

Thermal and Rheological Behavior of Reactive Blends from Metallocene Olefin Elastomers and Polypropylene

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Abstract: Reactive blends of metallocene polyolefin elastomers (POE)/polypropylene (PP) with 60/40 composition were prepared with an organic peroxide, 2,5-dimethyl-2,5-di-(t-butylperoxy)hexane, and a bis-azide derivative, diphenyloxid-4,4'-bis(sulfonylazide) (BSA). Ethylene-1-butene (EB) and ethylene-1-octene (EO) copolymers and elastomeric polypropylene (ePP) were used as the elastomeric phase. The effect of elastomeric phase on the thermal, rheological, morphological and mechanical properties of the thermoplastic vulcanizates (TPVs) or dynamic vulcanizates were studied. All TPVs depicted pseudoplastic behavior and blends cured with azide curative showed higher viscosities. The TPVs showed both dispersed and continuous phase morphology that depends on the elastomeric phase type revealing a limited degree of compatibility between PP and the elastomers EO or EB. On the other hand, the TPV PP/ePP showed a uniform morphology suggesting an improved compatibility. Substantial changes observed in physical properties were explained on the basis of blends' morphology and dynamic vulcanization. The results confirm that the mechanical properties are more influenced by the elastomeric phase than by the curative agent. This study revealed a broad new range of opportunities for POE-based TPVs.

Keywords: *Reactive blend, thermoplastic vulcanizates, metallocene polyolefin elastomers, rheology.*

Introduction

Thermoplastic elastomers (TPEs) based on rubber and plastic blends are materials that combine properties of thermoplastic and elastomeric materials, not achievable by other means. Thermoplastic Vulcanizates (TPVs) – a sub-class of TPEs^[1], are engineering materials obtained by blending elastomeric and plastic polymers through a process called dynamic vulcanization^[2]. Dynamic vulcanization is a process in which the elastomeric component is vulcanized in situ under continuous flow and shear to avoid coalescence and expedite dispersion. This process produces a characteristic and stable morphology where the crosslinked elastomer can become the dispersed phase with dimensions on the order of 1 μm , immersed in the thermoplastic matrix. The TPV morphology is attained even if the thermoplastic polymer is present as the minority component^[3], and the material shows elastic properties at room temperature approaching those of thermoset elastomers, and even can be melt reprocessed. These materials were first described by Gessler^[2], and commercially introduced in the 70's by Fisher^[4], and studied by several authors having a wide variety of elastomer-plastic systems afterwards^[5-11]. In particular, the most significant work in TPV technology was developed by Coran yielding "fully" crosslinked compounds^[6].

Rubber elasticity of TPV is usually attributed to a result of combined factors as morphology, plastic matrix, processing conditions, dispersed rubber microstructure and its particle size domains^[7]. In recent work, Arroyo^[8] summarizes the long time regarded knowledge that optimum dispersion of rubber particles guide to superior physical properties and are practicable by matching viscosities of the polymer pair. Also, some reports indicated that due to the small interfacial tension and the limited degree of compatibility, the methylol-phenolic crosslinked

ethylene-propylene-diene terpolymer/polypropylene (EPDM/PP) pair had presented the best balance of physical properties and achieved the biggest commercial significance^[9-10], calling attention of many industrial players and a large number of academic researchers^[11-23].

The advent of Metallocene Single-site Constrained geometry catalysts allowed the production of tailor made polymers with narrow molecular weight distribution and consistent co-monomer incorporation in levels not achievable by using conventional Ziegler-Natta type of catalysts^[18,19]. New polymer families of ethylene α -olefin copolymers with elastomeric behavior are now commercially available, reported as impact modifiers for polypropylene rich blends^[20], and recently it had been considered for use as modifiers in soft olefin based blends^[21], and TPVs^[22,23].

In addition to this scenario, Waymouth and co-workers^[24] reported a new way to synthesize a thermoplastic elastomeric PP based on an unbridged metallocene using oscillating stereo control. The isotacticity of the polymer, described by the isotactic pentad content, namely measured by the [mmmm] content, suggests a block structure PP with different stress-strain profile and unusual elastomeric properties. Whereby they are claimed elastomeric in its nature, and also could potentially play a role in dynamic vulcanized blends both as a plastic matrix or even as a dispersed elastomeric phase provided using a suitable curing agent^[25].

The emergent new classes of polyolefin elastomers (POEs) coupled with dramatically improved means of controlled synthesis through metallocene-catalyzed polymerization and with new alternatives for curing polyolefins^[26] have opened up a wider range of potential commercial applications than ever thought possible in TPE/TPV arena.

The present study focuses on the properties of blends using random polypropylene copolymer (PP) as the hard component and polyolefin elastomers (POE) as the soft ingredient. The POEs consists of two (ethylene- α -olefin) copolymers, and one elastomeric polypropylene are metallocenic polymers. The blends compositions contain higher concentration of the elastomeric component and were evaluated before and after the dynamic vulcanization. The material characterization is mainly concerned with the polymer crystallization, melt rheology, viscoelastic behavior, physical properties, and morphology of such blends.

Experimental

Typical properties of the PP and the POEs employed in this work are listed in Table 1. Both (ethylene- α -olefin) copolymers, poly(ethylene-1-butene) (EB) and poly(ethylene-1-octene) (EO), and the elastomeric polypropylene (ePP) were produced with commercial metallocene catalysts, and were used as elastomeric phase in the blends with a commercial Ziegler-Natta polypropylene as described in a previous paper²⁷.

The blends and TPVs formulations (in phr) are described in detail in Table 2. The polymers were melt blended at 190 °C in a Haake Mixer using small bowl (69 cm³) with cam type rotors at 75 rpm. All raw materials were used as received. First the PP and the elastomer were added until melting, followed by the plasticizer and last the curative and co-agent until constant torque is reached. The blends and the TPVs were prepared with constant elastomer/plastic ratio of 60/40 (w/w). Two different curatives were evaluated an organic peroxide: 2,5-dimethyl-2,5-di-(*t*-butylperoxy)hexane, and a bis-azide derivative: diphenyloxid-4,4'-bis(sulfonylazide) (BSA). After removed from the mixer, the mixtures were compression molded in a hot press at 190 °C and then cold pressed to cut samples for testing.

Differential scanning calorimetry was carried out on a TA Instruments DSC 2920, using a three step technique with cooling

Table 1. Properties of polymers used in this study.

Resin	Density	Melt Index	Comonomer
	g.cm ⁻³	dg/min	(wt. (%))
	(ASTM D-792)	(ASTM-1238)	
PP	0.902	1.5 ^a	n.m.
EO	0.863	1 ^b	38
EB	0.880	0.8 ^b	20
ePP	0.866	9 ^b	[mmmm]=43%

^a230 °C; ^b190 °C.

Table 2. Formulations of POEs/PP blends and dynamically cured TPVs.

	EO			EB			ePP		
	EO1	EO2	EO3	EB1	EB2	EB3	ePP1	ePP2	ePP3
Curative type	--	Peroxide ^a	BSA ^b	--	Peroxide	BSA	--	Peroxide	BSA
Curative level	0	1.0	0.3	0	1.0	0.3	0	1.0	0.3
EO	100	100	100						
EB				100	100	100			
ePP							100	100	100
PP					67				
Paraffinic oil ^f					30.0				
Coagent ^d					0.3				
Antioxidant ^e					1.0				

^aPerkadox 101(Akzo Chemicals) 2,5-dimethyl-2,5-di-(*t*-butylperoxy)hexane; ^bBSA (Nobel Dynamite) diphenyloxid-4,4'-bis(sulfonylazide); ^cSunpar 2280 (Shell); ^dPermalink 300 (Akzo Chemicals) tri allyl cyanurate (TAC); ^eIrganox 1076 (Ciba) octadecyl-3,5-di-(*t*-butyl-4-hydroxyhydrocinamate).

and heating rates of 10 °C/min, to determine the melting point and relative crystalline content.

Rheological properties, as a function of shear rate, were examined using a Rheometric Scientific, Inc ARES (Advanced Rheometric Expansion System) dynamic mechanical spectrometer, at 190 °C, using dynamic frequency range from 0.1-100 rad/s parallel-plate mode with a 2 mm gap and 15% strain. The samples were loaded and compressed to 2.1 mm, trimmed and compressed to the final 2 mm gap. The tests were run after the equilibration step (400s hold, no strain). Power law flow index (*n*) and Rheology Ratio (RR) were calculated from the linear regression of log shear stress vs log shear rate plots and from the $\eta_{app}^{0.1 \text{ rad/s}}$ divided by $\eta_{app}^{100 \text{ rad/s}}$ relationship respectively.

The blends were examined in a Scanning Electronic Microscope and captured with a Philips EM400T SEM operating at 5 kV. Samples were cryogenically fractured in liquid Nitrogen, etched with hexane and then gold coated to protect the surface.

Stress-strain data were obtained using an Instron model 1123 with a 1 kN load cell and a constant crosshead speed of 127 mm/min performed according ASTM procedure 1708 at room temperature. Shore A was recorded 10s after contact with the sample.

Results and Discussion

The properties of POE/PP blends and dynamic vulcanizates were studied as function of the elastomeric component (EO, EB and ePP) and crosslinking agent type (organic peroxide and BSA). All the components have the same chemical nature and a certain degree of crystallinity due to the long crystallizable sequences of ethylene in the (ethylene- α -olefin) copolymers and isotactic propylene blocks in the elastomeric iso-block PP. At 190 °C, during the melt mixing for the blends preparation, the polymers reach the amorphous state and crosslinking occurs between the polymers chains in the melt. At the end of the process the temperature decreases and the polymers partially re-crystallize, since the dynamic vulcanization process hinders the polymers crystallization by thermodynamic or/and kinetic factors. At room temperature, independently of the POE component used the dynamic vulcanizates showed elastomeric behavior as will be presented in the following discussion.

Thermal properties

Figure 1 shows the second heat DSC endothermic curves of the POE/PP blends over the temperature range of -100 to 200 °C and Table 3 summarizes the thermal properties determined for the pattern polymers and POE/PP blends and TPVs. As expected, the random propylene copolymer (PP) endothermic curve displays

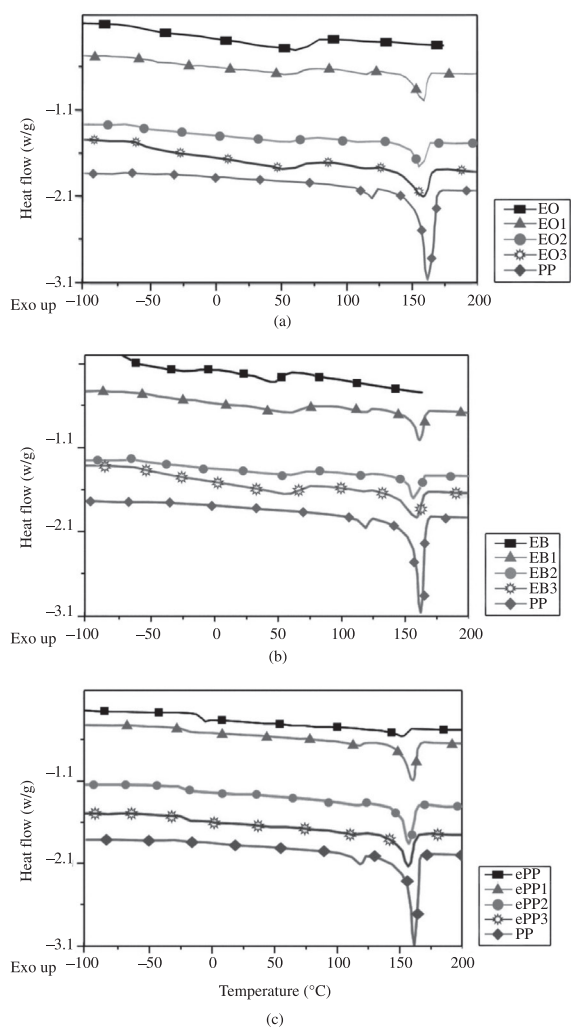


Figure 1. Second heat DSC plots for (a) EO, (b) EB and (c) ePP blends with PP and dynamic vulcanizates.

Table 3. Thermal Properties from DSC.

	Tc (peak)	Tm (peak)	Total Xtal %
PP	118.0	162.5	29.4
EO	42.3	57.2	17.7
EO1	106.7	162.1	9.8
EO 2	114.2	155.2	12.7
EO 3	131.6	159.0	13.6
EB	48.5	61.6	17.0
EB1	118.8	160.9	10.0
EB2	114.8	155.5	14.1
EB3	120.7	159.9	14.8
ePP	78.1	152.4	6.0
ePP1	105.8	159.7	13.7
ePP2	108.0	158.0	13.6
ePP3	125.8	157.4	12.5

a sharp melting peak at 162.5 °C, characteristic of the α -form of iPP, and a weak peak at 120 °C due to a small polyethylene (PE) fraction^[28]. In contrast, both EO and EB copolymers present a broad melting range with peak apex at 57 and 61 °C, respectively. In the EO2, EO3, EB2 and EB3 TPV the PE crystallization is hindered

since the endothermic peaks tends to disappear showing that the PE molecules must be involved in the chains crosslinking process. On the other hand, the PP melting peak also decreased significantly by the same reason or by others effects related to kinetic factors since at the PP crystallization temperature range the entropy is higher due to the higher mobility of the (ethylene- α -olefin) copolymers, which Tg values are much lower than that showed by the PP. As could be observed (Table 3), regarding the pattern polymers, there was a decrease in the crystallinity content of all POE/PP blends and TPVs and thus an increase in the amorphous content of the final material. As noted already, the residual crystallinity acts, in blends and TPVs, as a physical crosslink totally reversible by changing the temperature. The ePP endothermic curve shows a single and very weak peak at 152 °C and a noticeable transition temperature (Tg) at -6 °C. In contrast, in the ePP/PP blends and TPV the PP melting peak remains stronger than in the POE/PP ones, since it contains crystallizable isotactic sequences similar to those in the PP which ones may co-crystallize. The higher decrease in the crystallinity of the ePP/PP blend and TPV related to the POE ones is much more a consequence of the lower crystallinity of the ePP than due to hinder effects. In this case, the chains crosslinking seems to be less effective since there was no variation in the ePP/PP TPV crystallinity compared to the simple blend ePP1.

The melting process associated with both the elastomeric and plastic phases was evident in all blends of PP with EO and EB by the three peaks characteristics of the melting of α -olefin copolymer, of the polyethylene fraction and of the α -form of PP. The advent of the chain crosslinking maintained higher the overall crystallinity. It is known that rubber phase alters the crystallization structure of a plastic matrix^[15], by changing the number and average size of spherulites induced. Thus both EO and EB copolymers decreased the PP crystallinity and in the TPV they are preferentially crosslinked among them and with the PE chains of the random PP since the peak at 120 °C disappear in the DSC curve. On the other hand, the ePP1 blend, a broadened PP copolymer envelope is observed followed by a decrease in total crystallinity, suggesting a higher degree of miscibility between the pair since the chains of both PP may co-crystallize during cooling of the mixture (Figure 1-c).

Rheological behavior

The effect of shear rate on the log of apparent viscosity at 190 °C over the shear rate range of 0.1-100 rad/s is depicted in Figure 2 (a to c) for the POE/PP blends and TPV. It was observed that the viscosities of neat polymers and all blends decreased by increasing the shear rate, as reported previously^[26]. Likewise simple blends of PP and EO follow the additivity principle as described by Ferry^[29]. The power law relationship was calculated according to $\sigma = K\dot{\gamma}^n$, where K is the consistency, and n is the flow exponent. The results obtained are reported in Table 4. As far as n flow index is considered the higher the value suggests that the material is less shear sensitive in the Power Law region of the spectrum.

It can be observed the value of n decreases and Rheology Ration (RR) increases when samples are dynamically cured, what was specially noted when the azide derivative is used as crosslinking agent^[7]. Again dependency of blend composition and morphology are playing a major role to define rheological properties^[30].

For POE/PP reactive blends, EO2, EO3 and EB2, EB3, a typical behavior of a crosslinked material is observed due the use of peroxide and the azide. Thus at low frequencies the dynamically vulcanization imposes a higher viscosity when compared to the non-crosslinked blends, EO1 and EB1. However both cure agents increase the shear sensitivity as the viscosity drops with increasing

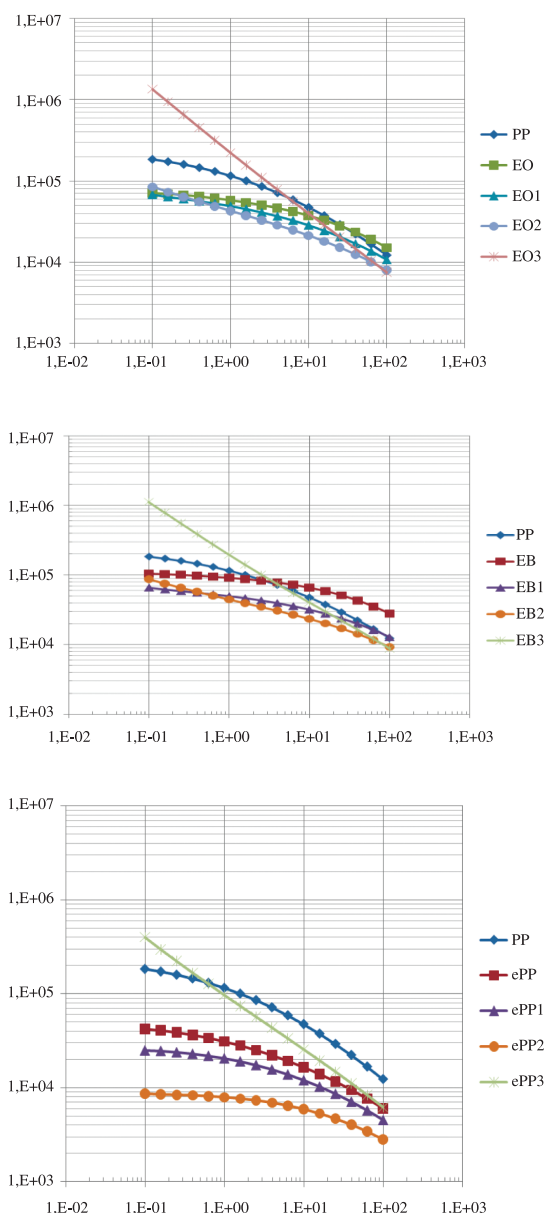


Figure 2. Apparent viscosity profile for (a) EO, (b) EB and (c) ePP polymers and its blends.

Table 4. Rheological Parameters of the materials studied and their blends.

	n^a	RR^b	η_{app} 100 rad/s	$\frac{\eta_{PP}/\eta_{POE}}{\phi_{POE}^c/\phi_{PP}^c}$
PP	0.36	14.9	12291	--
EO	0.52	4.7	15106	1.22
EO1	0.50	6.4		
EO2	0.52	10.6		
EB	0.52	3.8	27755	0.66
EB1	0.52	5.2		
EB2	0.53	9.4		
ePP	0.50	7.5	5996	3.08
ePP1	0.51	5.5		
ePP2	0.61	3.1		

^aFlow index from power law region of the curve; ^bRheology Ratio = η_{app} 0.1 rad/s/ η_{app} 100 rad/s; ^cViscosity Ratio 190° and 100 rad/s; values >1 POE tends to be the continuous phase; <1 PP tends to be continuous.

angular frequency, consistent with the values for Rheology Ratio presented in Table 4. As one can see for ePP2 the effect of peroxide decreases the viscosity probably due the degradation of both polymers as suggested before, nevertheless the azide acts the same way as for the ethylene copolymers increasing viscosity and shear thinning. It is also important to point out that all the azide modified blends showed higher viscosity, probably because it allows the interaction between both phases extending some grafting and part of the crosslink to the thermoplastic matrix^[31].

Blends Morphology

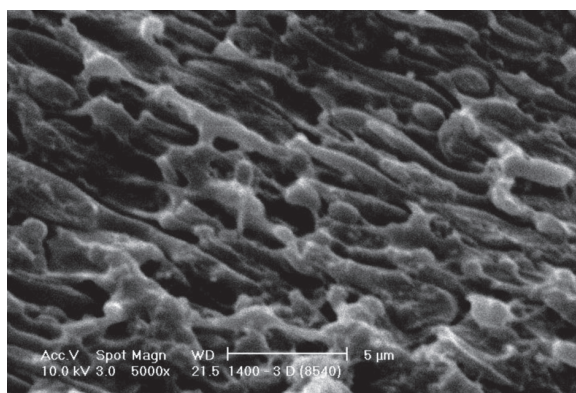
The interfacial chemistry control and the polymer microstructure are key variables to the development of multiphase morphology during processing in polymer blends. Eventually the objective of blending two polymers is to create novel materials with synergic properties and the developed morphology plays an important role defining blend properties. In order to guarantee blend homogeneity it is crucial to attain good interaction at interface and stabilization of morphology during processing^[32]. Among the important parameters for droplet formation and breakup in viscoelastic fluids are viscosity and elasticity ratios, interfacial tension, blend composition and type of flow^[33]. An extensional flow field as present in an internal mixer is believed to be more effective for tread formation and breakup, moreover a broader viscosity ratio can be used and still lead to small particle size^[34]. Usually for polyolefins the interfacial tension is low enough to not significantly affect the morphology. The co-continuity in polymer blends was described by Paul and Barlow^[35], which obey the rheological viscosity/volume fraction equation expressed as $\frac{\eta_P}{\eta_E} \cdot x \frac{\phi_E}{\phi_P} \cong 1$, where P ascribes for plastic and E for elastomeric phases, respectively. When the left side value of the equation is greater than 1, the elastomer tends to be the continuous phase, when it is less than 1, the plastic shows the tendency to be continuous.

Table 4 shows the volume fraction for each system under study and dual-phase morphology is foreseen. We included the torque data collected during mixing for pure polymers for the sake of comparison, which also shows a good correlation with the polymer viscoelasticity and morphology prediction. Utraki^[36] reported the critical volume fraction for a continuous phase, ϕ_{cr} is around 0.156 supporting the SEM micrographs trend towards dual-phase continuity. Same behavior was observed for EPDM-PP blends^[13]. In 1998 Coran^[11] presented an extensive study about SEM sample preparation to evaluate morphology development of HDPE/NR, indicating that SEM has some advantages over complex TEM's sample preparation.

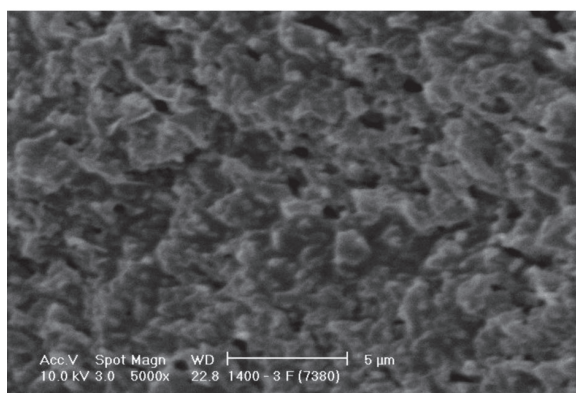
Figure 3 depicts the electron scanning micrograph of the POE/PP (60:40) blends surface after cryofracture and etching off the elastomeric phase.

Main problem for elastomer rich blends is the lack of plastic to keep rubber particles apart. The nodular nature of phases for elastomeric α -olefins is consistent with a shear dispersion mechanism, and a spinodal decomposition followed by coarsening mechanism from a soluble system is not likely to occur. This indicates a limited degree of compatibility between the polymers, which suggests that the comonomer type does not affect this feature.

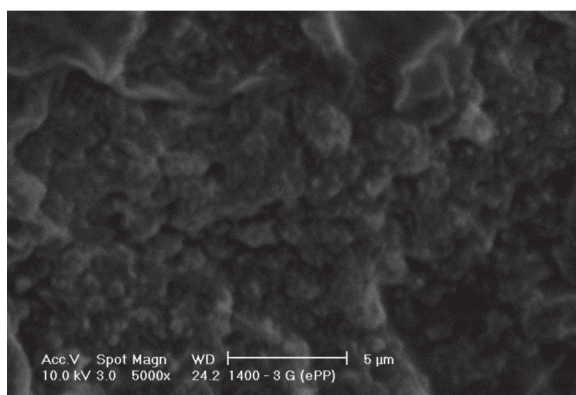
On other hand the ePP/PP blends (Figure 3c) blend showed a uniform morphology in SEM analyses suggesting an improved compatibility between the phases. As expected, dynamic vulcanizations leads to phase inversion (Figure 4), and a new morphology is developed where small domain dispersed particles of elastomer prevails. The substantial changes observed in physical properties can be explained on the basis of morphology and dynamic vulcanization^[37].



(a) EO1



(b) EB1

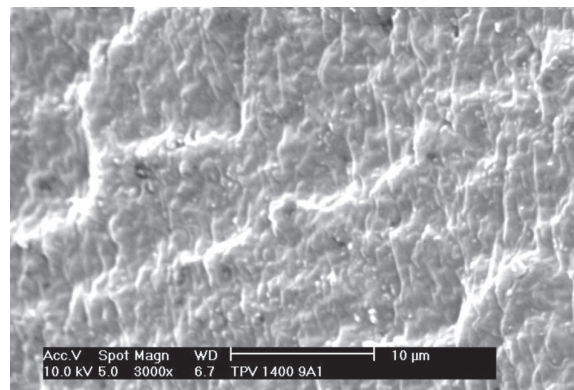


(c) ePP1

Figure 3. SEM of a 60:40 bi-blends of POEs and PP.

Mechanical properties

Table 5 shows the physical mechanical properties for the POE/PP blends. The blends named EO1 and ePP1 showed intermediate result between the pure components, while EB1 becomes more elastic. When POE phase is continuous, it will also provide some elastic response at the experiment's time scale specially if it is semicrystalline and the polyethylene has long chain branching^[38]. In case of more compatible blends such as EB/PP, it is expected that long chain branching promote entanglements across the interface, suggesting that the 1-butane rich fraction of EB is incorporated into the amorphous region of the polypropylene. After cooling,

**Figure 4.** SEM of dynamic vulcanized blend EO2.

such locked-in molecules should improve interfacial adhesion. The spherulites then are deformed and plastic deformation occurs during elongation, meanwhile the EO/PP blends are more incompatible showing lower elongation due to disruption of crystallites, decreasing the overall crystallinity of the blend accompanied by segregation between the phases. A rapid expansion of supercritical solution study^[39] reported slight thermodynamic miscibility of polypropylene EB copolymer (80% wt. 1-butene) with polypropylene in the molten state, typically the lower co-monomer level reduces miscibility. Once again crosslink of rubber phase helps to reduce domain of dispersed particles.

In the cure of (ethylene- α -olefins) copolymers with peroxides, the mechanism of crosslinking resultant from the recombination of a secondary alkyl macroradical^[40] is the dominant reaction path, and with polypropylene it is known the deleterious effect of peroxides explained by β -scission. Such effect is minimized by addition of co-agents, typically reactive polyfunctional monomers that minimize undesirable polymer disproportionation and scission, suggesting that the double bonds of the multifunctional monomer stabilize the free radical of polymer, therefore increasing crosslink efficiency. Lopes recently reviewed^[12] a benzene sulfonyl azide derivative for an EPDM based TPV, as an alternative to overcome peroxide chain scission of PP. It acts through C-H insertion bond on both phases EPDM and polyolefin, matching crosslink density needed and performing better than sulfur curatives.

The data on Table 5 shows that at lower levels of curative a slight increase in properties occurs suggesting that both crosslink and vis-broken are occurring.

The use of peroxide in the POE/PP blends caused a decrease in elongation. This effect is magnified in the ePP2 compound were peroxide curative causes loss of properties, probably due the effect on both polymers with reduction on average molecular weight by chain scission. In semicrystalline polymers, the residual crystallinity at a given temperature is the major responsible for the properties therefore; the dynamic vulcanization is expected to improve the properties, unless the crosslinks act as local defects reducing the total crystallinity of the system. Accordingly, the variation of the thermal properties values for the TPVs studied corroborates these results (Table 3). Azide crosslinked blends (EO3, EB3, and ePP3) showed tensile stress-strain curves typical of hard and brittle polymer, while peroxide modification imparted softness and toughness. Although a not fully crosslinked elastomeric phase is achieved obviously this process can be advantageously used to improve high temperature properties of such blends even at low gel levels without affecting thermoplastic workability^[30,41].

Table 5. Curatives effect on physical properties of POEs/PP TPVs and blends.

	EO			EB			Epp		
	EO1	EO2	EO3	EB1	EB2	EB3	ePP1	ePP2	ePP3
Curative type	--	Peroxide	BSA	--	Peroxide	BSA	--	Peroxide	BSA
Curative level	0	1.0	0.3	0	1.0	0.3	0	1.0	0.3
Hardness [Shore A]	80	82	87	76	87	88	89	86	89
Tensile Strength [MPa]	16,1	9.7	13.7	7,5	7.4	17.5	11.9	11.0	14.1
Elongation at Break [%]	913	504	213	980	193	260	923	735	600
Gel Content [%] ^a	0	37.5	3.5	0	24.5	0.0	0	11.3	1.9

^aASTM D-2765.

Conclusions

The properties of dynamically modified POE/PP blends were studied as function of the elastomeric component (EO, EB and ePP) and crosslinking agent (organic peroxide and BSA). The effect of dynamic vulcanization in the thermal, rheological and mechanical properties of all blends is evident and can be explained on basis of morphological changes. Power law behavior was observed after reaction with curing agents, suggesting phase inversion also in accordance with microscopy. The use of BSA as a modifier for POE/PP blends improved mechanical properties without adverse effects on flow and processability. The use of this technology combined with the unique properties of elastomeric polypropylene and new metallocene ethylene-copolymers availability will open a broad new range of opportunities for POE based TPVs.

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References

- Legge, N. R.; Holden, G.; Quirek, R. & Schroeder, H. E. (eds.). – “Thermoplastic Elastomers”, Hanser publishers, New York (1996).
- Gessler, A. M. & Haslett, W. H. – “Process for preparing a vulcanized blend of crystalline polypropylene and chlorinated butyl rubber”, Patent US3.037.954 (1962).
- Thomas, D. A. & Sperling, L. H. – “*Interpenetrating Polymer Networks*”, in: *Interpenetrating Polymer Networks*, S. Newman & D. R. Paul (eds.): Academic Press, New York (1978).
- Fisher, W. K. – “Thermoplastic blend of partially cured monoolefin copolymer rubber and polyolefin plastic”, Patent US3.758.643 (1973).
- Gomes, A. C. O.; Soares, B. G.; Oliveira, M. G. & Paranhos, C. M. - *Polimeros*, **19**, p.196 (2009).
- Coran, A. Y.; Das, B. & Patel, R. P. – “Thermoplastic vulcanizates of olefin rubber and polyolefin resin”, Patent US4.130.535 (1978).
- Coran, A. Y.; Chung, O. & Laokijcharoen, P. - *Kaut. Gummi Kunst.*, **51**, p.342 (1998).
- Lopez-Manchado, M. A.; Arroyo, M. & Kenny, J. M. - *Rubber Chem. Technol.*, **74**, p.211 (2001).
- Coran, A. Y. & Patel, R. - *Rubber Chem. Technol.*, **53**, p.144 (1980).
- Wang, Z.; Cheng, X. & Zhao, J. - *Mater. Chem. Phys.*, **126**, p.272 (2011). <http://dx.doi.org/10.1016/j.matchemphys.2010.11.027>
- Chung, O. & Coran, A. Y. - *Rubber Chem. Technol.*, **70**, p.781. (1997). <http://dx.doi.org/10.5254/1.3538460>
- Li, Z. & Kontopoulou, M. - *Polym. Eng. Sci.*, **49**, p.34 (2009). <http://dx.doi.org/10.1002/pen.21265>
- Pechurai, W.; Nakason, C. and Sahakaro, K. – *Polym. Test.*, **27**, p.621 (2008). <http://dx.doi.org/10.1016/j.polymertesting.2008.04.001>
- Caihong, L.; Xianbo, H. & Fangzhong, M. - *Polym. Adv. Technol.*, **18**, p.999 (2007).
- Vennemann, N.; Bokamp, K. & Broker, D. - *Macromol. Symp.*, **245-246**, p.641 (2006). <http://dx.doi.org/10.1002/masy.200651391>
- Nakason, C.; Worlee, A. & Salaeh, S. – *Polym. Test.*, **27**, p.858 (2008). <http://dx.doi.org/10.1016/j.polymertesting.2008.06.011>
- Cossa, M. M.; Costa, L. M. M.; Sirqueira, A. S.; Bretas, R. E. S.; Soares, B. G. & Gregório Filho, R. – *Polimeros*, **19**, p.190 (2009).
- Schellenberg, J. – *Adv. Polym. Technol.*, **16**, p.135 (1997). [http://dx.doi.org/10.1002/\(SICI\)1098-2329\(199722\)16:2%3C135::AID-ADV6%3E3.0.CO;2-V](http://dx.doi.org/10.1002/(SICI)1098-2329(199722)16:2%3C135::AID-ADV6%3E3.0.CO;2-V)
- Silva, A. L. N.; Rocha, M. C. G.; Guimarães, M. J. O. C.; Lovisi, H.; Coutinho, F. M. B. & Santa Maria, L. C. - *Polimeros*, **11**, p.135 (2001). <http://dx.doi.org/10.1590/S0104-14282001000300013>
- Huang, H. J.; Xie, B. H.; Yang, W.; Shen, Y. X. & Yang, M. B. - *J. of Macrom Sci - Part B*, **49**, p.231(2010).
- Guimarães, M. J. O. C.; Coutinho, F. M. B.; Rocha, M. C. G.; Bretas, R. E. S. & Farah, M. – *Polimeros*, **13**, p.135 (2003).
- Chee, H. J.; Min, J. H.; Byung, Y. L. & Chang, H. C. – “Olefin-based crosslinked thermoplastic elastomers and a process of preparation thereof”, Patent US6.143.828 (2000).
- Finerman, T. & Abdou-Sabet, S. – “Modification of thermoplastic vulcanizates with a thermoplastic random copolymer of ethylene”, Patent US6.399.710 (2002).
- Coates, G. W. & Waymouth, R. M. – *Science*, **267**, p.217 (1995). PMID:17791342. <http://dx.doi.org/10.1126/science.267.5195.217>
- Ternbrueggen, R. H.; Drumright, R. E. & Ho, T. H. – “Process for preparing thermoplastic vulcanizates”, Patent US6.277.916 (2001).
- Chodak, I. - *Prog. Polym. Sci.*, **20**, p.1165 (1995). [http://dx.doi.org/10.1016/0079-6700\(95\)98859-N](http://dx.doi.org/10.1016/0079-6700(95)98859-N)
- MacNally, T.; McShane, P.; Nally, G. M.; Murphy, W. R.; Cook, M. & Miller, A. – *Polymer*, **43**, p.3785 (2002).
- D’Orazio, L.; Mancarella, C.; Martuscelli, E.; Cecchin, G. & Corrieri, R. – *Polymer*, **40**, p.2745 (1999).
- Ferry, J. D. - “*Viscoelastic Properties of Polymers*”, Wiley and Sons, New York (1980).
- Babu, R. R.; Singha, N. K. & Naskar, K. - *J. Polym. Res.*, **18**, p.31 (2011). <http://dx.doi.org/10.1007/s10965-010-9388-2>
- Marinovic, T.; Susteric, Z.; Dimitrievski, I. & Vekšli, Z. - *Kaut. Gummi Kunst.*, **51**, p.189 (1998).

32. Favis, B. D. – Can. J. Chem. Eng., **69**, p.619 (1991). <http://dx.doi.org/10.1002/cjce.5450690303>
33. Tokita, N. - Rubber Chem. Technol., **50**, p.292 (1977). <http://dx.doi.org/10.5254/1.3535144>
34. Wu, S. - Polym. Eng. Sci., **27**, p.335 (1987). <http://dx.doi.org/10.1002/pen.760270506>
35. Paul, D. R. - Adv. In Chem. Series, **211**, p.3 (1985). <http://dx.doi.org/10.1021/ba-1986-0211.ch001>
36. Utracki, L. A. - “Polymer Alloys and Blends”, Hanser Publishers, New York 1989.
37. Eby, R. K.; Mareanukruoh, M.; Scavuzzo, R. J. & Preuschen, J. - Rubber Chem. Technol., **73**, p.912 (2000).
38. Guimarães, M. J. O. C.; Coutinho, F. M. B.; Rocha, M. C. G.; Farah, M. & Bretas, R. E. S. – Polym. Test., **22**, p.843 (2003).
39. Han, S. J.; Lohse, D. J. & Sperling, L. H. – J. App. Polym. Sci., **77**, p.1478 (2000).
40. Kim, B. K. & Kim, K. J. *Adv. – Polym. Technol.*, **12**, p.263 (1993). <http://dx.doi.org/10.1002/adv.1993.060120304>
41. Rowland, M. E.; Turley, R. R. ; Hill, J. J.; Kale, L. T.; Kummer, K. G.; Lai, S. Y. & Chum, P. S. – “Rheology-modified polyolefins”, Patent US6.114.486 (2000).

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