is clearly seen in the case of PP/PE blend. The addition of SEBS leads to a significant increase in the complex viscosity, especially at low frequencies. This is probably due to the rubbery nature of SEBS. The compatibilized blend behavior is considered to be linear viscoelastic. The compatibility can be achieved by the affinity that the middle block (EB) of SEBS presents towards the two homopolymers.

The variation of the complex viscosity with frequency for the b/PA blends (Figure 3) shows a viscoelastic behavior, and it can be seen that the viscosity increases when the frequency decreases and the PA content increases. This behavior indicates the existence of a yield stress not only in the SEBS-g-MAH compatibilizers, but also in the blends. The compositions containing 80 and 100%PA exhibit a Newtonian behavior. The storage modulus  $G'$  of the compatibilized b/PA blends is plotted against the frequency (Figure 4). In this figure  $G'$  increases with increasing frequency. The presence of the compatibilizer significantly increases  $G'$  for all the blends studied, except for the composition containing 80%PA. The curve in this last case is in between those of the pure components.



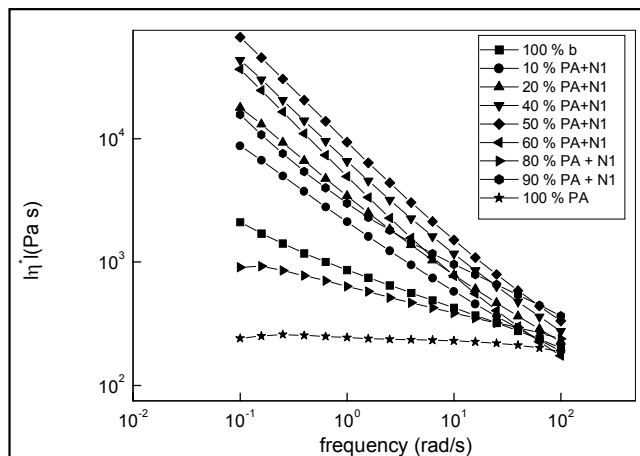


Figure 3: Complex viscosity versus frequency for the b/PA compatibilized blend

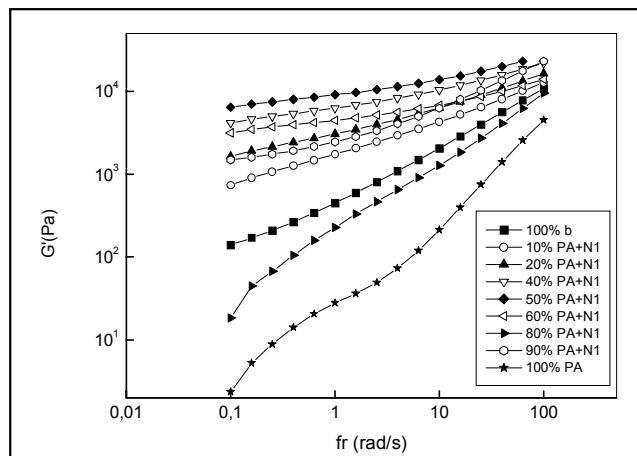


Figure 4: Storage modulus versus frequency for the b/PA compatibilized blend

In blends showing a viscoelastic behavior, the contribution of the elastic component is given by  $G'$  and that of the viscous component, by  $G''$ . Plots of  $\log G'$  versus  $\log G''$  illustrate the relative contribution of the  $G''$  respect to that of  $G'$ . The increase in  $G'$  could be attributed to the presence of entanglements in the compatibilized blend, as it has been demonstrated by Han<sup>[6]</sup>.

The change in the microstructure of the blends and the compatibility of the polymers could also be predicted from the variation of the  $G'$  versus  $G''$ <sup>[7]</sup>. The relationship between  $G'$  and  $G''$  is shown on figure 5. We observe that all the b/PA blends are positioned over a narrow range, except for the blend containing 80%PA. This means that the structures of these blends do not change significantly by increasing the amount of PA. The data also show that the blends are more elastic (storage modulus is  $G'$  is higher at equal  $G''$ ) than PA, b, and the blend containing 80%PA. According to some interpretations, the increase of storage modulus  $G'$  can be related to an elastic interfacial contribution from the dispersed phase, which depends on, both, the drop size and the volume fraction of this phase.

### Phase inversion prediction

There are several models to estimate which phase forms the matrix, by predicting the phase inversion composition. These models are based on the viscosity variation of the blends.

Assuming the validity of Cox-Merz rule, relating steady shear viscosity with the absolute value of complex viscosity<sup>[8]</sup>, the viscosity ratio ( $\eta_{PA}/\eta_b$ ) of 0.93 can be estimated at a mean shear rate of  $100s^{-1}$ .

In this study, three models, i.e., those of Paul<sup>[9]</sup>, Utracki and Metelkin<sup>[10]</sup>, were used for the phase inversion prediction in b/PA blends. The calculated values are summarized in TABLE 2.

For the b/PA blends, the phase inversion occurs when the volume ratio is equal to the viscosity ratio between the blend components. According to Paul, this relationship can be expressed by:

$$\eta_{PA} / \eta_b * \Phi_b / \Phi_{PA} = 1 \quad (1)$$

where  $\eta$  and  $\Phi$  denote the viscosity and volume fraction of the blend components, respectively.

The model proposed by Utracki includes the intrinsic viscosity  $[\eta]$ , and can be expressed by:

$$\Phi_b = (1 - \log(\eta_{PA} / \eta_b) / [\eta]) / 2 \quad (2)$$

TABLE 2: Predicted phase inversion composition according to the three models

Weight percent of PA (%PA)	10	20	40	50	60	80	90
Volume percent of PA ( $\Phi_{PA}$ )	0.082	0.17	0.35	0.45	0.54	0.76	0.88
$\eta_{PA} / \eta_b$ (Paul)	0.09	0.2	0.54	0.82	0.174	3.16	7.33
$\eta_{PA} / \eta_b$ (Utracki)	0.0258	0.0557	0.27	0.645	1.42	9.8	27.8
$\eta_{PA} / \eta_b$ (Metelkin)	0.2879	0.45263	0.73656	0.9051	1.085	1.8368	2.9698

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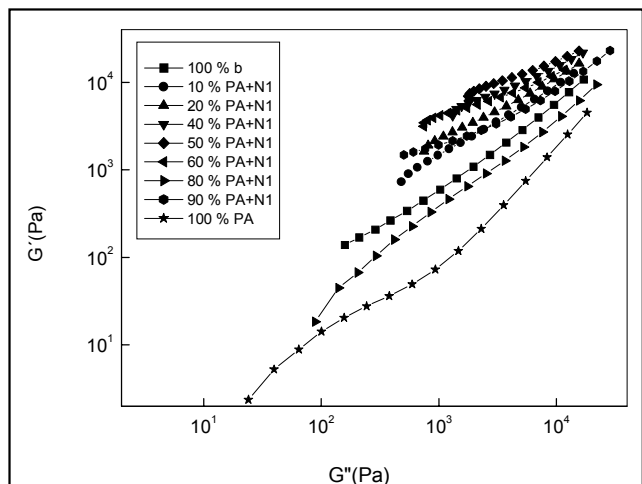


Figure 5: Storage modulus versus loss modulus for the b/PA compatibilized blend

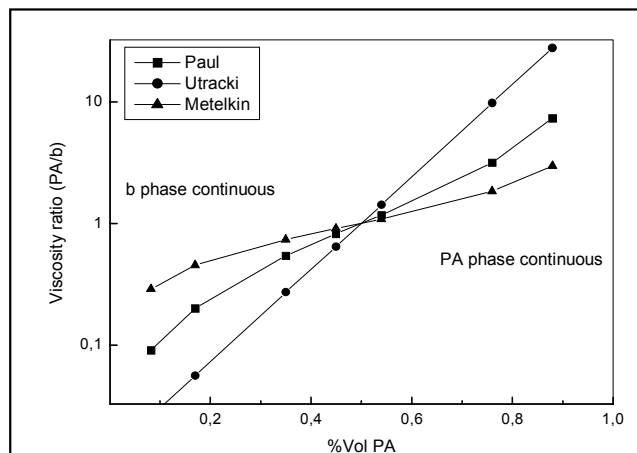


Figure 6: Phase inversion prediction in the b/PA compatibilized blend, according to the three models

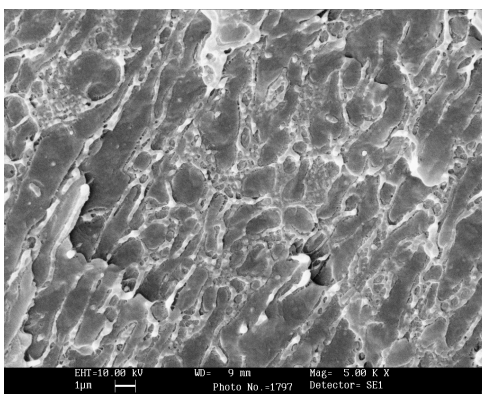


Figure 7: SEM micrograph of the cryofractured surface of PE/PP blend sample, without compatibilizer (scale 1  $\mu\text{m}$ )

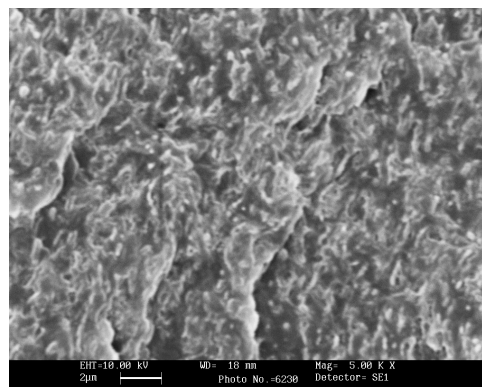


Figure 8: SEM micrographs of the cryofractured surface of PE/PP+10% SEBS blend sample (scale 2  $\mu\text{m}$ )

The intrinsic viscosity value was estimated equal to 1.9 for spherical domains.

The expression adapted to this system, according to Metelkin, can be written as:

$$\Phi_{PA} / \Phi_b = \eta_{PA} / \eta_b * F(\eta_{PA} / \eta_b) \quad (3)$$

According to Utracki, F is expressed as:

$$F(\eta_{PA} / \eta_b) = 1 + 2.25 \log(\eta_{PA} / \eta_b) + 1.81 [\log(\eta_{PA} / \eta_b)]^2 \quad (4)$$

Taking into account these models, the phase inversion prediction is found to be at a 50%PA composition (Figure 6).

### Morphological observations

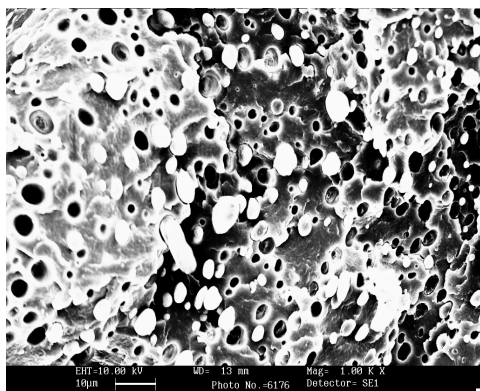
Figure 7 represents SEM micrograph of cryo-fractured surface of an injection-molded sample of PP/

PE (50/50) blend. It appears from the micrograph that the contrast is not good enough to distinguish between the two existing phases in the system. From the rheological measurements, it has been deduced that PE constitutes the continuous phase and PP the dispersed one.

The addition of the compatibilizer SEBS to the PP/PE leads to a significant change in the morphology of this blend (see figure 8). The dispersion of the minor phase is finer; and the system becomes more homogenous than in the same blend without compatibilizer.

The morphology of the compatibilized b/PA blends seems to be homogeneous in all composition, except for the blend containing 80%PA. The SEM micrograph of this later system (see figure 9) shows

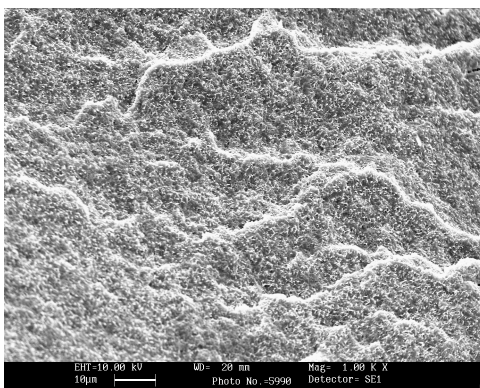
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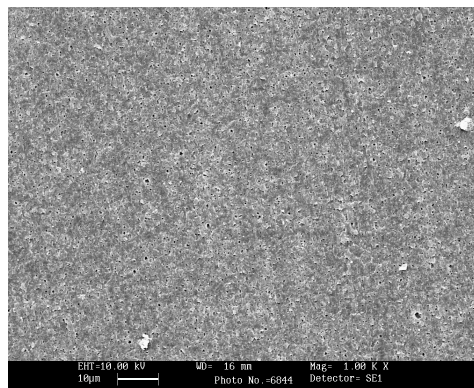
**Figure 9:** SEM micrograph of the cryofractured surface of b/PA(20/80)+15%SEBS-MAH blend sample (scale 10  $\mu\text{m}$ )

compatibilized blend. This separated phase morphology explains the low values obtained in rheology and impact strength tests for this composition.

For the rest of compositions, the system is more homogeneous, indicating a reduction of the interfacial tension and an increase of the phase adhesion (see figure 10a, 11a, 12a and 13). The morphology of the etched surface of these blends appears coarse co-continuous, with a regular distribution of PA particles having diameters of 0.3 to 0.8  $\mu\text{m}$ , see, for example, figure 11b corresponding to the b/PA (50/50) blend. Particle size is significantly reduced, and it changes in dependence on PA concentration (see figure 10b, 11b and 12b). The presence of the compatibilizer influences the particles dimension and

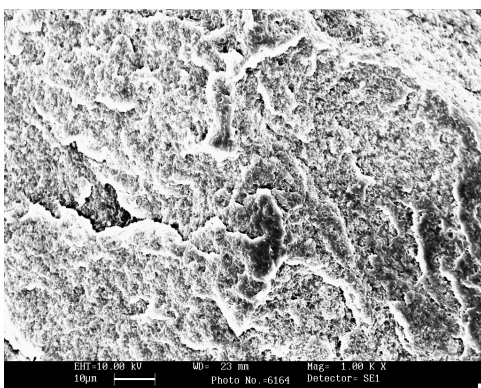


(a)

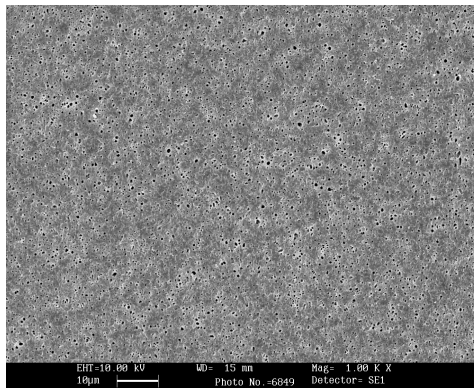


(b)

**Figure 10:** SEM micrograph of the cryofractured (a) and etched (b) surface of b/PA(60/40)+15%SEBS-MAH blend sample (scale 10  $\mu\text{m}$ )



(A)



(b)

**Figure 11:** SEM micrograph of the cryofractured (a) and etched (b) surface of b/PA(50/50)+15%SEBS-MAH blend sample (scale 2  $\mu\text{m}$ )

two phases clearly distinguished: a continuous one associated to the PA, and a great number of large and non-uniform dispersed particles having diameter from 2 to 8  $\mu\text{m}$ , associated to the polyolefin

the dispersion homogeneity in the matrix, favoring a better interfacial adhesion. Therefore, there are no evident holes on fracture surface caused by detachment.

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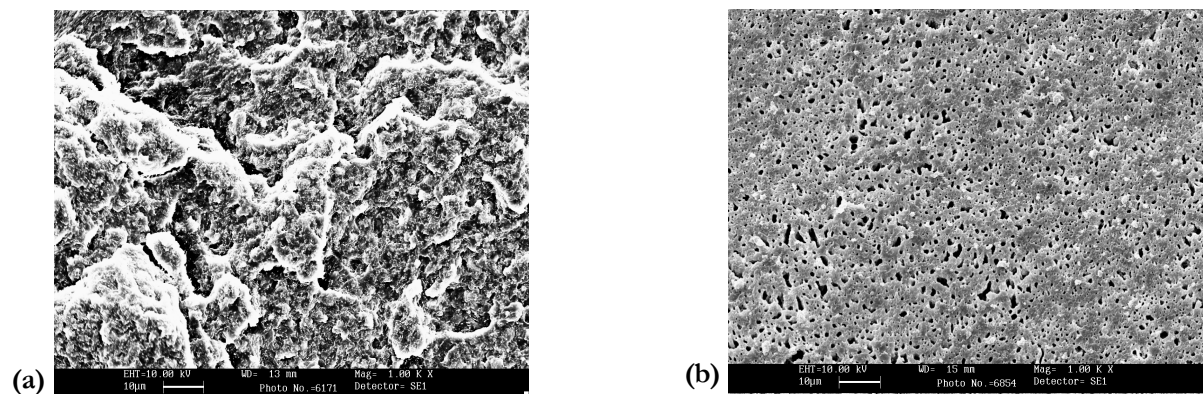


Figure 12: SEM micrograph of the cryofractured (a) and etched (b) surface of b/PA(40/60)+15%SEBS-MAH blend sample (scale 10 µm)

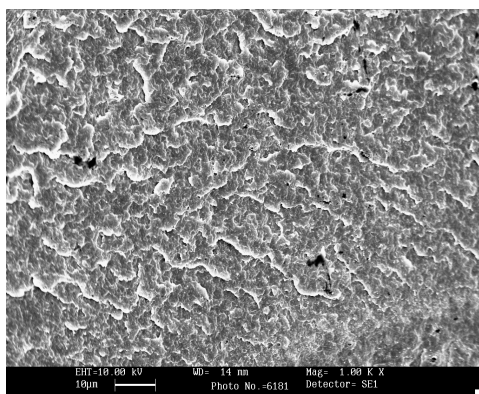


Figure 13: SEM micrograph of the cryofractured surface of b/PA(10/90)+15%SEBS-MAH blend sample (scale 10 µm)

The morphology was successfully correlated with the impact strength for all the blends investigated.

### CONCLUSIONS

The impact strength was improved with SEBS-g-MAH compatibilizer.

A maximum value was obtained for the blend containing 90%PA.

The increase in viscosity at low frequencies indicates the existence of a co-continuous structure. This structure seemed to be connected with the yield stress of the compatibilizer due to its elastomeric component. Most of the blends investigated are more elastic than PA and compatibilized polyolefin blend.

Interactions between the blend components were evident in the blend morphology of the samples studied.

Phase separation morphology was observed in the blend containing 80%PA.

Phase inversion composition according to the three models of Paul, Utracki, and Metelkin was located at a 50%PA content.

### ACKNOWLEDGMENTS

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