

Blend Compatibilizers Based on Silane- and Maleic Anhydride-Modified Polyolefins

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ABSTRACT: Polypropylene (PP)/polyamide blends were compatibilized with PP modified with vinylsilane or maleic anhydride and ethylene-propylene random (EPR) copolymer modified with maleic anhydride. The thermal behavior, mechanical properties, and morphology of the blends were investigated. Thermal analysis showed that the polyamide crystallization temperatures shifted downward with all compatibilizers, whereas its melting behavior did not change. On the other hand, polypropylene crystallization temperatures shifted upward in all cases, except for blends

containing EPR modified with maleic anhydride. Tensile strength and elongation at break increased for blends compatibilized with modified PP. Blends containing up to 7% of EPR modified with maleic anhydride did not show good yield stresses. The morphology of the blends showed a finer dispersion of the polyamide minor phase in the PP matrix. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2492–2498, 2003

Key words: blends; compatibilization; polyamides; poly(propylene) (PP); thermal properties

INTRODUCTION

Polymer blending has been widely used as an alternative to improve the properties of commercial polymers. Polypropylene (PP) and polyamide (PA) blends may offer a wide range of desirable characteristics when properly compatibilized. These blends combine PA's high strength and excellent resistance to organic liquids, heat, abrasion, and wear with PP's moisture resistance, high elongation at break, and low cost.¹ However, because these polymers are thermodynamically immiscible, their blends usually lead to multiphase systems whose properties depend largely on the mutual dispersion of the components. In general, the desired properties are achieved only with the addition of a compatibilizing agent that improves the interfacial adhesion and the phase dispersion.

In 1974, Ide and Hasegawa² showed that addition of PP modified with maleic anhydride (MA) caused a significant reduction in the phase size of dispersed particles in PP/PA blends containing 20 wt % of polyamide-6 (PA-6). These results were followed by enhancements in tensile strength, elongation at break, and impact strength. They proposed a chemical linkage among functional groups from the modified poly-

olefin and the terminal amino groups of the polyamide.

Since then, numerous works reported compatibilization effects through the addition of PP functionalized with MA, acrylic acid, or carboxylic acid groups.^{3–6} Apart from the more homogeneous morphology, changes in thermal behavior were reported for compatibilized blends. Marco et al.⁷ showed that increasing the concentration of the compatibilizing agent caused a reduction in the associated crystallization enthalpy of the polyamide and a reduction in the nucleating effect of the polyamide with respect to the matrix phase.

Recently, new functional molecules have been used as PP modifiers by means of radical reactions. Among these, itaconic acid,⁸ glycidyl methacrylate,⁹ and vinylsilanes^{10–12} have been studied. PP molecules usually show chain-scission reactions during functionalization, leading to polymers with lower molecular weights. The modified PP can be used as a blend compatibilizer.

Other modified polymers have been cited as compatibilizers for polyamide/polypropylene blends during the last few years, such as ethylene-propylene-diene copolymers (EPDM), styrene-ethylene-butylene-styrene block copolymers (SEBS), and ethylene-vinyl acetate copolymers (EVA) modified with maleic anhydride.^{13–16}

The purpose of this work was to compare the compatibilizing effect of three distinct agents in PP/PA blends. Two compatibilizers were based on PP modified with either maleic anhydride (PP-MA) or vinyl-

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triethoxysilane (PP-VTES) and the third was an ethylene-propylene copolymer (EPR-MA) modified with maleic anhydride.

EXPERIMENTAL

Materials

Polypropylene, highly isotactic [melt index (MI) = 15.4 g/10 min (230°C; 2.16 kg)], was obtained from OPP Química (Brazil); ethylene-propylene random (EPR) copolymer (55 wt % ethylene, low molecular weight) was from DSM Elastomers (Brazil); polyamide-6 [PA-6, MI = 6.6 g/10 min (230°C; 2.16 kg)] was from Companhia De Millus S.A. (Brazil); maleic anhydride, 99.5%, was from Produtos Químicos Elekeiroz S.A. (Brazil); vinyltriethoxysilane (Silan GF 56) was from Wacker (Germany); and dicumyl peroxide 70% was from Aldrich Chemical (Milwaukee, WI); all materials were used as received.

Polymer modification and blending procedures

The reactions of modification and blending were performed in a mixer chamber Rheomix 600p (Haake, Germany), previously saturated with argon, equipped with two corotating rotors, at 50 rpm.

The chemical modifications of PP with maleic anhydride and vinyltriethoxysilane were described elsewhere.^{11,17} Reactions of EPR with MA were performed at 170°C.¹⁷

For blending experiments, all components were pre-mixed with an antioxidant (Irganox B215, 0.15 wt %; Ciba, Summit, NJ). They were processed at 240°C for 5 min. At the end, products were pressed at 180°C, 2.5 kN, for 2 min.

Characterization

Thermal analyses were performed in a Perkin-Elmer DSC-4 calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT). Blend samples were heated to 260°C, at 10°C/min, held at that temperature for 5 min, then cooled to 40°C at -10°C/min, to eliminate thermal history. The melting and crystallization behaviors were taken from the second heating and cooling cycles. Crystallinities were calculated using an extrapolated value of enthalpy corresponding to the melting of 100% crystalline samples ($\Delta H_{PP} = 207 \text{ J/g}^{18}$; $\Delta H_{PA-6} = 109 \text{ J/g}^{19}$).

Tensile tests were performed in a Wolpert machine (Karlsruhe, Germany) at 2 mm/min, 500 N, room temperature. Specimens were cut from samples prepared in a Carver press (Wabash, IN). Reported data are the results of an average of about 10 measurements.

TABLE I
Compatibilizing Agents (CA) and Their
Functionalization Degree (F)

CA	Polymer	Modifier	F (wt %)
PPMA 0.20	PP	MA	0.20
PPMA 0.70	PP	MA	0.70
PPVTES 0.77	PP	VTES	0.77
PPVTES 3.04	PP	VTES	3.04
EPR 0	EPR	—	0
EPRMA 0.19	EPR	MA	0.19
EPRMA 0.71	EPR	MA	0.71

The morphology of the blends was determined by scanning electron microscopy using a JEOL microscope (JSM 5800 model, JEOL, Peabody, MA) operating at 10 kV. Samples were prepared by fracturing the blends under liquid nitrogen, and the fractured surfaces were gold coated.

Melt flow indices were obtained in a Ceast equipment, Junior Model, 2.16 kg/10 min, at 230°C.

RESULTS AND DISCUSSION

Table I provides information about the compatibilizing agents (CA) used in the blends. All blends contained 30 wt % of polyamide-6 and variable amounts of PP and CA, as shown in Table II. Crystallization temperatures (T_c) and degrees of crystallinity (X_c) are also shown.

Thermal analyses

The cooling thermograms of PP and PA-6 homopolymers and of the binary blend are shown in Figure 1. It may be observed that the uncompatibilized blend (curve c) shows two exothermic peaks, indicating that PP and PA-6 did not cocrystallize.

One can observe that the crystallization temperature of the PP component shifted to a higher temperature because of the nucleating effect of the crystallized PA, as described elsewhere.^{7,20}

PA-6 is known to have two crystalline forms,²¹ with more perfect crystals obtained at higher temperatures. By cooling PA-6 at an intermediate cooling rate²² (e.g., 10°C/min), two crystallization peaks may be seen. Thus, the crystallization exotherm of PA-6 homopolymer showed a peak at 169°C, with a shoulder at about 183°C (Fig. 1, curve b). In the binary blend the PA-6 component showed only one crystallization peak (the one at the higher temperature, 183°C).

The exotherm peaks of PP and PA-6 in the blends containing EPR were similar to those of the binary blend, indicating that EPR homopolymer did not interact with these components. However, addition of any modified EPR or PP to the blends changed PA-6

TABLE II
Composition and Thermal Properties of Polypropylene/Polyamide Blends

CA	CA (wt %)	PP (wt %)	PA-6 (wt %)	T_c PP (°C)	X_c PP (%)	T_{c1} PA-6 (°C)	T_{c2} PA-6 (°C)	X_c PA-6 (%)
—	—	100	—	113	58	—	—	—
—	—	—	100	—	—	169	185	28
—	—	70	30	118	53	—	183	28
PPMA 0.20	4	66	30	121	63	154	—	38
PPMA 0.20	7	63	30	121	64	155	—	38
PPMA 0.70	4	66	30	120	58	157	—	37
PPMA 0.70	7	63	30	120	63	152	—	35
PPVTES 0.77	4	66	30	119	56	158	181	30
PPVTES 0.77	7	63	30	119	58	168	182	33
PPVTES 3.04	4	66	30	118	58	165	181	34
PPVTES 3.04	7	63	30	119	59	162	180	31
EPR 0	4	66	30	118	55	—	184	30
EPR 0	7	63	30	119	56	—	184	28
EPRMA 0.19	4	66	30	113	57	161	184	36
EPRMA 0.19	7	63	30	113	52	163	183	37
EPRMA 0.71	4	66	30	112	54	157	—	36
EPRMA 0.71	7	63	30	114	53	161	—	33

crystallization behavior. Thermograms of these blends showed that polyamide crystallized in a wider temperature range and its crystallization peaks shifted to lower temperatures when modified polyolefins were added (Figs. 2–5). This behavior has been reported for several PP/PA compatibilized blends.^{7,23} These effects could be explained in terms of a fractionated crystallization process attributed to the large number and small size of dispersed nylon particles.²⁴ Chemical or physical interactions between the compatibilizer and the PA component could also explain this behavior,

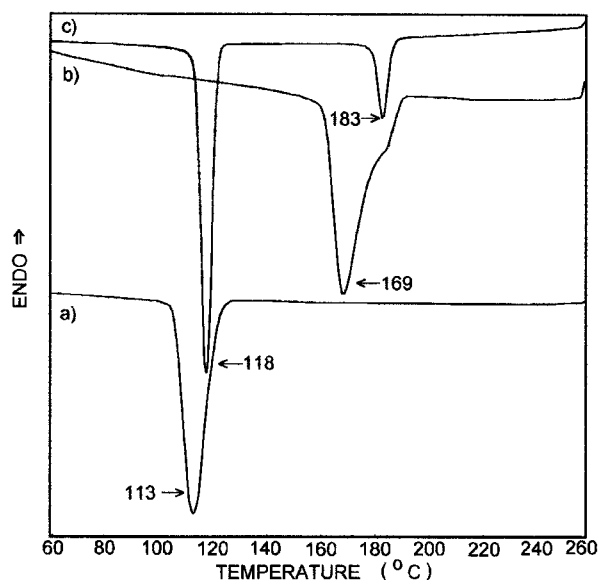


Figure 1 Cooling thermograms: (a) PP; (b) PA-6; (c) PP/PA-6 blend (70/30).

given that they could reduce the segmental motion of PA molecules, thus hindering the crystallization process. In this sense, the use of PP modified with MA showed the greatest effect on the polyamide crystallization behavior (Fig. 2), probably because of the formation of PP grafts on the polyamide chains. The crystallization temperature of polyamide showed a more slight decrease in blends containing EPR modified with MA (Fig. 3), suggesting a poorer compatibilizing effect.

Cooling thermograms of blends compatibilized with PP modified with VTES showed two well-separated PA-6 crystallization peaks, whose relative areas varied with the degree of silane incorporated into the

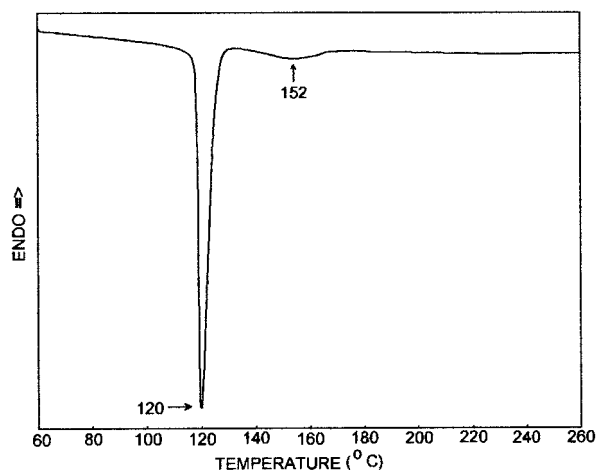


Figure 2 Cooling thermogram of the blend PP/PA-6/PPMA 0.70 (63/30/7).

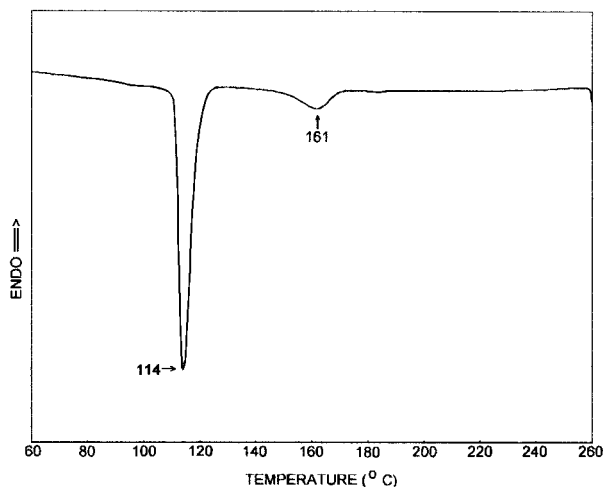


Figure 3 Cooling thermogram of the blend PP/PA-6/EPRMA 0.71 (63/30/7).

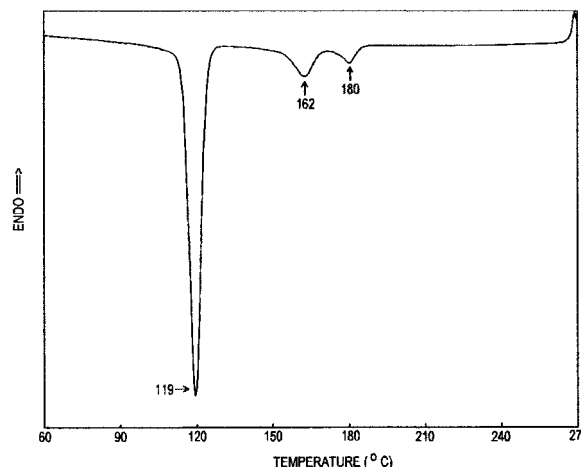


Figure 5 Cooling thermogram of the blend PP/PA-6/PPVTES 3.04 (63/30/7).

PP chains (Figs. 4 and 5). Recent work²⁵ showed that organosilanes could form adducts with compounds containing electron-donor groups. These unstable complexes were formed through interactions between the silicon atoms and the electron-donor groups. Amino and carbonyl groups formed the strongest adducts. This kind of interaction could explain the compatibilizing effect of PP modified with silane in our blends, attributed to the presence of amino and carbonyl groups in the polyamide. However, new studies should be conducted to investigate this interaction.

The crystallization temperature of polypropylene was higher than that of the pure homopolymer in almost all compatibilized blends, except when EPR modified with maleic anhydride was employed as compatibilizer. Although the interaction between

modified PP and the polyamide favored the formation of nucleating sites for the PP component, it is believed that grafting EPR onto polyamide chains could reduce this nucleating action because of the flexibility of the grafted EPR chains.

Whereas the enthalpy associated with the crystallization of polyamide was clearly dependent on the kind of compatibilizer (in addition, it diminished when compared with the pure polyamide), the melting behavior of polyamide in the blends was always very similar (Fig. 6). The heating thermograms of the blends showed well-defined endothermic peaks from PP and PA-6. Moreover, the degrees of crystallinity determined from the enthalpies of fusion indicated an increase in PA-6 crystallinity in compatibilized blends

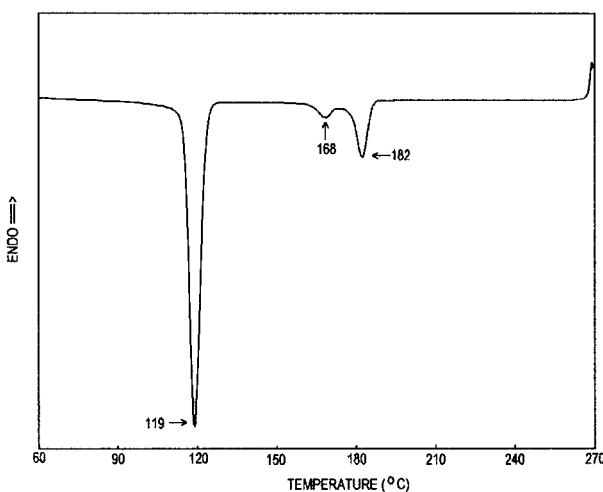


Figure 4 Cooling thermogram of the blend PP/PA-6/PPVTES 0.77 (63/30/7).

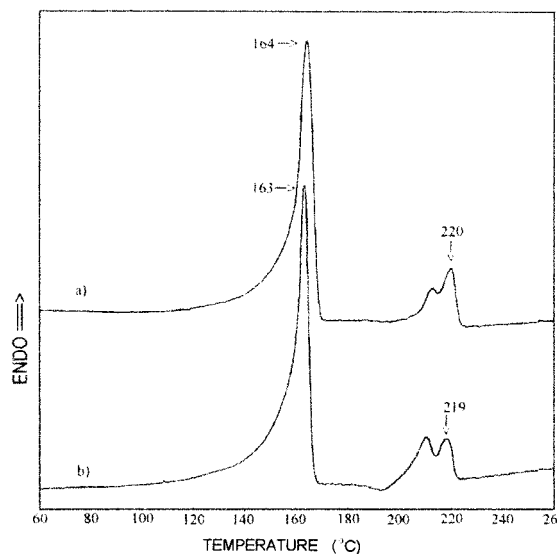


Figure 6 Heating thermogram of the blends: (a) PP/PA-6 (70/30); (b) PP/PA-6/PPMA 0.70 (63/30/7).

TABLE III
Mechanical Properties of PP/PA-6 Blends^a

CA	CA (wt %)	Yield stress (MPa)	Elongation at break (%)	MI (g/10 min)
—	—	96.2 ± 18.6	4.1 ± 0.9	14.4
PPMA 0.20	4	238.1 ± 17.0	11.0 ± 1.3	9.6
PPMA 0.20	7	264.2 ± 23.8	11.2 ± 2.3	8.6
PPMA 0.70	4	251.5 ± 17.4	11.2 ± 1.6	8.4
PPMA 0.70	7	263.9 ± 9.9	15.8 ± 1.6	10.4
PPVTES 0.77	4	158.8 ± 12.5	4.9 ± 0.8	19.9
PPVTES 0.77	7	177.2 ± 46.5	6.3 ± 3.3	17.7
PPVTES 3.04	4	134.3 ± 42.4	3.6 ± 1.2	21.8
PPVTES 3.04	7	143.8 ± 12.2	4.0 ± 1.1	22.2
EPR 0	4	139.2 ± 9.9	6.5 ± 1.3	16.2
EPR 0	7	142.3 ± 8.8	6.9 ± 1.3	16.2
EPRMA 0.19	4	108.7 ± 9.9	7.5 ± 2.5	11.9
EPRMA 0.19	7	77.6 ± 8.1	8.6 ± 3.0	—
EPRMA 0.71	4	130.4 ± 8.7	6.4 ± 1.0	10.1
EPRMA 0.71	7	80.2 ± 11.6	6.0 ± 1.2	10.0

^a Composition: PP/PA-6/AC. PA-6 = 30 wt %.

with respect to the homopolymer and the uncompatibilized blend (Table II).

Mechanical properties

Table III shows results from tensile tests. It can be seen that blends compatibilized with PP-MA showed the greatest tensile strength among all the blends (Fig. 7). They had the highest elongation at break, indicating good adhesion between the phases. High yield stresses were also observed for blends compatibilized with PP-VTES, even though the yield stress and the elongation at break were not as good as for the PP-MA compatibilized blends. These observations indicated that in the last cases adhesion between phases was weaker or less efficient.

Yield stresses did not increase in all cases for blends compatibilized with EPR-MA. Although one could expect a good interaction between EPR-MA and PA-6,

the results greatly varied with concentration and kind of EPR-MA. Yield stresses decreased when 7 wt % of EPR-MA was used. These results indicated that, although polyamide and compatibilizer could show a good interaction, the adhesion with the PP phase did not necessarily increase. This probably happened as a result of the dissimilarities between PP and EPR. However, it was observed that elongation at break was improved in these systems compared to that of the binary blend, probably because of the elastomeric characteristics of the EPR.

Melt behavior

The melt index values determined are shown in Table III. The use of compatibilizers modified with MA decreased the melt indices of the blends probably attributable to the strong interactions between the compatibilizer and the PA-6 phase. Meanwhile, blends compatibilized with PP-VTES showed the highest melt indices. Blends containing nonmodified ethylene-propylene copolymer showed a MI slightly higher than

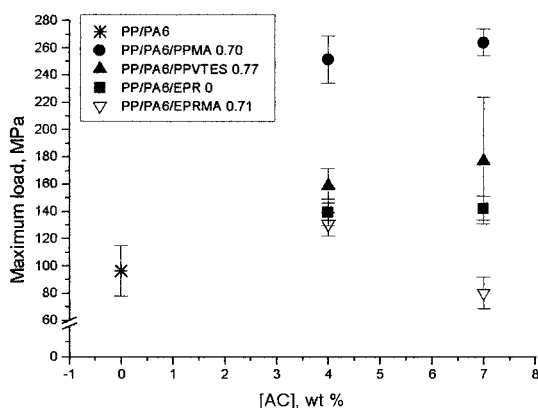


Figure 7 Maximum load of the blends.

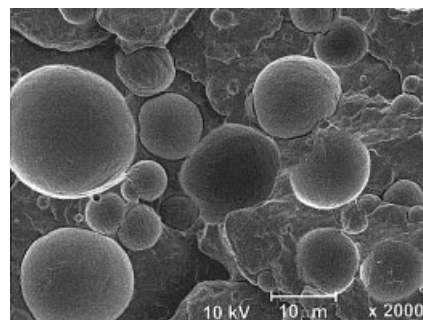


Figure 8 SEM micrograph of PP/PA blend (70/30).

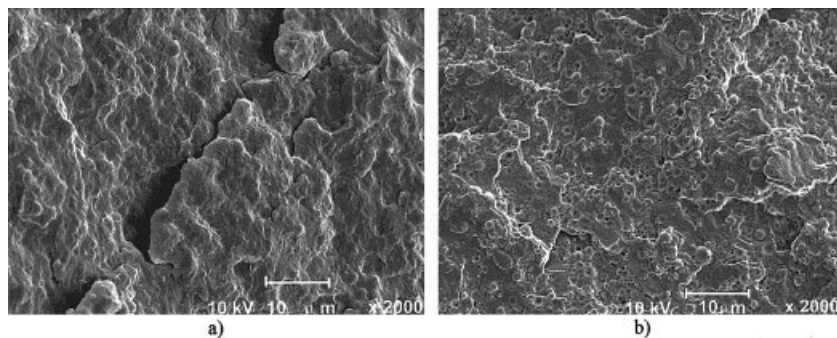


Figure 9 SEM micrographs: (a) PP/PA/PPMA 0.70 (63/30/7); (b) PP/PA/EPRMA 0.71 (63/30/7).

that of the binary blend. In these cases the low molecular weight EPR probably acted as a plasticizer.

Morphology

The effect of each compatibilizer was clearly observed in the morphology of the blends. In the uncompatibilized blend the minor PA-6 component was readily observable as spherical particles dispersed in the PP matrix (Fig. 8). These particles were notably heterogeneous in size. More homogeneous systems were obtained when PP and EPR modified with MA were used as compatibilizers (Fig. 9a, b). A finer dispersion of the polyamide phase was observed, showing the interfacial action of the new components. According to Ide and Hasegawa,² a reaction between anhydride groups from the modified polyolefin chains and the terminal amino groups from PA-6 could form polyolefin-polyamide block copolymers. Such copolymers could explain the compatibilizing effect.

When PP modified with silane was used as the third component, the PA-6 particles underwent a reduction in size compared with that of the binary blend (Fig. 10a, b), although this reduction was less effective than that promoted by MA-modified polyolefins. The particle size reduction effect was more pronounced when the PP-VTES concentration increased. On the other hand, increasing the degree of functionalization did

not reduce the particle size, provided that the same PP-VTES concentration was used.

The addition of EPR without chemical modification did not show changes in blend morphology, indicating no compatibilizing effect.

CONCLUSIONS

PP and EPR modified with maleic anhydride and PP modified with vinyltriethoxysilane showed a compatibilizing effect in PP/PA-6 blends containing 30 wt % of polyamide. Thermal analysis showed that polypropylene and polyamide crystallized separately and that interfacial agents changed the crystallization behavior of the components of the blends.

All systems became morphologically more homogeneous, with a finer dispersion of the polyamide phase after addition of compatibilizers.

PP-MA proved to be the best interfacial agent within those used, in that it reduced polyamide particles to a greater extent and produced blends with the highest tensile strength. EPR-MA affected polyamide particle sizes more than did PP-VTES; however, the mechanical properties of their blends were inferior, probably because of the characteristics of the EPR component by itself.

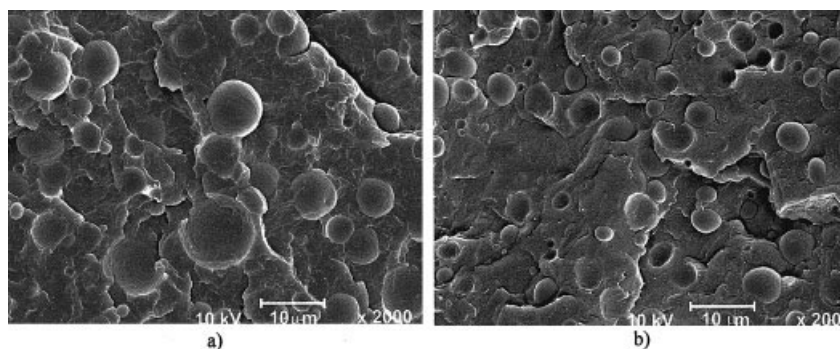


Figure 10 SEM micrographs of PP/PA/PPVTES 0.77: (a) 66/30/4; (b) 63/30/7.

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