

Influence of Type of Vulcanization on Rheological and Thermal Properties of PP/NR Blends

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Summary

Rheological and thermal behavior of isotactic polypropylene (PP) and natural rubber (NR) blends were studied, with special reference to the type of vulcanization (dynamic and static). It was found that dynamic crosslinking of the NR phase increases the viscosity of the system, while it decreases crystallinity degree. Statically vulcanized blends show similar properties regardless curing time while dynamically vulcanized blends show enhanced properties if compared to the corresponding uncured blends.

Introduction

Polymer blends are gaining increasing industrial importance as a means of improving the overall properties and processability. In the last decades, several researchers have based their studies on thermoplastic-elastomer blends, since this type of blends combine the excellent processing characteristics of thermoplastics at higher temperature and a wide range of physical properties of elastomers at service temperature. In particular, melt flow studies of thermoplastic elastomer blends have become important in optimizing the processing conditions, and in developing new processing equipment and the dies necessary for the production of various types of extruded and injection molded products.

Different research groups have studied the rheological behavior of polymer blends and that of polymers containing gel and crosslinked particles [1-8].

Thermal studies have also been a point of interest for thermoplastic-rubber blends. Yoon et al [6] studied the reactive extrusion of polypropylene/natural rubber 90/10 blends in terms of thermal and mechanical properties. Norzalia [9] also studied the incorporation of a rubber phase into polypropylene, obtaining no noticeable change in degree of crystallinity, melting and crystallization temperatures.

The objectives of the present study were to explore the processability of PP/NR blends and to evaluate its rheological and thermal properties. Due to the complexity of NR processing in conventional thermoplastics equipment, an alternative method consisting of a combination of static and dynamic vulcanization was studied.

Experimental

Isotactic Polypropylene (PP) J-600 having a melt flow index (MFI) of 7 g/10 min (230 °C, 2.16 Kg) supplied by Propilven S.A and Natural Rubber SGR-10 (NR) were used. Mixing took place in a Berstorff ECS 2E25 co-rotating twin screw extruder at a temperature profile of 200 °C and screw speed of 200 rpm.

Vulcanized blends were prepared from the formulation shown in Table 1. Vulcanization methods employed were dynamic and static. For the dynamically cured blends (DV), all compound ingredients were physically blended and then fed into the twin-screw extruder for mixing and vulcanizing. In order to assure the crosslinking reaction of the NR phase during the extrusion process, rheometric curves were obtained using a Zwick oscillating disk rheometer at 210 °C, oscillation arc of 5° and torque range of 226.8 kgf.m. The 90% cure time value was set as the minimum residence time needed in the extruder so the dynamically vulcanization reaction could take place. Concerning statically cured blends (SV), vulcanization of the rubbery phase took place in a Carver Hydraulic press at 200 °C. Different curing times were employed (t_{30} , t_{50} , t_{70} and t_{90}) corresponding to 30, 50, 70 and 90% of maximum torque value obtained from rheometric curves. Partially vulcanized rubber sheets were then grounded and mixed with PP in the extruder according to conditions previously mentioned in order to continue vulcanization and obtain the so-called “statically vulcanized blends”.

Rheological measurements were done in a Göttfert capillary rheometer (model 2000) at different plunger speeds varying from 0.01 to 1.00 mm s⁻¹. The melt was extruded through the capillary at predetermined plunger speeds after a warm-up period of 6-8 min. Tests were done at a temperature of 200 °C. Melt Flow Index of extrudates was measured at 200 °C and 3.36 kg loading using a Davenport plastometer according to ASTM D1238. Thermogravimetric analysis was carried out in a Mettler Toledo TGA equipment. Samples were scanned from 30 to 600 °C at a heating rate of 5 °Cmin⁻¹ in nitrogen atmosphere. Initial decomposition temperature was calculated at the point where the derivative separates from the base line in graphs of weight loss (1- α) versus temperature. Thermal behavior of PP/NR blends was studied using a Mettler Toledo DSC821 thermal analyzer. This analysis was performed under nitrogen with a heating rate of 10 °Cmin⁻¹ up to 200 °C, and maintained for 10 min. Samples were then cooled to room temperature at constant cooling rate of 10 °Cmin⁻¹ with identical settings of the instrument for all the systems studied. Samples fractured under liquid nitrogen were observed by a scanning electron microscope Hitachi S-24000. Specimen's surface was coated with gold.

Table 1. Vulcanization system for natural rubber.

Ingredients	phr
NR	100
ZnO	5.0
Stearic acid	1.0
MBTS ^a	1.0
Sulphur	2.5

^a Dibenzothiazole disulfide

Results and Discussion

Rheological properties

Melt Flow Index (MFI) values give an idea about the processing behavior of polymers; even though the actual processing conditions (such as temperature and shear rate) employed in product development differ from those of the conditions used in MFI tests. However, MFI is widely calculated as an empirical parameter influenced by the physical properties and structure of the material. Results show that for a fixed ratio of 70/30 PP/NR the dynamically vulcanized blend presents lower values of MFI (1.9 g/10min) if compared to the respective uncured blend (8.4g/10min), since mobility of the polymer chain from the higher molecular weight NR micro gel decreased due to the chemical crosslinks. These results are in accordance with studies presented by several researchers, where a higher viscosity was achieved when a crosslinking agent was added to a dynamic vulcanization process [10].

The influence of curing time on the NR static crosslinking process was also studied. This analysis reflects that, as in dynamic crosslinking, MFI is lower when compared to the respective uncured blend regardless curing time. Moreover, Table 2 shows that MFI decreases slightly when static curing time of NR decreases, being the lower value obtained the one corresponding to 30% curing time. It should be reminded that for the so-called statically vulcanized blends, vulcanization time presumably continues in the extruder via dynamic vulcanization. Instead, for higher curing times (90%) the crosslinking mechanism of the NR phase takes place almost independently of the mixing with PP. So the final blend is formed by two incompatible phases, where the agglomerated NR particles are more subject to deformation, hence MFI increases.

If we analyze together both crosslinking procedures, one could presume that the dynamic process is more efficient, since the rubber phase is being vulcanized simultaneously with components mixing, by means of the shear action of the extruder screws, high temperatures and high pressures applied. This efficiency induces a rapid formation of a uniform three dimensional rubber network, with its corresponding increase on viscosity, hence lowering MFI [11].

Table 2. Melt Flow Index values for 70/30 PP/NR statically vulcanized blends.

MFI (g/10 min)			
90% curing time	70% curing time	50% curing time	30% curing time
5.0	4.8	4.6	4.5

Concerning capillary rheometry results, Figures 1 and 2 show the influence of shear rate on melt viscosity for all blends. In all cases, melt viscosity decreases with increasing shear rates indicating pseudoplastic nature, due to the random orientation and highly entangled state of the molecules, which under high shear are disentangled and become oriented, resulting in a reduction of viscosity. The decrease in viscosity at higher shear rate may also be due to the shearing away of the dispersed phase of the incompatible blend [3]. Besides, a considerable rise on viscosity is obtained when vulcanization takes place, especially at low shear rates (see Figure 1). The uncrosslinked rubber particles in the blend are elongated at the entrance of the capillary and are broken down into smaller particles whereas, the crosslinked particles

which are less deformable, retain the morphology of the blend. Similar results were obtained by Kuriakose [11].

If the effect of curing time on melt viscosity for the blends with statically cured NR is analyzed, Figure 2 shows that there are no significant differences when curing time changes. However, if vulcanization methods are compared, results indicate that the dynamically cured blend is the one with the highest viscosity (Figure 1). Firstly, upon dynamic crosslinking, the rubber phase is crosslinked and finally transformed into fine particles which are dispersed in the continuous PP matrix. This morphology is highly stable as the crosslinked particles are highly resistant to agglomeration, as it can be seen on Figure 3. Since crosslinked particles are less deformable, the system shows higher viscosity [11]. All these findings are in accordance with MFI tendency. Secondly, for the statically vulcanized blend crosslinked particles are more subject to deformation when a stress is applied. Moreover, statically cured rubber is presumably acting like a filler. At low shear rates, the high curing degree (SV 90%) makes the system more rigid; a relaxation process can take place in the rubbery phase in such a manner that a noticeable influence on viscosity is observed, while at high shear rates there is little influence of the dispersed phase on the system viscosity [12].

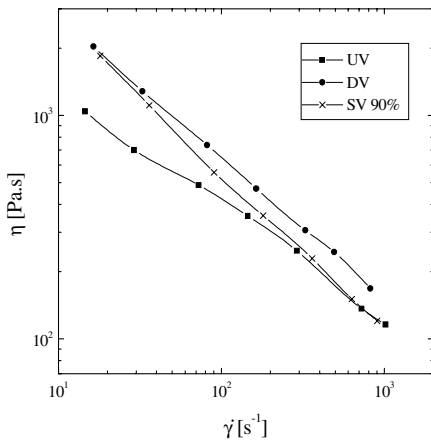


Figure 1. Influence of shear rate on melt viscosity for 70/30 PP/NR blends.

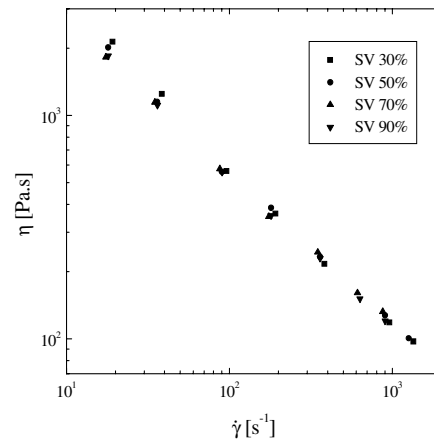


Figure 2. Influence of shear rate on melt viscosity for statically vulcanized 70/30 PP/NR blends.

An analysis of the Power Law followed by all blends was also performed. Table 3 shows the “n” (power law exponent) and “k” (consistency constant) calculated. The values presented in Table 3 confirm that the blends studied present a pseudoplastic behavior, since all “n” values are lower than unity. As explained earlier, the applied force disturbed the long chain polymer from its equilibrium position and the molecules were disentangled in the direction of the force, causing a reduction in viscosity [3].

Concerning the vulcanization method employed, one can see that the vulcanization process, static or dynamic, increases the pseudoplasticity of PP/NR blends. López et al. [13] and Ichazo et al. [2] obtained similar results for PP/EPDM and PP/SBS blends respectively.

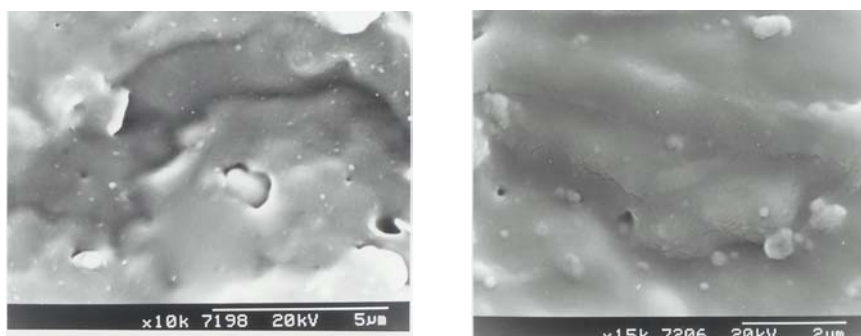


Figure 3. SEM micrographs of 70/30 PP/NR blends: (left) unvulcanized UV, (right) dynamically vulcanized DV.

Table 3. Power Law values for 70/30 PP/NR blends.

Blend	n	k (Pa.s ⁿ)
PP/NR UV	0.5034	2595.6
PP/NR DV	0.3712	3174.7
PP/NR SV 30%	0.2726	2348.6
PP/NR SV 50%	0.3065	2418.8
PP/NR SV 70%	0.3268	2427.8
PP/NR SV 90%	0.3059	2300.8

Thermal Properties

If thermal behavior is analyzed, one can see that with the incorporation of a rubbery phase to the blend, the melting peak (T_f) does not differ significantly from the pure polypropylene ($T_f = 162$ °C). However, there is a slight decrease on T_c when NR is present in the blend if compared to the pure polymer ($T_c = 119$ °C) indicating a dilution effect, thus retarding the crystallization process.

Concerning the blends statically vulcanized, there are no significant variations on T_c or T_f values; nonetheless, a decrease on fusion enthalpy is adverted since the crystallization process can be interfered by the vulcanization reactions. Moreover, fusion enthalpy decreases with increasing vulcanization time previous to mixing in the extruder. This is due to the fact that for smaller curing times (SV 30%), the vulcanization process (dynamic) can continue in a greater extent during extrusion, thus a smaller particle size can be achieved, acting this particles as nucleating agents. This cannot be observed in the micrographs presented due to the great difference in particle size between the agglomerates and the smaller particles. In the case of greater vulcanization times (SV 90%), NR particles produce local defects, not allowing the close packing of polymer chains (Figure 4). On the other hand, when the blend is

dynamically vulcanized, rubber particle size decreases and the crystallization process is less interfered, hence, fusion enthalpy increases if compared to the unvulcanized blend. Crystallinity degree of all blends respect to PP ($\Delta H_f = 121$ J/g) diminishes since the crosslinked NR particles may restrict the spherulitic growth and regular arrangement of the spherulites of PP (Figure 3).

Table 4. Thermal properties of 70/30 PP/NR blends.

Blend	T _c (± 1 °C)	T _f (± 1 °C)	ΔH _f (± 1 J/g)	T _{id} (± 1 °C)
PP/NR UV	115	163	74	317
PP/NR DV	115	163	86	322
PP/NR SV 30%	114	163	76	294
PP/NR SV 50%	115	164	75	292
PP/NR SV 70%	116	164	69	294
PP/NR SV 90%	114	164	63	292

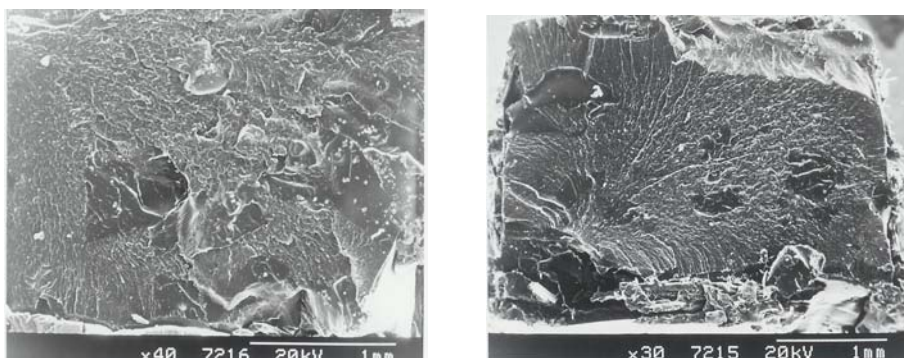


Figure 4. SEM micrographs of 70/30 PP/NR statically vulcanized blends: (left) SV 30%, (right) SV 70%.

Thermal stability of blends was determined using TGA technique. Figure 5 shows the thermograms obtained from PP/NR 70/30 blends unvulcanized (UV), dynamically vulcanized (DV) and statically vulcanized (SV 90%). It can be observed that in the thermograms of the unvulcanized or dynamically vulcanized blends there is only one slope. However, in the case of the statically vulcanized blend, two slopes are observed, which implies that two decomposition processes, one corresponding to PP and the other to the crosslinked rubber, are taken place. When increasing temperature, a change on decomposition mechanisms is adverted from the curves, depending on the percentage of vulcanization the rubbery phase has achieved.

On the other hand, it can be seen that T_{id} decreases for the blends statically vulcanized if compared to its unvulcanized peer, since vulcanized particles act like rigid fillers and the adhesion between phases is very poor as can be seen in Figure 4. These two factors accelerate the degradative process of the PP/NR blend. However, T_{id} slightly increases for the dynamically crosslinked blend.

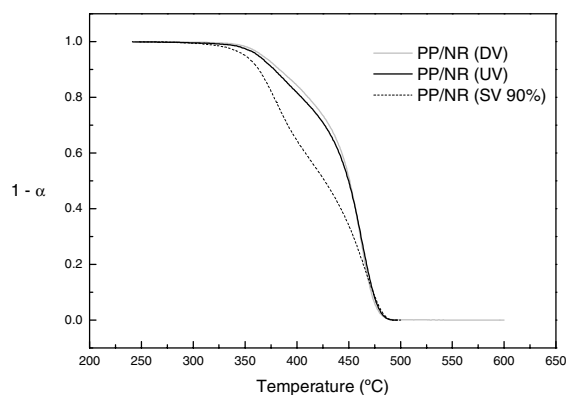


Figure 5. Thermogram of PP/NR blends unvulcanized (UV), dynamically vulcanized (DV) and statically vulcanized (SV).

Conclusion

Rheological and thermal properties of PP/NR blends statically and dynamically vulcanized have been studied. Results show that dynamic crosslinking of the NR phase increases the viscosity of the system. Also, melt viscosity of the blends decreases with increase in shear rate indicating a pseudoplastic nature. The low values of the flow behavior index confirm this pseudoplasticity. Statically vulcanized blends show similar rheological and thermal properties regardless curing time. However, the presence of NR retards the crystallization process of PP. In addition, a decrease in fusion enthalpy and decomposition temperature is adverted for statically crosslinked blends, while dynamic crosslinking gives better thermal stability to the PP/NR blend.

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