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Use of Differential Scanning Calorimetry (DSC) in the Characterization of EPDM/PP Blends

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Abstract New polyolefinic thermoplastic elastomers based on the ethylene–propylene-diene monomer (EPDM) and polypropylene (PP) containing an EPDM elastomer of the last generation (Nordel NDR 47130), obtained by polymerization in the gaseous phase with metallocene catalysis, were prepared and characterized. The melting and crystallization behavior of these blends was investigated by differential scanning calorimetry. It is observed that the melting temperature, crystallization temperature, and crystallinity degree increase with an increase of PP loading. The influence of the blend composition on the physico-mechanical characteristics was discussed using statistical processing of the experimental data. Two compatibilizing procedures were utilized to improve the physico-mechanical characteristics of the samples: an addition method using different compatibilizing agents and dynamical vulcanization with three types of crosslinking systems. Significant improvements of the tensile strength and tear strength were noted by dynamic crosslinking, and the best results were obtained using a crosslinking system based on phenolic resin and tin chloride.

Keywords Crystallization · Differential scanning calorimetry (DSC) · EPDM/PP blends · Mechanical properties

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1 Introduction

The ethylene–propylene-diene monomer (EPDM) exhibits better physical characteristics such as high heat resistance, ozone resistance, and cold and moisture resistance to permanent deformation and impact. Because of the poor impact resistance, especially at room and low temperatures of polypropylene (PP), blends of EPDM with PP may be very attractive in order to improve the impact toughness of PP and to extend its applications. EPDM/PP blends are the most frequently used polyolefinic thermoplastic elastomers because they are less expensive than polyurethanes, they are resistant to oxidizing agents, and they are flexible even at low temperatures. Their characteristics are comparable to S–EB–S (styrene–ethylene–butylene–styrene copolymers) thermoplastic elastomer properties [1–4]. These blends are obtained by mixing of EPDM rubber with PP in the molten state. When the mixture becomes homogeneous, compatibilizing agents, vulcanization agents, etc. are added to the system. Because of the very large range of the obtained products, profitable cost-performance relationship, and particularly acceptance of these materials by the car manufacturing industry [5], these thermoplastic elastomers were studied in order to obtain enhanced mechanical properties using different compatibilizing procedures. The compatibilization must accomplish: (a) optimization of interfacial tension; (b) stabilization of the morphology against high stress during forming; and (c) enhanced adhesion between the phases in the solid state [6–8]. Compatibilizing methods can be divided into two categories: compatibilization by addition and reactive compatibilization [9–16]. Using differential scanning calorimetry (DSC), the modifications occurring in the EPDM/PP blends can be estimated depending on the compatibilization procedures or composition changes and their influence on the structural or physico-mechanical characteristics of these thermoplastic elastomers can be evaluated. Differences in the mechanical properties of the blends can be attributed to some changes in the crystallization behavior of PP in the elastomer matrix [17,18].

For this study, blends of ethylene–propylene terpolymer rubber and PP were prepared using an EPDM elastomer of the last generation, obtained by polymerization in the gaseous phase with metallocene catalysis [19].

2 Experimental

2.1 Materials

The following raw materials were used: (1) EPDM Nordel NDR 47130 (ethylene content 67 %, 5-ethylidene-2-norbornene (ENB) content 4.9 %, crystallinity degree 9 %, density 0.97 $\mathrm{g \cdot cm^{-3}}$, Mooney viscosity at 125 °C: 130); (2) PP Moplen HP200R (density 0.900 $\mathrm{g \cdot cm^{-3}}$, MFI 20 g/10 min at 230 °C/2.16 kg); (3) compatibilizing agents: chemically modified polyethylene by grafting with maleic anhydride (mPE) Polybond 3009 (with 0.2 % maleic anhydride content, MFI 5 g/10 min at 190 °C/2.16 kg), chemically modified PP by grafting with maleic anhydride (mPP) Polybond 3002 (with 1 % maleic anhydride content, MFI 7.0 g/10 min at 230 °C/2.16 kg) and maleinized ethylene propylene terpolymer rubber (mEPDM) Royaltuf 498 (with 1 % maleic anhydride content, Mooney viscosity at 125 °C: 30); (4) vulcanization agents: (a) sulfur (S) with vulcanization accelerators: mercaptobenzothiazole (MBT) and tetramethylthiuram disulfide (TMTD), (b) di(*tert*-butyl peroxy-isopropyl)benzene Perkadox 14-40B-GR (40 % peroxide) with trimethylolpropane trimethacrylate TMPT DL 75 C (pH 9.2, 74.2 % active agent), and (c) phenolic resin Ribetak 75-30 (8.8 % methyl) with tin chloride dihydrate (98.6 % purity); and (5) antioxidant: Irganox 1010.

2.2 Blend Preparation

EPDM/PP blends were obtained by mixing in a 70 cm^3 Plasti-Corder PLV 330, Brabender, Duisburg, Germany, device at 80 rpm, at a temperature of 190 °C for 10 min. After adding the vulcanization agents, the EPDM/PP blends were mixed for 3 min. Blends were homogenized on a laboratory roller mill heated at 155 °C to 165 °C. Plates required for physico-mechanical tests were obtained by pressing in an electrical press at 180 °C, for 5 min and at a pressure of 150 MPa. After molding, the mix was cooled under pressure at room temperature.

2.3 Blend Characterization

Differential scanning calorimetry (DSC) measurements were carried out with a Perkin Elmer Pyris Diamond (USA) calorimeter. Thermograms were run at heating and cooling rates of $15\,^{\circ}\mathrm{C}\cdot\mathrm{min}^{-1}$. The melting temperature (T_{m}), crystallization temperature (T_{c}), and heat of fusion (ΔH_{f}) were determined from DSC data. The crystallinity (X_{c}) was evaluated from the relation, $X_{\mathrm{c}} = 100\,\Delta H_{\mathrm{f}}/\Delta H_{\mathrm{o}}$, where ΔH_{o} is the heat of fusion for a perfect crystal of PP ($207\ \mathrm{J}\cdot\mathrm{g}^{-1}$) [20,21].

The hardness, in units of Shore A, was measured by means of a hardness tester according to ISO 7619/2001. Tensile properties were measured by means of a Schopller strength tester. The tensile strength was determined using dumbbell-shaped specimens according to ISO 37/1997. The tear strength was measured according to ISO 34-1/2000 using angular test pieces (type II). The elasticity was determined with a test machine of type Schob (according to ISO 46662/1986). Test specimens were cut from plates of 150 mm × 150 mm × 2 mm by means of an automatic punching die. The melt flow index of the thermoplastic materials was measured by means of an extrusion plastometer (capillary rheometer) at 210 °C, and a 5 kg load was employed according to ISO 1133/2003. Three measurements were carried out to obtain each data point.

2.4 Statistical Processing

Statistical processing of data was performed in the SPSS version 13. It was aimed at explaining the relationship between the resulting variable (analyzed blend characteristic) and causal independent variable—the PP percentage in blends, based on a mathematical relation known as a regression model.

Statistical models are applied to enable predictions of future states based on information resulting from previous states. They deal certainly with a prediction based on probable statistical elements, accompanied by some risks assumed previously to this prediction process [22,23].

3 Results and Discussion

The effect of blend composition and compatibilizing methods on the thermal properties was estimated from DSC measurements in a nitrogen atmosphere. The glass transition temperature values obtained from thermograms are displayed in Table 1. The T_g values of EPDM/PP blends are located in the same temperature range as those for EPDM (−39.77 °C) (Table 1). DSC thermograms were presented in Fig. 1 for EPDM/PP blends. In the DSC determinations, one broad melting peak at about 161 °C to 164 °C for EPDM/PP blends was found. The melting temperature for the used PP is 164.13 °C (Table 2). Melting temperatures of the blends are smaller than that of PP, except for the composition with a high level of PP, due to the decrease of the size and perfection of PP crystals as well as to the increase in the amorphous domains in an elastomer which hinders the PP crystallization [24]. The increase in height of the melting peak of the blend with a high level of PP indicates a higher crystallinity, and the crystals were bigger due to the lowering of the interfacial tension between PP and EPDM. In the case of a vulcanized blend, the reduction of T_m is noted as shown in Fig. 1, which means that the dynamic crosslinking influenced the crystallinity and the blend melt at lower temperatures.

As the PP content increased in the polymer blends, the melting temperature shifted to a higher temperature and an increase of the melting enthalpy was observed. Also, the inclusion of maleated polyolefin results in a decrease in the melting temperature, probably due to the amorphous domains of the two polymers that leads to a lowering of T_m of the blends.

Because the melting peaks of the blends are situated in a small temperature range for the EPDM/PP blends, we can conclude that the addition of the compatibilizer does practically not alter the crystalline structure of polyolefin [25].

The crystallization thermograms of EPDM/PP blends and the characteristic parameters are given in Fig. 2 and Table 1. It can be observed that the crystallization

Table 1 Physical properties of EPDM/PP blends

Sample	T_g (°C)	T_m (°C)	ΔH_f ($J \cdot g^{-1}$)	X_c (%)	T_c (°C)	ΔH_c ($J \cdot g^{-1}$)
60 % EPDM/40 % PP	−39.79	160.91	39.23	18.9	116.37	39.6
20 % EPDM/80 % PP	−39.82	163.96	82.64	39.9	127.02	80.2
57 % EPDM/38 % PP/5 % mPP	−39.35	162.60	41.59	20.1	120.50	41.2
54 % EPDM/36 % PP/10 % mPP	−40.07	162.29	44.47	21.5	121.63	43.5
60 % EPDM/40 % PP/8 phr resin/1.6 phr $SnCl_2$	−37.11	162.54	36.15	17.5	121.48	37.4
EPDM Nordel	−39.77					
PP		164.13	85.57	41.34		
mPP		164.48	78.75	38.04		

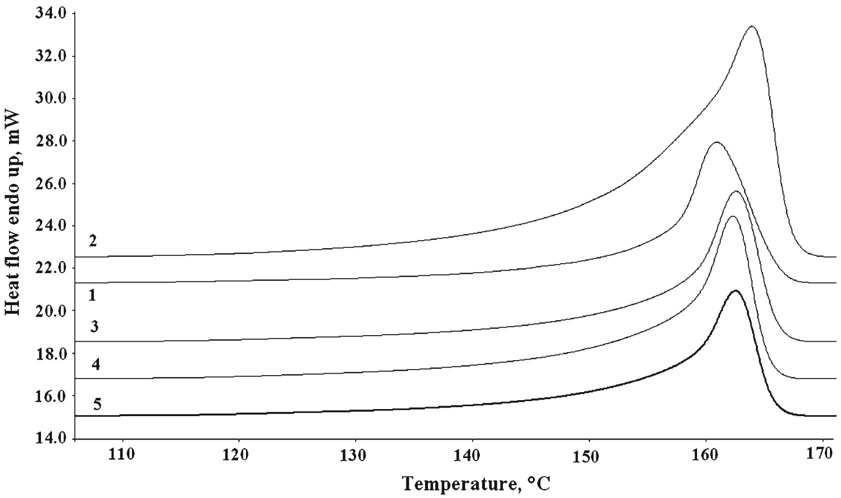

Fig. 1 Melting behavior of EPDM/PP blends: (1) 60 mass% EPDM/40 mass% PP; (2) 20 mass% EPDM/80 mass% PP; (3) 57 mass% EPDM/38 mass% PP/5 mass% mPP; (4) 54 mass% EPDM/36 mass% PP/10 mass% mPP, and (5) 60 mass% EPDM/40 mass% PP/8 phr resin/1.6 phr $SnCl_2$

Table 2 Estimated characteristics for a probability of 95 % of a blend with 40 mass% PP

Characteristics	Estimated values on the basis of the relations from Figs. 3, 4, 5, 6, 7 ($\hat{y}_{40\,\%}$)	Standard model error ($\sqrt{\text{SSE}}$)[a]	Standard estimation error ($s_{\hat{y}_{40\,\%}}$)[b]	Confidence interval[c]	
0	1	2	3	4	5
Hardness (°ShA)	95.145	1.177	0.467	94.042	96.248
Elasticity (%)	29.820	4.475	1.659	25.993	33.647
Tensile strength ($\text{N}\cdot\text{mm}^{-2}$)	7.844	1.050	0.367	7.013	8.674
Tear strength ($\text{N}\cdot\text{mm}^{-1}$)	76.012	10.136	3.544	67.996	84.028
Melt flow index (g/10 min)	1.327	0.619	0.245	0.727	1.928

[a] $\text{SSE} = \sum_{i=1}^{n}\left(y_i - \hat{y}_i\right)^2/n-k-1$ where y_i = experimental values; $\hat{y}_i$ = values adjusted based on the regression model; and $\overline{y}$ = the mean of the experimental values

[b] $s_{\hat{y}_{40\,\%}} = \sqrt{\frac{\text{SSE}}{n-k-1}\left[1+\frac{1}{n}+\frac{(40-\overline{P}_{\%})^2}{\sum_i^n\left(P_{\%i}-\overline{P}_{\%}\right)^2}\right]}$ where $\overline{P}_{\%}$ is the medium level of PP content (%) corresponding to the experimental data domain

[c] $\hat{y}_{40\,\%} \pm t_{\alpha/2;n-k-1}\cdot s_{\hat{y}_{40\,\%}}$ where $t_{\alpha/2;n-k-1}$ is the value for the student repartition (see table footnote "d") as a function of the certainty level α (this was considered 0.05 because a probability of 95 % for the results was desired) and the number of degrees of freedom $df = n-k-1$, where n is the number of observations and k is the number of parameters in the model

[d] Testing of the significance of the regression model parameters was performed by means of the student's t-test, considering a number of experimental values less than 30

$t_{\text{calc}} = \frac{b_i-\beta_i}{s_{b_i}}$ where β_i is the parameter i of the single factor regression model (if assuming that it has no statistical significance, it is 0; b_i is the parameter i estimator for the regression model obtained from the experimental data; and s_{b_i} = standard deviation of the b_i estimator

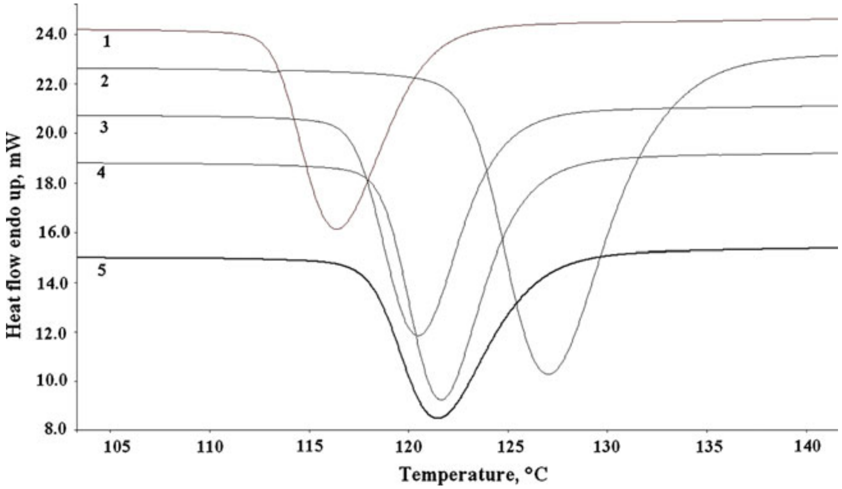

Fig. 2 Crystallization behavior of EPDM/PP blends: (1) 60 mass% EPDM/40 mass% PP; (2) 20 mass% EPDM/80 mass% PP; (3) 57 mass% EPDM/38 mass% PP/5 mass% mPP; (4) 54 mass% EPDM/36 mass% PP/10 mass% mPP, and (5) 60 mass% EPDM/40 mass% PP/8 phr resin/1.6 phr $SnCl_2$

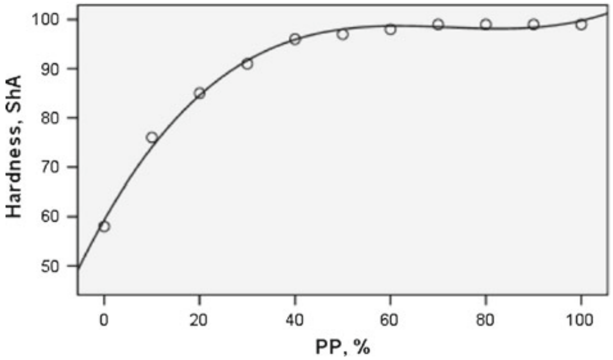

Fig. 3 Hardness versus the PP level; $H = 59.308 + 7.7PP_{\%} - 0.0241PP_{\%}^2 + 0.0001PP_{\%}^3$

temperature (T_c) increased with an increase of the PP concentration or with the introduction of mPP in the mixture. A similar trend was found in the vulcanized mixture.

The review of physico-mechanical characteristics according to the composition of the EPDM and PP blends has revealed the following: The increase in the PP percentage from 0 up to 40 mass% (parts to 100 parts polymer) has led to a significant increase in the hardness (Fig. 3) and a marked decrease in the elasticity (Fig. 4), as in this percentage range, the continuous phase is made up of EPDM for low percentages, and thereafter both phases are co-continuous. At percentages above 40 mass%, the continuous phase is made up of the thermoplastic polymer that imparts the surface characteristics in the samples.

The tensile strength (Fig. 5) and tear strength (Fig. 6) have increased with an increase in the PP mass percentage in the blends.

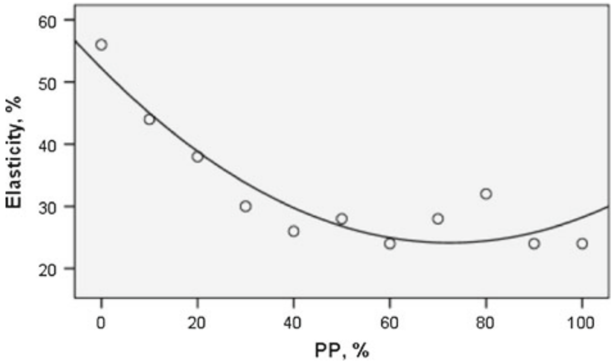

Fig. 4 Elasticity versus the PP level; $E = 52.224 - 0.7761 PP_{\%} + 0.0054 PP_{\%}^2$

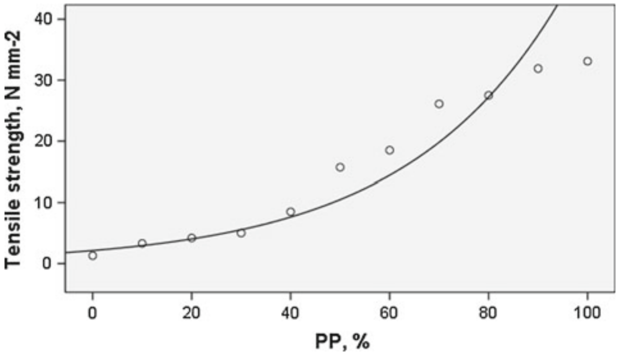

Fig. 5 Tensile strength versus the PP level; $TlS = 2.19883\mathrm{e}^{0.0318 \cdot PP_{\%}}$

The melt flow index (Fig. 7) at 210 °C and a pressure of 5 kg has shown an exponential increase with an increase in the PP mass percentage in the blends; a blend containing 40 mass% PP has shown a good value for the melt flow index, enabling good injection processing.

Due to the fact that the viscosity of EPDM is lower than that of PP, PP is covered by EPDM. Figure 7 shows that with an increase in PP loading, the melt flow index increases which indicates that PP becomes more fluid than EPDM.

Starting from the obtained experimental data, the effect of the estimation of causal variable modifications (PP content) on the characteristics of EPDM/PP blends was analyzed by advanced statistical methods and econometrical modeling. Regression models presented in Figs. 3, 4, 5, 6, and 7 have been validated for a probability not less than 95 %. Taking into account the above, the analysis of the changes in the characteristics of EPDM/PP blends as a function of composition gives the possibility to select materials for a variety of applications.

The characteristics of a blend containing 40 mass% of PP were evaluated for a probability of 95 % on the basis of previously made models (Figs. 3, 4, 5, 6, 7; Table 2).

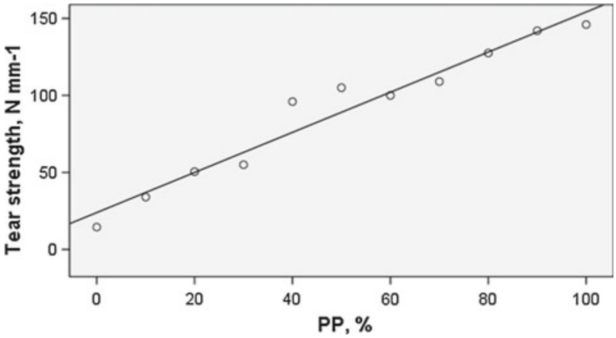

Fig. 6 Tear strength versus the PP level; $TrS = 23.933 + 1.302PP_{\%}$

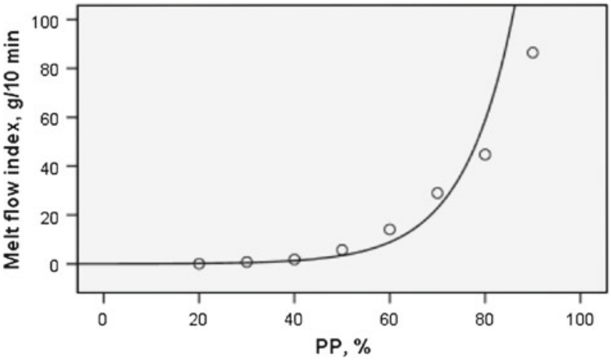

Fig. 7 Melt flow index versus the PP level; $MFI = \mathrm{e}^{-3.477+0.094PP_{\%}}$

To improve the physico-mechanical characteristics of EPDM/PP blends, both compatibilization methods were used: addition of a compatibilizer and reactive compatibilization.

Compatibilization by addition utilized the following compatibilization agents: PE grafted with maleic anhydride (mPE) Polybond 3009, PP grafted with maleic anhydride (mPP) Polybond 3002, and EPDM grafted with maleic anhydride (mEPDM) Royalene 498. The physico-mechanical characteristics of 57 mass% EPDM, 38 mass% PP blend, and 5 mass% compatibilizing agent content (Table 3) was not modified significantly. These modifications are in the limits of the confidence interval of the reference blend for a probability of 95 %, with the exception of EPDM/PP compositions containing mPP and mEPDM. In the first case, the tensile strength and tear strength increase while the elasticity exhibits a small decrease. In the last case, the tensile strength and tear strength show a decrease with the presence of mEPDM. The increase of mPP quantity in the blend to 10 mass% does not lead to any significant improvement of the characteristics.

Reactive compatibilization between both phases in the EPDM/PP blends has been used for the crosslinked copolymer formation strategy; this was accomplished by

Table 3 Physico-mechanical characteristics of the EPDM/PP blends

Sample	Hardness (°ShA)	Elasticity (%)	Tensile strength ($N \cdot mm^{-2}$)	Tear strength ($N \cdot mm^{-1}$)
60 % EPDM/40 % PP (reference)[a]	96	26	8.6	71.5
60 % EPDM/40 % PP[b]	94–96	26–33	7.0–8.7	68–84
57 % EPDM/38 % PP/5 % mPP	96	25	11.2	92.0
57 % EPDM/38 % PP/5 % mPE	96	28	7.6	75.5
57 % EPDM/38 % PP/5 % mEPDM	94	28	6.1	63.5
54 % EPDM/36 % PP/10 % mPP	97	24	12.7	92.5
60 % EPDM/40 % PP/6 phr peroxide/3 phr TMPT	96	22	11.2	98.0
60 % EPDM/40 % PP/3 phr peroxide/1.5 phr TMPT	97	22	12.5	107.0
60 % EPDM/40 % PP/8 phr resin/1.6 phr $SnCl_2$	97	21	18.6	126.5
60 % EPDM/40 % PP/4 phr resin/0.8 phr $SnCl_2$	96	22	16.1	114.5
60 % EPDM/40 % PP/2 phr S/1 phr Th/0.5 M	96	22	15.9	121.5
60 % EPDM/40 % PP/1 phr S/0.5 phr Th/0.25 M	97	20	17.0	116.0

[a] Experimental data

[b] Confidence interval for estimation of the characteristics of the reference blend with a probability of 95 % (Table 2, columns 4 and 5)

vulcanization, employing three different classes of modifiers: peroxides, phenolic resins, and sulfur. The physico-mechanical properties of EPDM/PP (60:40 by mass) blends are improved by dynamical crosslinking (Table 3).

Thus, significant increases of the tensile strength and tear strength were found while the hardness values were not practically modified. The best results were observed for compositions with 8.0 phr of phenolic resin and 1.6 phr of tin chloride contents. These modifications are due to the dynamical vulcanization of the elastomer that leads to the formation of crosslinking bridges both in the elastomer and between the elastomer and thermoplastic polymer.

4 Conclusions

In the use of DSC in the characterization of EPDM/PP blends, it is observed that the melting temperature, crystallization temperature, and crystallinity degree increase with an increase of PP loading.

The increase of PP content in EPDM/PP blends led to an increase of the hardness, tensile strength, tear strength, and to a decrease of elasticity. All these trends were analyzed by statistical methods using suitable models. The characteristics of an EPDM/PP blend with 40 mass% PP were estimated for a probability of 95 % based on the proposed regression models.

Significant improvements of the tensile strength and tear strength were noted by dynamic crosslinking, and the best results were obtained using a crosslinking system based on phenolic resin and tin chloride.

The melt flow index shows good values for blends with over 40 mass% PP allowing better processing by methods specific for plastics, thus removing the vulcanization operation required in the case of elastomers.

Due to their performance characteristics, the new polyolefinic thermoplastic elastomers can be used for manufacturing of products used in the cable industry and automotive industry as shock absorbers, etc.

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