Study of the Impact Resistance of Physically and Dynamically Vulcanized Mixtures of PP/EPDM

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Summary: Physically and dynamically vulcanized (TPV) mixtures of polypropylene (PP) and ethylene propylene diene terpolymer (EPDM) are prepared by extrusion in order to improve the impact resistance of PP. To enhance the chemical compatibility and provide better interaction between the PP and EPDM in the physical mixtures, both polymers are modified with maleic anhydride (MAH) in solution using xylene as solvent and dicumyl peroxide (DCP) as initiator. The qualitative and quantitative determination of the degree of grafting is study by Fourier Transform Infrared Spectroscopy (FTIR) and varying the amount of DCP and/or amount of MAH in order to determine the optimum amounts to obtain the highest degree of grafting. The effect of the relation of PP/EPDM, the amount of reinforcement filler and mix rate are studied for modified polymer mixtures (PP-g-MAH/EPDM-g-MAH). For the TPV of PP/EPDM the effects of amount and triallylisocyanurate (TAC) as coupling agent in presence of different amounts of DCP are studied. The physical mixtures of modified polymers prepared with a PP/EPDM ratio of 80/20 and the TPVs blends prepared with a PP/EPDM ratio of 70/30 and containing 15% filler at 60 rpm show the highest impact resistance. The impact resistance, melt flow index and hardness of the different mixtures are measured to determine their possible applications to prepare front panels and bumpers for automobiles by injection molding.

Keywords: DSC; ethylene propylene diene terpolymer (EPDM); extrusion; FTIR; impact resistance; poly(propylene) (PP)

Introduction

Mixtures of polymers give material with properties different from the properties of the individual constituent polymers. Mixtures are therefore widely used industrially since their properties can be adjusted to cover a specific necessity by varying the chemical structure of the components, the composition of the mixture and the processing conditions.

PP presents excellent processability, resistance to water and chemicals but it has poor resistance to impact especially at low temperatures due to its crystalline nature. It has been mixed with different inorganic materials such as glass fiber and organics such as EPDM in order to obtain a material with better mechanical properties and impact resistance. Successful dispersion of fine and homogeneous particles of elastomeric EPDM with a low degree of crystallinity into a PP matrix with good interfacial adhesion enhances the impact strength of PP but it decreases its processability[1–5].

Most of the mixtures are thermodynamically incompatible and the individual components exist as separate phases with large domains and with little adhesion among the components. This lack of compatibility results in poor properties and has limited the use of such mixtures[6,7]. Improved properties can be achieved with a good selection of the components, followed by an appropriate method of compatibilizing and processing conditions[8]. PP does not contain functional

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groups capable of interacting with other polymers therefore its funcionalization is recommended to increase the compatibility of their mixtures. Maleic anhydride (MAH) has been used to modify PP in order to improve interfacial adhesion in polymeric composites. One of the most common methods to achieve polyolefin modification with MAH is reactive processing in the presence of a peroxide[9,10]. The main advantages of such reactive processing are the absence of solvent, short reaction time and the fact that it is a continuous process. However, besides the main reaction, degradation and crosslinking are the most often cited side reactions in reactive processing[11].

An alternative to reactive processing is polymer modification in solution[12]. This method provides little or no crosslinking, no thermal degradation and also affords appropriate conditions to study the structural effects of the original polymer or the reactants on the grafting reactions. The main disadvantages are the large amount of residual solvent and long reaction time[13]. There are other ways to improve the compatibility among different polymers, like addition of compatibilizer, typically block or grafted copolymer[14,15] or inducing chemical reaction between polymers[16,17] leading to a modification of interfaces in two phase blends, and thereby tailoring of phase structure and properties. Reactive extrusion using an interfacial-active coupling agent can improve the interfacial adhesion of an inherently immiscible polymer blend. Coupling agents used in reactive extrusion are typically polymeric peroxides or multifunctional monomers such as trimethylolpropanetriacrylate (TMPTA) or triallylisocyanurate (TAC)) in presence of peroxide [18–19].

The objective of this work is to study systematically the effect of DCP peroxide percentage, the amount of MAH and the reaction time on the degree of MAH grafting onto EPDM and PP, and determine the effect of this modification, the relation of PP/EPDM, the amount of reinforcement filler and mixing rate on the impact resistance of physically and dynamically vulcanized (TPV) mixtures of PP/EPDM samples. These new materials will be able to be used in diverse applications that demand good impact resistance as front panels and bumpers for automobiles.

Experimental

Materials

The EPDM, Keltan 5508 contents 70 wt% ethylene, 25.4% propylene and 4.6 wt% ethylydenenorbornene with Mooney viscosity of 55 ± 4 MU. PP with MFI at 230 °C and 2.16 Kg of 12 g/10 min., Rockwell hardness of 76 R and 17,5 J/m. Charpy impact. A commercial maleic anhydride (99% Purity),dicumyl peroxide (Fluka), triallylisocyanurate (Aldrich), 99.5% methanol, acetone (99.9% purity), xylene (99 % purity), stearic acid (99%), calcium carbonate and parafinic oil are used without further purification. Flectol (2,2,4-trimethyl-1,2 dihydroquinoline) and Santoflex 6ppd (n-(1,3-dimethylbutyl)-n-phenyl-p-phenylene diamine) from Flexsis.

Functionalization of EPDM and PP with MAH

Funcionalization of EPDM MAH: In a glass reactor under nitrogen atmosphere 5 g of EPDM are dissolved in 100 ml of xylene at 132 °C. 10% MAH and 0.25% DCP are dissolved previously in 20 ml and 10 ml xylene respectively and added to the reactor after complete dissolution of the EPDM. The reaction time was 3 hours under constant stirring. This procedure is repeated for different amounts of dicumyl peroxide (1.0, 3.0. 6.0 and 7.5%). The amount of DCP is an important variable in the funcionalization reaction since it reacts with the unstaurated C=C bonds of the EPDM. The final products are precipitated with 300 ml acetone, washed several times with acetone to eliminate the residual initiator, cooled and vacuum filtered. After drying, the modified EPDM-MAH is extracted with methanol for 24 hours in a Soxhlet apparatus to remove the unreacted MAH.

To study the effect of reaction time on the degree of grafting, physical mixtures are prepared with the same molar ratio of EPDM/MAH and 3 wt-% peroxide which gives the highest degree of grafting and the reaction times of 30, 60, 100, 150, 210 min. The samples are subjected to the same purification process.

Functionalization of PP with MAH: The same procedure as described above is used for the functionalization of PP but in this case the effect of different amounts of DCP y MAH is analyzed. The different percentages used with respect to PP are in Table 1. The samples are named according their MAH and DCP percentage, for example Samples A are prepared with 1% MAH and different % DCP: A1 if the DCP is 0.25%, A2 if DCP is 0.5% or A3 if DCP is 0.75%.

Preparation of the EPDM-MAH and PP-MAH Standards

Several samples of EPDM are impregnated with different MAH amounts to be used as standards in the determination of grafting degree. The mixtures are prepared by dissolution in chloroform of 2,0 g EPDM and 0,1 ,0,5, 1,0, 3,0, 6,0% of MAH under stirring until complete solvent evaporation.

The PP is granulated by dissolution in xylene, then the PP is washed, dried and mixed with 0.2196, 0.7818, 2.1360, 3.008 and 3.6% of MAH, then KBr disks are prepared for posterior analyses.

Preparation of the Physically and Dynamically Vulcanized Mixtures

To determine the effect of the ratio of PP/EPDM, the amount of reinforcement filler and mixing rate on the impact resistance of physical samples of PP-g-MAH/EPDM-g-MAH, several mixtures are prepared varying the PP/EPDM ratio (70/30, 80/20 and 90/10), mixing rates (60,120 and 180 rpm) and filler concentration (10%, 15% and 20%) at 200 °C in a laboratory mixer extruder (LME) from Atlas Electric Devices Company. All the mixtures are prepared using the same amount of stearic acid as filler dispersion agent (1.5% with respect to calcium carbonate), two antioxidant agents Flectol and Santoflex 6 PPD and paraffin oil as processing agent at 0,75 phr, 1.0 phr, 10% with respect polymer mixture respectively. The mixtures are extruded four times for each mixing rate.

The TPV mixtures are prepared under the same condition as the physical mixtures PP/EPDM using triallylisocyanurate (TAC) as an interfacially active coupling agent at different percentage of DCP (0,25, 0,5, 0,75).

Table 1.
Percentage of DCP y MAH for the functionalization reaction

Samples	% MAH	% DCP
A	1.0	0.25 (1)
B	2.0	0.5 (2)
C	3.0	0.75 (3)
D	4.0	
(E)	5.0	

Characterization of Materials

Determination of Degree of Grafting

FTIR Spectroscopy of EPDM-g-MAH

The FTIR spectra of the EPDM impregnated MAH mixtures and EPDM-g-MAH films are recorded in a Perkin Elmer, model Spectrum One. The films are prepared by compression molding using a laboratory press with constant thickness. A calibration curve is prepared by analysis of EPDM impregnated MAH mixtures taking into account the absorbance of the carbonyl groups from 1698 cm^{-1} to 1856 and the absorbance at 720 cm^{-1} of CH_2 with $n \geq 5$ used as the internal standard. The degree of grafting is denominated carbonyl index and it is calculated by the following equation:

$$I_c = (A_{C=O}/A_{720})/(A_{1460}/A_{720})$$

FTIR Spectroscopy of PP-g-MAH

A calibration curve is prepared by analyzing the physical mixtures of PP/MAH taking into account the absorbance of the carbonyl groups from 1698 cm^{-1} to 1856 and the absorbance at 1420 cm^{-1} of CH_2 used as the internal standard with respect of

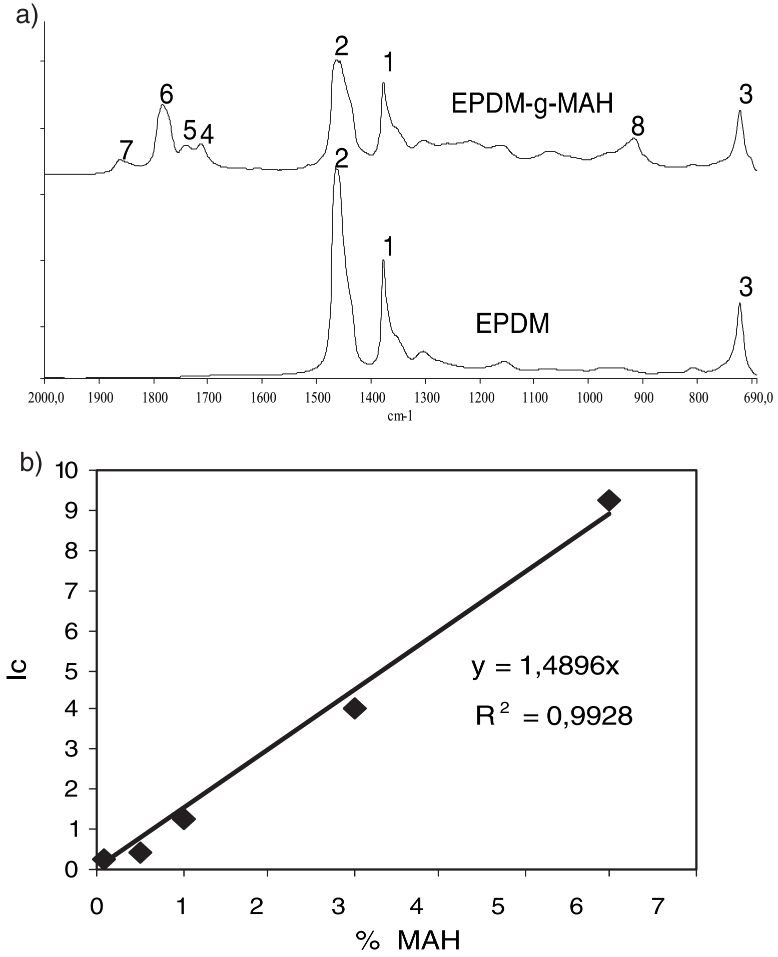

Figure 1.
a. FTIR Spectra: EPDM and EPDM-g-MAH. b. Calibration curve EPDM-g-MAH.

Table 2.
FTIR Characteristic Infrared Bands of the EPDM y EPDM-g-MAH

Band Number	Band Intensity	ν cm^{-1}	Group	Vibration Mode
EPDM				
1	Medium	1375	CH_3	Angular deformation
2	Strong	1460	CH_2	Angular deformation
EPDM-g-MAH				
3	Low	1707	C=O of Acid	Symmetric stretching MAH hyd.
4	Low	1739	C=O of Ester	Symmetric stretching
5	Medium	1783	C=O of Cyclic Anhydride	Symmetric stretching
6	Low	1859	C=O of Cyclic Anhydride	Asymmetric stretching
		922	OH of Anhydride	Angular deformation

absorbance at 720 cm^{-1}. The degree of grafting is denominated carbonyl index and is calculated by the following equation:

$$I_c = (h_{C=O}/h_{720})/(h_{1460}/h_{720})$$

Characterization of the Physically and Dynamically Vulcanized Mixtures

Impact Resistance Test

The Charpy impact resistance tests are made according to ASTM D-256 at room temperature using 25 J in a CEAST Spa Resil 25 equipment, Torino Italia.

Melt Flow Index (MFI)

El MFI of the physical and dynamical vulcanized mixtures are made according to the ASTM D-1238 standard test method. Approximately 4 g of sample are put into the cell at 230 °C, a load of 2,16 Kg is applied to force the material to pass through the die. The extrudate is collected and weight. The MFI is calculated using the following equation:

$$\text{Flux rate} = (600/t \times W\ \text{extrudate})\quad (t = \text{time in sec})\ \text{in g/10 min.}$$

Hardness Analyses

The analyses are made according to ASTM D 2240 standard test method. The samples of 4 mm thickness are put on the surface; the indenter is parallel pressed against the sample surface for one second. The analyses are made in triplicate.

Table 3.
%MAH Grafting

%Peroxide	%Graft
0.25	1.825
1	2.611
3	2.698
6	2.182
7.5	1.736

Results and Discussion

Determination of the Degree of Grafting of EPDM-g-MAH

Figures 1a and 1b show the FTIR spectra of EPDM, EPDM-g-MAH and the calibration curve to determine the porcentage of MAH grafting on EPDM. The bands are denominated according to the numbers assigned to the different vibrations, as seen in Table 2. Since the unreacted MAH gives rise to the absorption bands in the same region as the grafted anhydride, it is of great importance to eliminate all unreacted MAH. Elimination of unreacted MAH can be verified by the disappearance of the characteristic absorption band at 700 cm^{-1} assigned to the C=C bond of MAH. Analyzing the absorption bands of the EPDM-g-MAH, we can deduce that MAH is grafted particularly in anhydride form onto the EPDM and there is no MAH free. The absorption band at 720 cm^{-1} assigned to methylene group bending $(CH_2)_n$ with $n \geq 5$ that is used as an internal standard and does not change with the degree of grafting.

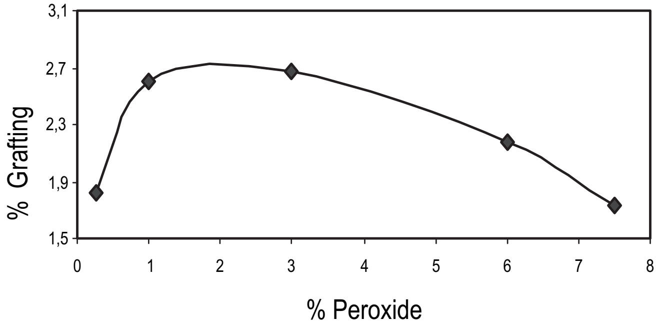

Figure 2.
% MAH Grafting vs. [Peroxide].

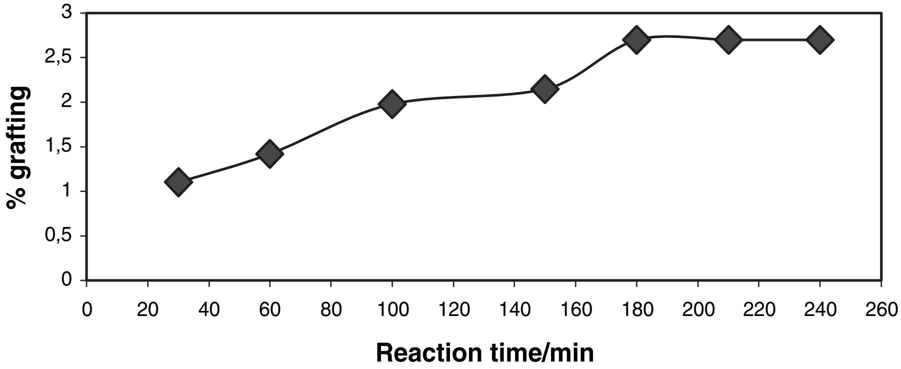

Figure 3.
Percentage of MAH Grafting on EPDM vs. Reaction Time.

Effect of Peroxide Content

Table 3 and Figure 2 show the degree of grafting of maleic anhydride on the EPDM obtained from the calibration curve at different peroxide concentrations. It can be observed that the degree of grafting increases with increasing peroxide concentration until the maximum value of 2,698% at 3 wt % of peroxide is reached. This is because by increasing the initiator content more

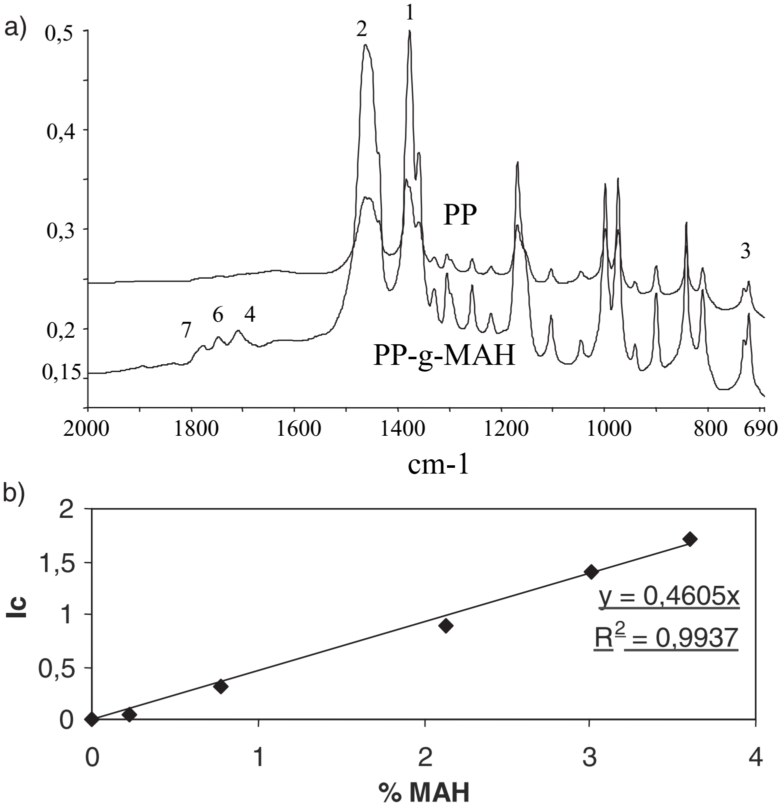

Figure 4.
a. FTIR spectra of PP and PP-g-MAH b. Calibration curve PP-g-MAH.

polymer radicals are formed, leading to a higher degree of grafting. Further increase in peroxide decreases the percentage of grafting; this indicates that the free radicals generated from the peroxide dissociation participate in other competing reactions such as cross linking reactions, scission of PP chains of the EPDM, EPDM radical recombination reactions and homopolymerization of MAH[17].

Table 4.
Percentage MAH Grafting vs. Carbonyl Indices Content (I_c).

0,25 % DCP			0,5% DCP			0,75 % DCP		
M	% Graf.	I_c	M	% Graft	I_c	M	% Graft	I_c
A_1	0,05	0,02	A_2	0,08	0,04	A_3	0,12	0,05
B_1	0,13	0,06	B_2	0,20	0,09	B_3	0,31	0,14
C_1	0,28	0,13	C_2	0,30	0,16	C_3	0,49	0,23
D_1	0,40	0,18	D_2	0,61	0,28	D_3	0,94	0,43
E_1	1,13	0,52	E_2	1,31	0,60	E_3	1,53	0,70

Effect of the Reaction Time

Figure 3 shows percentage of MAH grafting onto EPDM vs. reaction time at 132 °C for the sample containing 3% peroxide and 10% MAH. The percentage of MAH grafting increases with the reaction time until a maximum value is reached at 180 minutes. This can be related to the radical's life time, at this time no more radicals are present and the grafting reactions stop. Since MAH and EPDM are miscible in xylene at 132 °C, the grafting reaction is not dependent on the rate of MAH diffusion onto the EPDM. The plateau can be explained since the EPDM radicals will combine with each other yielding a cross linked structure or homo polymerization reaction of MAH that is favored especially when the peroxide content is sufficiently high.

Determination of the Degree of Grafting of Physical PP-g-MAH Mixtures

Figures 4a and 4b show the infrared spectra of PP y PP-g-MAH and the corresponding calibration curve. The calibration curve has a linear behavior through the origin with a high correlation coefficient that indicating good confiability with respect to the degree of MAH grafting.

Effect of DCP and MAH Content

Table 5 shows the porcentage MAH grafting on PP calculated from the calibration curve for 1 to 5 % MAH from 0.25 to 0.75% DCP. The peroxide radicals can be consumed by the MAH and PP. If the MAH and DPC contents are low, the DCP can react first with the MAH. The unreacted radicals interact with PP to produce macroradicals. If the MAH content increases the degree of grafting increases and more radicals formed from DCP are consumed, thus decreasing PP degradation [20,21]. It seems that the DCP content used in this work is enough to induce MAH radicals and PP macroradicals formation but are not enough to detect the higher DCP content to

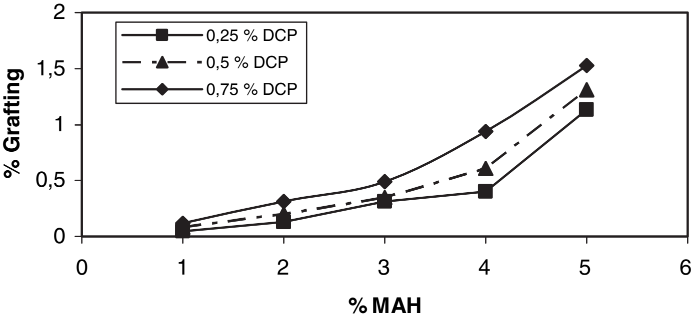

Figure 5.
Percentage MAH Grafting onto PP vs. Percentage MAH.

Table 5.
Impact resistance of TPV PP/EPDM Mixtures

N°	PP/EPDM	Carbonate %	Mixer Speed (rpm)	% DCP	Charpy impact (J/m)
1	70/30	10	60	0.25	60.2
2	70/30	10	60	0.75	62.5
3	70/30	15	60	0.25	62.5
4	70/30	15	60	0.5	87.5
5	70/30	15	120	0.75	62.5
6	80/20*	15	60	—	50

* Modified polymer mixture with higher impact resistant.

determine the optimum concentration for the higher % MAH grafting.

Figure 5 shows the degree of grafting of MAH vs. MAH content. The degree of MAH grafting increases with amounts of MAH and DCP. Since the radicals preferentially formed are the MAH radicals avoiding the formation of the PP radical.

Characterization of the Mixtures

Impact Resistance of the PP/EPDM Physical and TVP Mixtures

The highest impact resistances values are obtained for TVP PP/EPDM mixtures (Table 5) getting a maximum value of 87,5 J/m, at 60 rpm, 0,50 % DCP and 15% carbonate. The DCP concentration is a condition that should be optimized, in order to increase the interaction reaction and avoid the degradation and possible crosslinking at high concentration. The lowest mixing rate (60 rpm) or highest extruder mixing time yield the best dispersion of the EPDM into the PP matrix. The 15% carbonates is the best condition because have good reinforcement and do not form agglomerates.

The increase of impact resistance of vulcanized mixtures compared with the physical samples of functionalized polymers is due to increase of interaction by the formation of the copolymer PP-TAC- EPDM (Figure 6), as determine by infrared spectra (not shown).

Hardness Shore A and MFI

Table 6 presents the hardness values for the different mixtures. The behavior is contrary to the impact resistance. The mixture with highest hardness presents the lowest impact resistance.

The MFI values for the mixtures are higher than the MFI of PP indicating that the DCP caused PP scission. The degree of scission is different for the different samples since the DCP contents are different for each sample. The PP scission increases with increasing DCP concentration and mixing speed.

Conclusions

Taking into account the several factors that affect the degree of grafting such as the reaction time, temperature and mixing rate,

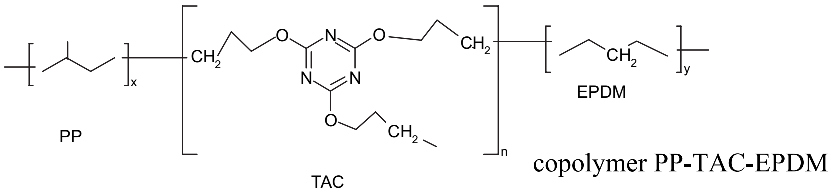

Figure 6.
Block copolymer PP-TAC-EPDM.

Table 6.
Hardness and MFI Results of the TPV PP/EPDM Mixtures

N°	MFI (g/10 min)	Hardness (Shore A)
1	18.57	25.1
2	35,45	25.8
3	19.16	25.7
4	18,66	18,7
5	50,12	25.7
6*	12.54	28,4

* Mixture of PP/EPDM functionalized.

we can conclude that graft efficiency is good since the EPDM utilized has only 4.6% of ethylydenenorbornen. The impact resistance for physical samples of functionalized polymers increases compared to the physical mixtures of non functionalized polymers but increases even more for the TPV mixtures, since the interaction between the polymers is higher for them due to the coupling agent TAC which forms PP-TAC- EPDM in-situ. The MFI is adequate for injection molding.

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