Compatibility Study of Polypropylene and Acrylonitrile Butadiene Rubber Blends

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ABSTRACT: Blends of polypropylene (PP) and acrylonitrile butadiene rubber (NBR) were prepared with different weight compositions with a plasticorder at 180°C at a rotor speed of 60 rpm for 8 min. The physicomechanical properties and mass swell of the prepared blends were investigated with special reference to the effects of the blend ratio. The prepared epoxidized linseed oil (EL) (i.e., $E_{0.5}L$, E_1L, $E_{1.5}L$, and E_2L using 0.5, 1, 1.5, and 2 mol H_2O_2/mole of unsaturation in linseed oil) and maleic acid anhydride (MAH) were melt mixed in various contents (i.e., 1, 5, 10, and 15 wt %) with a PP/NBR blend with a weight ratio of 70/30 and used as compatibilizers. The effect of the compatibilizer contents on the physicomechanical properties and mass swell of the binary blend was investigated. With an increase in the compatibilizer content up to 10 wt %, the blend showed an improvement in the physicomechanical properties and reduced mass swell in comparison with the uncompatibilized one. The addition of a compatibilizer beyond 10 wt % did not improve the blend properties any further. The efficiency of the compatibilizers (10 wt %) was also evaluated by studies of phase morphology (scanning electron microscopy). © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2056–2061, 2010

Key words: polypropylene (PP); acrylonitrile butadiene rubber (NBR); compatibility; physicomechanical properties; scanning electron microscopy (SEM); mass swell

INTRODUCTION

The simple blending of a crystalline thermoplastic and elastomeric polymer results in a new class of material termed a thermoplastic elastomer (TPE). The properties of the resultant TPE will be derived from the properties of each of the two polymers and dependent on the composition and the interaction between their phases. However, most TPE blends are immiscible and usually exhibit phase-separated morphology and poor interfacial adhesion between the phases.[1] These problems could be alleviated by the addition or *in situ* formation of compatibilizers or interfacial agents.[2] This phenomenon generally results in an improvement in compatibilization of the blend.

TPEs based on polypropylene (PP)/NBR combine the oil resistance and elastic properties of NBR as well as excellent chemical and moisture resistance, good ductility and stiffness, low density, and easy processing characteristics of PP. They can be successfully used for heat and oil resistance applications.[3] However, PP and NBR are highly incompatible because of poor physical, mechanical, and chemical interactions across the phase boundaries.[4] Several compatibilizing systems for PP/NBR have been studied and reported by many researchers.[3–8] George et al.[5–7] have investigated in detail and reported the effect of phenolic-modified PP and maleic-modified PP as compatibilizers on the properties of PP/NBR. Xiangfu et al.[9] have used glycidyl methacrylate-grafted PP/amino compound as a compatibilizer in their study on dynamically vulcanized NBR/PP and found that the modification of PP-based compatibilizer with amino compounds significantly increases the mechanical properties of the PP/NBR blend. Ismail et al.[10] have tested epoxy resin as a compatibilizing agent for PP/recycled acrylonitrile butadiene rubber (NBRr).

The aim of this work is the potential utilization of epoxidized linseed oil and maleic acid-modified PP as compatibilizers for PP/NBR blend and systematically investigates their effect on the compatibilization, physicomechanical properties, mass swell, and morphology of the blend samples.

EXPERIMENTAL

Materials

PP (isotactic) [Moplen EP-D60R, product of Montell Polyolefins, Italy] with a melt flow index = 0.35 g/

TABLE I
Characteristics of the Prepared Epoxidized Linseed Oil Samples

Sample	Epoxy group content[13] (equiv/100 g)	Hydroxyl group content[14] (equiv/100 g)	Total iodine value[15]
$E_{0.5}L$	2.8	6.4	141
E_1L	5.4	10.7	109
$E_{1.5}L$	7.2	26.5	70
E_2L	5.1	28.1	76

10 min (230°C, 2.16 kg). NBR was purchased from Bayer, Fiber Organic and Rubber Division, Germany, with CN content = 40%, density = 980 kg/m³, and Moony viscosity ML_4 100°C = 50 ± 5 L was supplied by Tanta of Flax and Oil, Egypt, with density = 931–936 kg/m³, saponification value = 188, iodine value = 177, and free fatty acids 2%. MAH was obtained from El-Nasr Pharmaceutical of Chemicals with melting point of 54–56°C and boiling point of 200°C.

Methods

Synthesis of epoxidized linseed oil EL

Epoxidation process was occurred using peracetic acid formed *in situ.* Linseed oil (1 L) solution (876 g, 6.27 mol) in *n*-hexane (220 g) was mixed with 22.5% H_2O_2 (405.5, 811, 1216.5, and 1622 mL) showing different moles of 0.5, 1, 1.5, and 2 per each mole of unsaturated linseed oil. Glacial acetic acid (286.4 mL, 3.13 mol) was dropped for 3 h with stirring at 25°C. The experiment was carried out according to the method described in Refs. 11 and 12. Characteristics of the prepared epoxidized linseed oil samples (i.e., epoxy group content,[13] hydroxyl group content,[14] and total iodine value[15]) are given in Table I.

Melt processing

PP/NBR blends of various weight compositions with and without compatibilizers were prepared with a Brabender plasticorder (PL 2100, 350S). EL (i.e., $E_{0.5}L$, E_1L, $E_{1.5}L$, and E_2L) and MAH were used as compatibilizers in various contents (i.e., 1, 5, 10, and 15 wt %). At the start, PP was introduced into the Brabender plasticorder preheated to 180°C for 2 min, the tested compatibilizer was incorporated, and NBR was added thereafter. The mixer was operated at 180°C; the rotor speed being maintained at 60 rpm for 6 min. The molten mix was quickly removed from the Brabender plasticorder and was subsequently passed through a two-roll mill (outside distance = 470 mm, working distance = 300 mm, speed of slow roll = 24 rpm, and a fraction ratio = 1.4 : 1). The blends were removed and subsequently

compressed in an electrically heated hydraulic press at about 150°C for 5 min into thin sheets about 1-mm thick, and from these, test specimens were papered. Upon using MAH, benzoquinone (0.75 parts) and dicumyl peroxide (3 parts) were added in a Brabender plasticorder at 180°C with the above mentioned technique[5,16] giving maleic acid-modified PP (MA-PP) as a compatibilizer.

Property evaluation

The tensile strength (σ_R), elongation at break (ε_R), and young's modulus (E) were determined with a universal tension testing machine (type M-10 Hunge Ta Instruments). The compressed sheets were cut into dumbbell-shaped specimens with appropriate punching dies with a width of 4 mm (DIN 53504 STABIN^EF). The specimens, with a width of 4 mm, a neck length of 50 mm, a thickness of 1–1.5 mm, were tested at a crosshead speed of 50 mm/min.[17] The hardness of test specimens at least 6-mm thick was measured with shore A durometer (PTC instrument of Model 306L[18]). Mass swell percentages of the test pieces were carried out in the benzene/acetone solvent mixture. About 0.1–0.2 g of each specimen (square test pieces with 5-mm dimensions and 1-mm thick) was weighed in a weighing bottle, which was covered with benzene/acetone solvent mixture 50/50 for 24 h. The swollen samples were weighed and then dried in an oven to a constant weight. The last weight was taken as the correct weight of the sample free from dissolved matter. The mass swell percentages Q of the samples were calculated as follows:

$$Q = [(m - m_o)/m_o] \times 100,$$

where m and m_o represent the weights of the samples after swelling and original one, respectively.[19] All these tests were performed at room temperature (25°C ± 1°C), and the reported results were averaged from a minimum of five specimens.

The Fourier transform infrared (FTIR) spectra were obtained using a Perkin-Elmer 2000 series instrument. The spectrum resolution was 4 cm⁻¹, and the scanning range was from 600 to 4000 cm⁻¹. The surface topography of the samples was analyzed by scanning electron microscopy (SEM). The samples were sputter coated with gold (JEOL-JFC-1100E ion sputtering device) and examined in a JEOL JSM-5400 scanning electron microscope (Japan).

RESULTS AND DISCUSSION

Polymer blending is a means of improving deficient properties of some traditional polymers. The attainment of desirable properties depends mainly on the extent of molecular interactions between the blend

TABLE II
Physicomechanical Properties and Mass Swell of the Pure Polymers and Uncompatibilized PP/NBR Blends

	Blend ratio		Physicomechanical properties				Mass swell Q (%)
Sample	PP	NBR	σ_R (MPa)	ε_R (%)	E (MPa)	Hardness Shore A	
PP_{100}	100	0	33.235	15.200	518.65	96	0
PP_{90}	90	10	25.023	66.666	437.53	96	0.41
PP_{80}	80	20	21.345	80.130	366.30	96	0.73
PP_{70}	70	30	17.213	92.00	278.53	93	1.26
PP_{60}	60	40	13.762	69.861	219.69	95	1.43
PP_{50}	50	50	8.750	45.733	161.37	94	1.40
PP_{40}	40	60	7.146	41.930	91.70	90	1.51
PP_{30}	30	70	3.622	38.640	52.78	83	1.82
PP_{20}	20	80	2.731	244.900	28.11	75	2.40
PP_{10}	10	90	1.624	663.810	5.26	64	2.41
PP_0	0	100	1.570	1250.000	1.67	31	3.50

ε_R, tensile strength; ε_R, elongation at break, %; E, Young's modulus.

components. By careful selection of component polymers, their blend ratios, and processing conditions, one can attain wide range of desirable properties in polymeric blends.[20,21] Final morphology has a controlling influence on the properties and end use of the blend.[22–27]

Uncompatibilized PP/NBR blends

Physicomechanical properties

The physicomechanical properties (σ_R, ε_R, E, and shore A hardness) of the pure polymers and the prepared blends without the compatibilizers are listed in Table II. It was observed that PP phase exhibited a high rigidity (σ_R, 33.235; E, 518.65; and hardness shore A, 96), while it failed at a relative small strain level (ε_R, 15.200). This was probably due to the brittle character of the PP phase. The reverse was true for pure rubber phase.[28] One can notice that the strength of the material (σ_R, E, and hardness shore A values) decreased and the flexibility (ε_R) increased with the incorporation of rubber particles in the PP phase. This might be mainly due to the rubber effect in decreasing the crystallinity of PP through a decrease of the spherulite size of PP in the presence of the elastomers.[5,10,29,30] This was confirmed for the blends with different contents of NBR phase (see Table II). However, the negative deviation of the uncompatibilized blends from the additive contribution of each component indicated poor interfacial adhesion between the phases which caused poor stress transfer between the matrix and dispersed phase.[31]

Mass swell

Also, the effect of the blend compositions on mass swell percentages of PP/NBR blends in the tested

solvent mixture acetone/benzene (50/50) for 24 h was studied and listed in Table II. It could be seen that the property increased with increasing rubber content in the composition. These results indicated that there was no adhesion between the two phases, suggesting the incompatibility of the components.

Compatibilized PP/NBR blends

Physicomechanical properties

Figures 1–5 summarize the effects of EL (i.e., $E_{0.5}L$, E_1L, $E_{1.5}L$, and E_2L) and MA-PP as compatibilizers with various contents (viz., 1, 5, 10, and 15 wt %) on the physicomechanical properties and mass swell of PP_{70} blend composition. The tested compatibilizers had an influence on the mechanical behavior of the blends because all the mechanical properties were improved in each case with respect to the uncompatibilized blends. With increase in compatibilizer concentration, the tensile properties were found to increase up to 10 wt % compatibilizer and then leveled off for all compatibilizers. The highest tensile
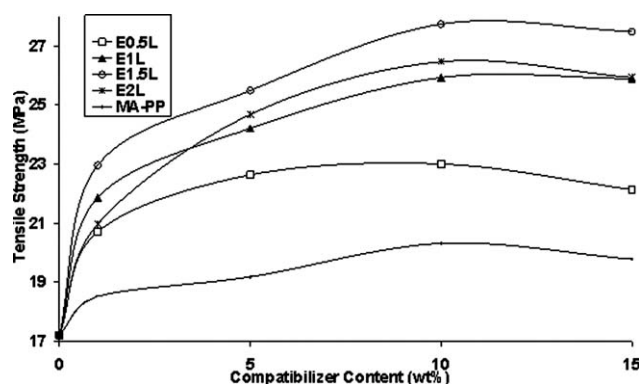

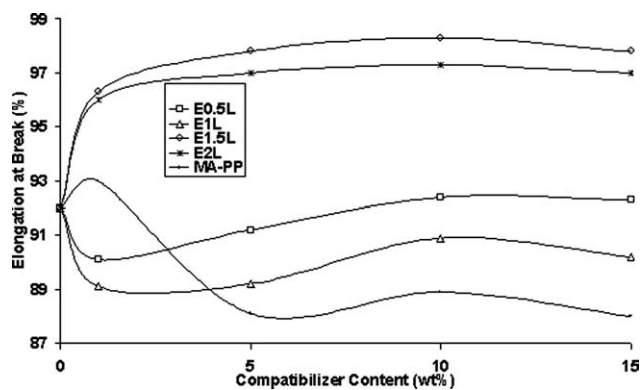Figure 1 σ_R values of the PP_{70} blends versus the compatibilizer content.

Figure 2 ε_R values of the PP_{70} blends versus the compatibilizer content.

Figure 4 Hardness of the PP_{70} blends versus the compatibilizer content.

properties of the 10 wt %. $E_{1.5}L$ compatibilized blend were due to the presence of epoxy group with higher content in $E_{1.5}L$ compared with that of E_1L, E_2L, and $E_{0.5}L$ (see Table I). The presence of epoxy group permits the following mechanism and the chemical reaction can be depicted as shown in Scheme 1[10]:

Thus, increasing the epoxy group content in the compatibilizer structure increased its efficiency in enhancing the interaction between PP and NBR phases. This increase in adhesion was evident from the scanning electron micrographs [Fig. 2(b)] with the lowest particle size of NBR domains in this system, as explained later. Also, compatibilized blends with E_2L exhibited better properties compared with those with E_1L and $E_{0.5}L$. This was due to increased hydroxyl group content of E_2L in comparison with E_1L and $E_{0.5}L$ (see Table I), which in turns increased the dipolar interaction and hydrogen bond formation with CN groups of NBR phase.

For MAH-compatibilized PP_{70}, it is believed that the peroxide catalyst initiates radical formation on the PP backbone by hydrogen abstraction and chain scission. The radicals then react with MAH to form maleated polypropylene MA-PP.[5,32] Scheme 2 shows
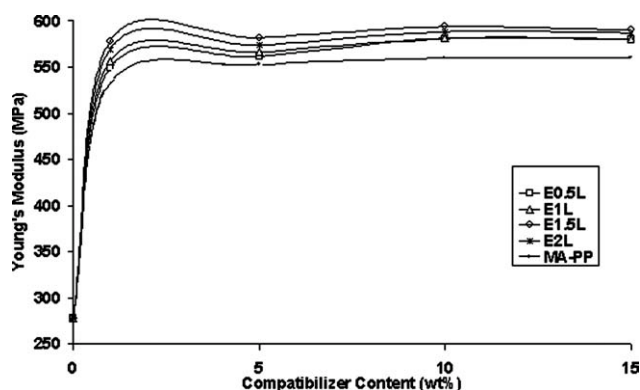
the reaction mechanism of MAH-grafted PP with NBR, which occurred during melt mixing.

The increase in tensile properties of MAH-compatibilized samples, when compared with uncompatibilized ones, was due to the increased dipolar interaction between the MA-PP and NBR phase, which caused an increase in interfacial adhesion between PP and NBR phases. MA-PP-compatibilized blend samples showed a decrease in tensile properties with a reduced flexibility with respect to EL ternary samples. This was confirmed by SEM, showing no reduction in particle size at 10 wt % MA-PP [Fig. 2(c)], as explained later. Similar results have been reported for the PP/NBR[5] and nylon/PP system.[33]

Thus, the variation of the mechanical data of the blends with different compatibilizers depends on the morphologies of the blends with respect to the size of the dispersed phase, interfacial adhesion, and dispersion of the minority phase in the matrix, as discussed later.

Mass swell

The effect of compatibilizer content on mass swell of PP_{70} blend samples in the tested solvent mixture is

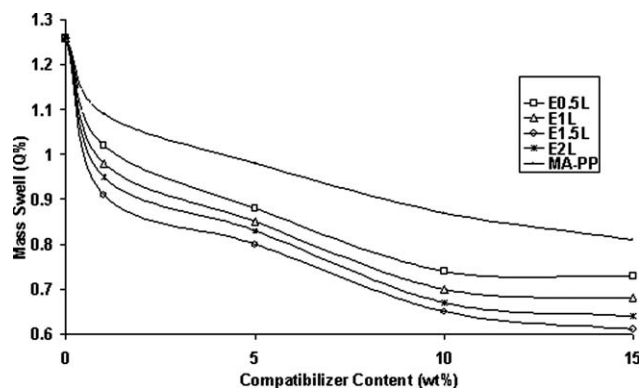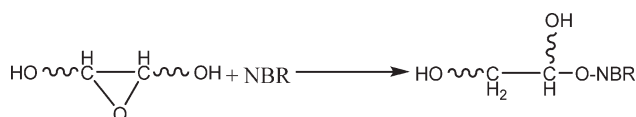**Figure 3** E values of the PP_{70} blends versus the compatibilizer content.

Figure 5 Variation of the mass swell of the PP_{70} blends in acetone/benzene (50/50) solvent mixture as a function of the compatibilizer type and content.

Scheme 1 Illustration of proposed reaction mechanism for epoxidized linseed oil with NBR.

illustrated in Figure 5. It was found that the property decreased with increasing compatibilizer content up to 10 wt % and then leveled off for all compatibilizers.. This decrease in mass swell at 10 wt % compatibilizer was due to the increase in adhesion between PP and NBR phases; more adhesion regions were expected to be formed between the two phases upon using $E_{1.5}L$. Thus, this would render the compatibilized PP_{70} blend with 10 wt % $E_{1.5}L$ stiffer and subsequently reduce the penetration by the solvent further. These results were in accordance with σ_R, E, and hardness values as shown in Figures 1, 3, and 4.

Fourier transform infrared spectroscopy analysis

The FTIR measurements of PP_{70} and compatibilized PP_{70} with $EL_{1.5}$ were in consistent with the spectra of Ismail et al.[10] and Supri and Ismail.[34] Although the spectrum of EL oil is in harmony with the spectrum of Téllez et al.,[35] the spectrum of PP_{70}/EL blends showed an absorption peak at around 3450–3400 cm^{-1}, assigned to the OH group of EL oil in the blends. The peaks of the stretching vibration of CN group and C=C double bond of NBR appeared at around 2300–2000 cm^{-1} and 1680–1620 cm^{-1}, respectively. The peaks appearing at around 1230 and 913 cm^{-1} were attributed to the epoxy group Of
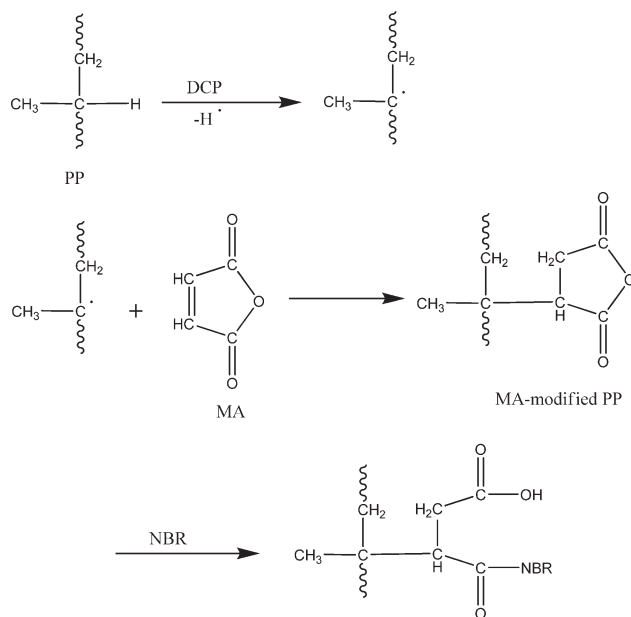
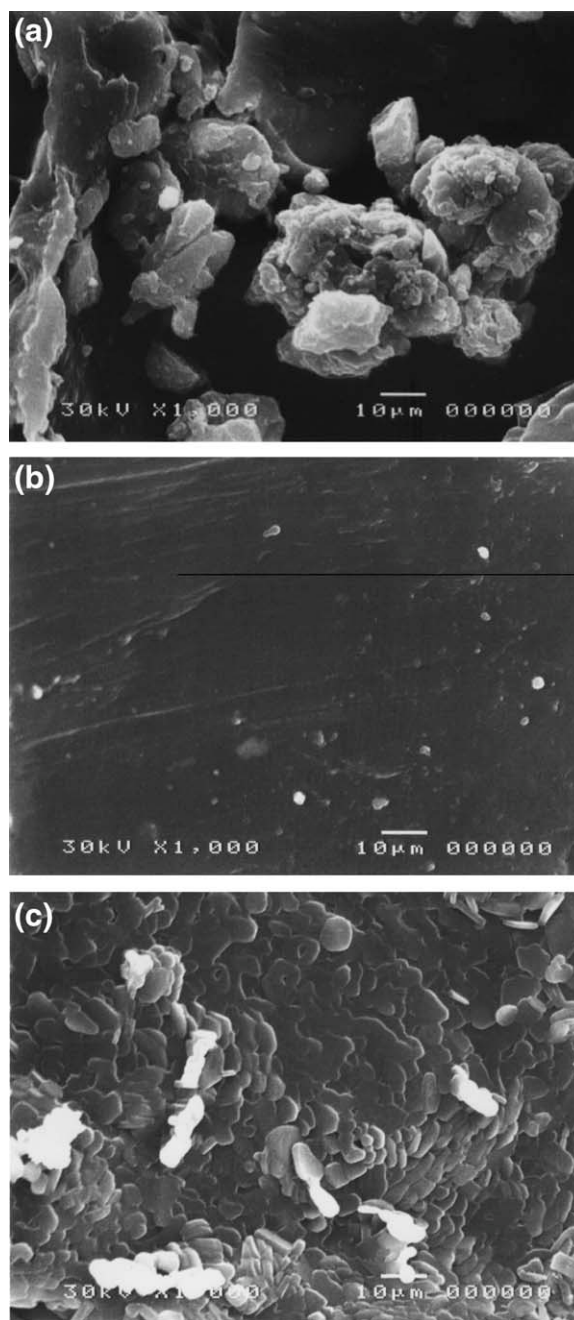**Scheme 2** Reaction mechanism of maleic anhydride-grafted PP with NBR.

Figure 6 SEM of the PP_{70} surfaces with (a) 0% compatibilizer, (b) 10% $E_{1.5}L$, and (c) 10% MA-PP.

EL. However, the absence of these two peaks in the spectrum of PP/NBR-EL blend might be due to the reaction of epoxy group with NBR. In addition, disappearance of the peak of the stretching vibration of CN group may also be evidence of a reaction between epoxy and NBR.

Thus, when EL was added to the PP/NBR blend, there is a possibility for the reaction between EL and NBR[10] as illustrated in Scheme 1. At the same time, PP is more compatible with the epoxidized linseed oil because it contains a long nonpolar hydrocarbon chain. Therefore, the interfacial interaction between

PP and NBR was improved by addition of epoxidized linseed oil into the PP/NBR blends, and the compatibilizing effect of epoxidized linseed oil might be due to the chemical reaction between EL and NBR and nonpolar physical interaction between EL and PP. On the other hand for PP/MAH, the absence of C—C double bond at 1600 cm^{-1} of MAH structure might be due to C—C radical of MAH, which grafted with PP. The FTIR spectra were similar to Ismail et al.[36] on the study of blend of waste poly(vinylchloride)/NBR using maleic anhydride as a compatibilizer.

Blend morphology

The fractured surface of the PP$_{70}$ blend with and without compatibilizers was observed by SEM to study the effects of the compatibilizer on the morphology. The fractured surfaces of the blends without compatibilizers possessed a coarse morphology [Fig. 6(a)] with a larger domain size in comparison with the compatibilized ones. The larger particle size, with no evidence of adhesion between the matrix (PP) and dispersed phase (NBR), confirmed the incompatibility of the two component, although the E$_{1.5}$L ternary blend [Fig. 6(b)] showed more regular dispersion of NBR nodules inside the PP matrix, a smaller nodule size and an improvement in interfacial adhesion with respect to the MA-PP ternary blend [Fig. 6(c)].

CONCLUSIONS

The compatibility of PP and NBR is poor and can be enhanced by the addition of compatibilizers. In this study, PP/NBR (70/30 wt %) blends were modified by the addition of compatibilizers, that is, EL and MAH. Ternary blends with compatibilizers (10 wt %) showed an improvement in mechanical properties and reduced mass swell compared with uncompatibilized ones. The addition of compatibilizers beyond 10 wt % did not improve the physicomechanical properties or mass swell any further. The overall improvement in properties with a reduction in the domain size of the dispersed NBR particles was obtained upon using E$_{1.5}$L, indicating the improvement of adhesion between the two phases. This suggests that E$_{1.5}$L can be used as an effective compatibilizer in PP/NBR blends.

While in the case of MA-PP (10 wt %), there was a slight reduction in particle size of NBR and showed different behavior as a compatibilizer in PP$_{70}$ compared with E$_{1.5}$L.

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