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Effects of Composition and Dynamic Vulcanization on the Rheological Properties of PP/NBR Blends

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Summary

Rheological behavior of isotactic polypropylene (PP) and nitrile rubber (NBR) blends, in the composition range of 10-30-wt % NBR content were studied, with special reference to the effect of blend ratio, dynamic vulcanization and compatibilization. All blends were prepared in a twin-screw extruder. Capillary Rheometry was employed. Pseudoplastic behavior of blends was favored by increasing rubber content. The incorporation of NBR into PP lowered activation energies. Compatibilization of unvulcanized blends did not produce significant changes on flow behavior. Dynamically vulcanized blends provide unique processing characteristics that enable to perform well in both injection molding and extrusion.

Introduction

The poor impact strength of polypropylene, especially at low temperature, has been overcome by melt blending with different elastomers such as ethylene-propylene diene rubber (EPDM), polyisobutylene (PIB) and styrene-butadiene block copolymer (SBS) (1). An approach to improve further the performance of rubber modified PP is to develop dynamically vulcanized thermoplastic blends (2-5). These blends have important technical advantages because they can be processed by such methods as extrusion and molding, even though they possess a cross-linked elastomer as one component. Several researchers have been working with PP/SBS blends (6), and with PP/EPDM (7), but not much work has been reported on systematic investigation of the effect of temperature on the rheological properties of unvulcanized and dynamically vulcanized PP/NBR blends. Besides, much of the studies done on these blends have employed internal mixers as main equipment. However, Cai e Isayev (8) found that the use of twin-screw extruders for dynamic vulcanization of Copolyester/ NBR blends resulted in a dispersed phase of smaller size and hence, better final blend properties. Blends of PP with NBR combine the excellent processing characteristics and tensile properties of PP with the oil resistance and flexibility of NBR. Nonetheless, these blends are incompatible and require compatibilization for better properties (9). In order to overcome the gross mutual incompatibility of olefin polymers and nitrile rubber such that compositions having improved ultimate properties can be obtained, the addition to the blend of polymers of a compatibilizing agent comprising a block copolymer having an olefin polymer compatibilizing segment chemically linked to a nitrile rubber-compatibilizing segment is proposed by A.Y.Coran (9). These compatibilizers are found to modify the morphology of the blends and improve the viscoelastic and mechanical properties (10). In this paper, we have studied the rheological properties of PP/NBR blends compatibilized and dynamically vulcanized. A very detailed study on activation energies at constant shear stress and constant shear rate was accomplished with the intention of discerning the influence of processing parameters on rheological behavior of blends, factor that has been scarcely studied.

Experimental

Propilven S.A supplied Isotactic Polypropylene (PP) J-600 having a melt flow index (MFI) of 7 g/10 min (230 °C, 2.16 Kg). Acrylonitrile-butadiene rubber (NBR) Arnipol BJLT having an acrylonitrile content of 30.5-34.5 % was obtained from Industrias PASA S.A. Maleic anhydride modified PP (MA-PP) Polybond 3150 supplied by Uniroyal Chemical was used as a compatibilizing agent.

NBR particles obtained from the bale were introduced in liquid nitrogen and immediately fed into a cutting mill in order to reduce its size. The unvulcanized PP/NBR blends of compositions 10, 20 and 30 wt % NBR content were prepared by melt mixing using a Werner and Pfleiderer ZSK-30 twin-screw extruder at a temperature of 210 °C and a screw speed of 60 rpm.. The binary blendsobtained are denoted as PP_0, PP_{10}, PP_{20}, PP_{30}, where the subscripts define the weight percentage of NBR in the blend. Dynamically vulcanized blends (30% NBR content) denoted as $PP_{30\text{-}v}$ were prepared from the formulation shown in Table 1. 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 NBR 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 0.5 Kp.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. Besides, both 70/30 PP/NBR blends unvulcanized and dynamically vulcanized were compatibilized with 5 wt % compatibilizer content. These blends are denoted as $PP_{30\text{-}c}$ and $PP_{30\text{-}v,\,c}$ respectively.

Rheological measurements were done in a Göttfert capillary rheometer (model 2000) at different plunger speeds varying from 0.01 to 5.00 mm s^{-1}. The melt was extruded through the capillary at predetermined plunger speeds after a warm-up period of 6-8 min. The tests were done at a temperature of 210 °C. However, for studying the effect of temperature, the samples were also analyzed at 190 and 230 °C. The morphology of the samples was analyzed using a scanning electron microscope Hitachi S-2400. The specimens were obtained from the extruded blends. They were prepared by cryogenically fracturing in liquid nitrogen and then coated with platinum/palladium.

Table 1. Formulation of dynamically vulcanized PP/NBR blends.

Ingredients	phr
NBR	100
ZnO	5
Stearic acid	2
CBS	2
TMTD	2.5
Sulphur	0.2

Results and discussion

The rheological curves for various PP/NBR blends are shown in Figure 1 (11). One can see that the melt viscosities decrease when shear rates increase indicating the pseudoplastic nature of the blends. This is because the randomly oriented and entangled polymer chains become oriented and disentangled on application of high shear rates, lowering the melt viscosity. Furthermore, in all cases the viscosity increases with increasing contents of NBR. This fact is more pronounced at low shear regions than at high shear regions as observed from the converging behavior of the flow curves at high shear rates. The thermoplastic/rubber blends can be considered as viscous emulsions where the elastomer, in droplets form, is dispersed into the plastic matrix. As the NBR content increases, the domain size increases. This is attributed to coarsening of NBR domains at higher concentrations, which makes it difficult for the material to flow and hence the viscosity increases (12). The micrographs shown in Figure 2 correlate this behavior.

Concerning Flow Behavior Index (n), the values shown in Table 2 obtained among unvulcanized PP/NBR systems do not differ very much from pure PP values except for the PP_{30} blend; George et. al (13) have reported such behavior for similar blends and Oomenn et. al (14) for PMMA/NR blends. This indicates that the addition of up to 20% of rubber does not affect markedly the flow behavior of PP. However, one can see that an increase in rubber content represents a slight decrease on flow behavior index, supporting the pseudoplastic behavior. Pseudoplasticity increases with the number of chain entanglements and with molecular weight, so the incorporation of rubber particles definitively favors this behavior. Similar results have been obtained with binary blends of PP/ABS (15) and with PE/UHMWPE (16), where pseudoplasticity increased with ABS content and UHMWPE respectively.

The ease of flow depends on the mobility of the molecular chains and the forces or entanglements holding the molecules together. That an increase in temperature decreases viscosity is widely known and in general is a property easily understood (17). The influence of temperature on melt viscosity of pure PP and the 70/30 PP/NBR blends unvulcanized and dynamically vulcanized was previously studied (11).

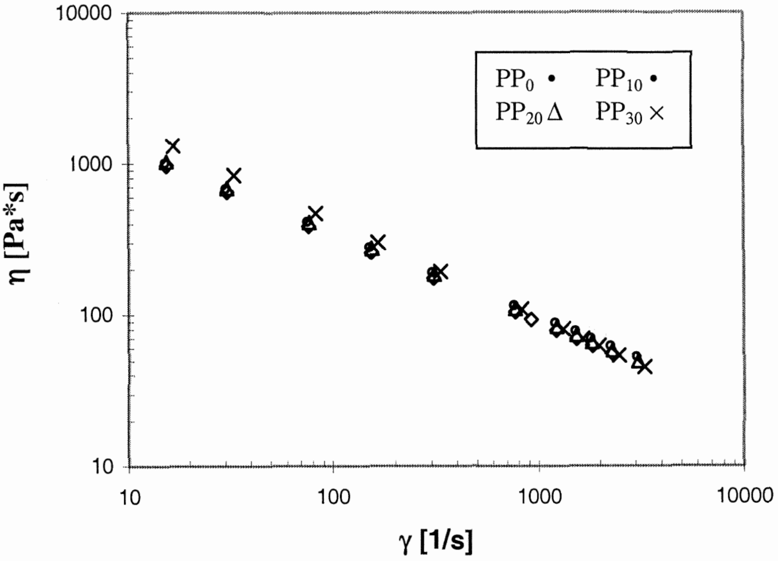
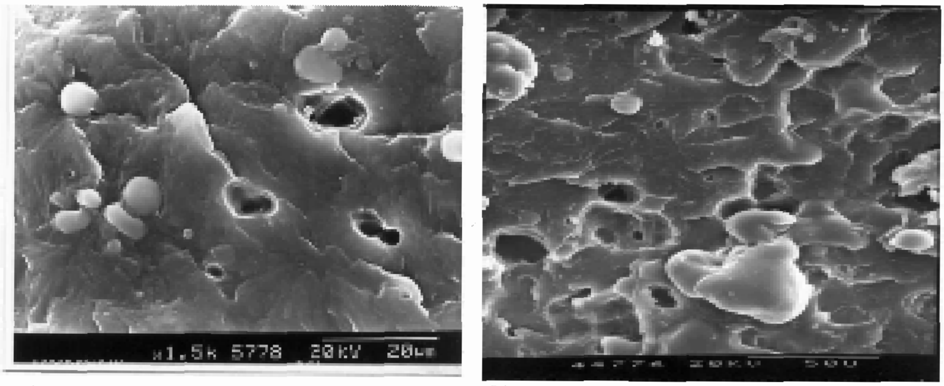


Figure 1. Effect of shear rate on the melt viscosity of unvulcanized PP/NBR blends (11).



a) **b)**

Figure 2. SEM micrographs of PP/NBR unvulcanized blends: a) PP_{10}, b) PP_{30}.

Results obtained (Figure 3) also indicate the addition of 30% NBR to PP lowers its sensibility to temperature even more at low shear rates, where the blend flow behavior depends markedly on rubber content. In the case of the dynamically vulcanized blend ($PP_{30\text{-}v}$), viscosity reduces upon increase in temperature from 190 °C to 210 °C, but rises from 210 °C to 230 °C. It is therefore assumed that at 230 °C the crosslinking mechanism of the NBR phase overshadows the degradation mechanism of the PP phase.

Activation energies calculated from the plot of log η versus 1/T (Arrhenius curves) are an important tool for studying the influence of temperature on viscosity. In this work, Tables 3 and 4 show the activation energies at constant shear rate and at constant shear stress for PP_0, PP_{30} and $PP_{30\text{-}V}$. Generally, the lower the activation energy, the less temperature sensitive the material's viscosity will be. One can see that blending PP with NBR decreases the activation energy, confirming that rubber phase incorporation makes the plastic/rubber blend less temperature sensitive. In addition, the activation energy for flow increases as the size of side groups increases and as the chain becomes more rigid. Therefore, the incorporation of NBR into PP furnishes flexibility to the system obtaining lower activation energies. Results also indicate vulcanization decreases chain mobility and activation energy by making the rubbery phase more rigid.

It is important to add that pseudoplastic behavior of all blends can be verified from the activation energies obtained, where the values at constant shear stress are always greater than the values at constant shear rates and that activation energy decreases upon increase in shear stress or shear rates. Based on results shown, it can be concluded that melt viscosity of PP/NBR blends results more sensitive to shear rates than to temperature.

Table 2. Flow behavior index for PP/NBR blends at 210 °C.

Blend	Flow index (n)
PP_0	0.43
PP_{10}	0.44
PP_{20}	0.43
PP_{30}	0.36
$PP_{30\text{-}c}$	0.36
$PP_{30\text{-}v}$	0.37
$PP_{30\text{-}v,\,c}$	0.34

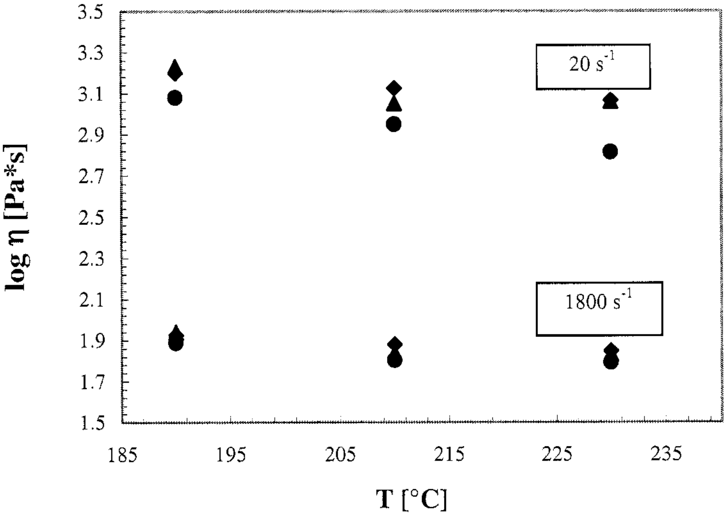


Figure 3. Effect of temperature on blends viscosity: PP_0 (•), PP_{30} (♦) and $PP_{30\text{-}v}$ (▲) (11).

This behavior has been confirmed on PP/EPDM blends (18, 19). In addition to evaluate rheological behavior of blends by determining Activation energies, these values are an useful issue for choosing the temperature to be fixed during processing routes such as extrusion, injection molding, etc.

The effects of dynamic vulcanization ($PP_{30\text{-v}}$) and compatibilizer addition ($PP_{30\text{-c}}$ and $PP_{30\text{-v, c}}$) on flow behavior index are also shown in Table 2. It is clear that neither the dynamic vulcanization nor the compatibilization of the unvulcanized blend produce significant changes on flow behavior index; however, for the dynamically vulcanized and compatibilized blend the n value does decrease. The compatibilizing action of MA-PP is due to the dipolar interaction between the maleic anhydride group of MA-PP and NBR. This causes a reduction in interfacial tension, which reduces the domain size of the dispersed phase (13). In this study, the addition of 5 wt % MA-PP produced a marginal reduction in particle size for the unvulcanized blend (Figures 2-b and 4-a). However, a reduction in domain size of 27% was seized for the dynamically vulcanized and compatibilized blend as shown in Figure 4-b). The size reduction explains the pseudoplasticity nature and decrease on n values, since small particle size favors interactions between domains, which are equivalent to more chain entanglements.

Table 3. Activation energies at constant shear rate for pure PP (PP_0), 70/30 unvulcanized (PP_{30}) and dynamically vulcanized ($PP_{30\text{-v}}$) PP/NBR blends.

γ (s^{-1})	$E\gamma$ (KJ/mol)		
	PP_0	PP_{30}	$PP_{30\text{-v}}$
20	12.90	6.49	8.30
60	10.90	5.82	7.56
120	9.63	5.41	7.10
600	6.70	4.43	6.02
1800	4.70	3.77	5.29

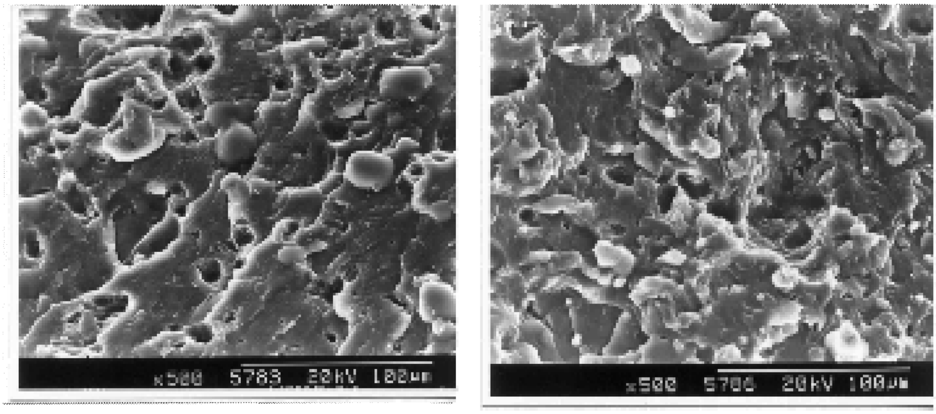
Table 4. Activation energies at constant shear stress for pure PP (PP_0), 70/30 unvulcanized (PP_{30}) and dynamically vulcanized ($PP_{30\text{-v}}$) PP/NBR blends.

τ (Pa)	$E\tau$ (KJ/mol)		
	PP_0	PP_{30}	$PP_{30\text{-v}}$
20000	28.85	19.34	23.15
50000	19.89	15.12	20.29
90000	14.15	12.42	17.18
150000	9.16	10.07	14.47
190000	6.85	8.98	13.22

The variation of flow behavior index with temperature was studied for pure PP and for 70/30 PP/NBR unvulcanized and dynamically vulcanized blends. Table 5 shows that a rise in temperature increases n values, that is to say a tendency to Newtonian behavior. One can see that variation among blends is less noticeable than variation with pure PP, confirming this fact the little sensitivity of blends to temperature. Then, it can be said that dynamic vulcanization could enhance the processing behavior of the studied blends, since they provide unique processing characteristics that enable to perform well in both injection molding and extrusion. The high viscosity at low shear rate provides the integrity of the extrudates during extrusion, and the low viscosity at high shear rate enables low injection pressure and less injection time. Besides, when working at high temperatures, a high production rate is obtainable with no noticeable loss of properties since temperature fluctuations do not affect the behavior of vulcanized blends.

Conclusions

Rheological behavior of isotactic polypropylene (PP) and nitrile rubber (NBR) blends was investigated. It was found that pseudoplastic behavior of blends was favored by increasing rubber content. Melt viscosity of PP/NBR blends was more sensitive to shear rates than to temperature. Activation energies at constant shear rate and constant shear stress decreased with the incorporation of NBR into PP and increased with dynamic vulcanization. Compatibilization of unvulcanized blends did not produce significant changes on flow behavior. Dynamically vulcanized blends provide unique processing characteristics that enable to perform well in both injection molding and extrusion.



a) **b)**

Figure 4. SEM micrographs of 70/30 PP/NBR blends: a) $PP_{30\text{-c}}$, b) $PP_{30\text{-v, c}}$.

Table 5. Flow behavior index variation with temperature for pure PP (PP_0), 70/30 unvulcanized (PP_{30}) and dynamically vulcanized (PP_{30-v}) PP/NBR blends.

Blend	**Flow Behavior Index (n)**		
	190 °C	**210 °C**	**230 °C**
PP_0	0.39	0.43	0.48
PP_{30}	0.35	0.36	0.38
PP_{30-v}	0.34	0.37	0.37

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