Comparison of Rheological and Mechanical Behavior of Dynamically and Statically Vulcanized PP/SBS Blends

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Summary

Rheological behavior of dynamically and statically vulcanized blends of isotatic Polypropylene (PP) and 20% wt Styrene-Butadiene-Styrene block copolymer (SBS) was studied with reference to the effect of extrusion conditions, curing agents (sulphur, peroxide) and curing times. All blends showed pseudoplastic behavior. When using sulphur, a slight increase on melt viscosity was observed, showing no differences with vulcanization method or with pre-vulcanization time. With peroxide, melt viscosity changed drastically. Dynamically vulcanized blends with sulphur showed a noticeable rise on elongation at break as well as on toughness while those statically vulcanized showed very low values on these properties.

Introduction

Considerable work has been carried out to improve the poor impact strength of polypropylene (PP) by incorporation of elastomers such as ethylene-propylene diene rubber (EPDM), polyisobutylene (PIB) and styrene-butadiene block copolymer (SBS)[1]. There are many ways to combine the desired features of each component of the blend. However, one effective approach is to prepare the blend by the dynamic curing method [2-3]. Improvements in properties from dynamic vulcanization include higher tensile strength, better elastic recovery, improved properties retention at high temperatures, greater resistance to attack and swell by fluids, greater stability of morphology and more consistent processability[4]. Further, dynamically vulcanized thermoplastic elastomer blends have been used in the plastics industry because of their advantages in processing; even with the presence of crosslinked elastomers, a thermoplastic nature can be obtained. Oomen et al.[5] and Kuriakose et al.[6] investigated the effect of various vulcanizing agents on the rheological behavior of PP/NR and HDPE/NR blends. Other researchers have been working with PP/SBS blends[7], and with PP/EPDM[8], but much of the studies done on these blends have employed internal mixers as main equipment. However, Cai e Isayev[9] found that the use of twin screw extruders for dynamic vulcanization resulted in a dispersed phase of smaller size and

hence, better final blend properties. Ichazo et al[10] studied the influence of vulcanization agents (sulphur and peroxide) on the rheological behavior of PP/SBS blends (90/10), where the rubber phase was statically cured. Sulphur cured systems showed higher viscosity values than peroxide cured systems attributing this behavior to the degradation of PP by peroxide. In this paper, rheological behavior of dynamically vulcanized PP/SBS 80/20 blends is studied, with special attention to the influence of shear conditions (screw speeds) and different curing systems (sulphur, peroxide). A comparative analysis is also made with blends where the 20% SBS phase is statically vulcanized before its blending with PP, with the intention of evaluating the possibility of using previously vulcanized rubbers as fillers for PP.

Experimental

Isotactic Polypropylene (PP) J-600 having a melt-flow index (MFI) of 7 g/10 min (230 °C/2160 g) was supplied by Propilven S.A. Styrene-Butadiene-Styrene copolymer (SBS) SOLPRENE with a density of 0.94 g/cm^3, a melt flow index of 6.4 g/10 min (200 °C/5000 g) and a styrene content of 30 % was supplied by INSA. PP/SBS blends dynamically vulcanized were prepared according to the formulations shown in Table 1 with concentrations of SBS of 10, 20 and 30 %wt and different curing systems. Curing agents for rubbers were sulphur (S) and dicumyl peroxide (DCP). The other components of the compound (tetramethyl thiuram disulfide (TMTD), benzothiazole disulfide (MBTS), stearic acid and zinc oxide (ZnO)) were all laboratory reagent grade. All compound ingredients were physically blended and then fed to a Berstorff ECS 2E25 co-rotating twin screw extruder at a temperature profile of 210 °C and screw speeds of 60, 75 and 90 rpm. Statically vulcanized blends were obtained by blending rubber with different components in a Farrel two roll mill (750 g capacity). Static vulcanization of SBS was done in a Carver hydraulic press at a temperature of 160 °C. Curing times chosen for this study (2 min and 4 min) correspond to intermediate points, above scorch time, within SBS curing curves for systems I and II; these curves were done in a Zwick oscillating disk rheometer at 160 °C. Vulcanized rubber sheets were cut and granulated with the intention of obtaining an appropriate particle size in order to be fed into the extruder when preparing the blend with PP. Finally, PP and 20% statically vulcanized SBS were blended in the molten state, using a Berstorff ECS 2E25 twin-screw extruder at a temperature of 210 °C and a screw speed of 75 rpm.
Melt Flow Index (MFI) measurements were done in a Davenport Plastometer at a temperature of 230 °C according to ASTM D1238 procedure. A Gottfert capillary rheometer (model 2000) was employed for rheological measurements at different plunger speeds varying from 0.01 to 5.00 mm/s. 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 using a capillary die with ratio L/D of 30/2. Rabinowitsch correction was applied in order to obtain viscosity curves. Tensile testing was done following the ASTM D638 test method using dumb bell shaped samples at a crosshead speed of 50 mm/min with a universal testing machine (Instron model 1125). These samples were obtained using a Reed Prentice injection molding machine at an injection temperature of 190 °C and an injection pressure of 600 psi. The gel content in statically vulcanized SBS and in dynamically vulcanized PP/SBS blends was determined by extraction of powdered samples in boiling xylene for 72 h.

**Table 1.** Formulation for statically and dynamically vulcanized SBS

Components	Curing System (phr)	
	I	II
SBS	100	100
ZnO	5	-
Stearic acid	1	-
MBTS	0.5	-
TMTD	1	-
S	2	-
DCP	-	1

Results and discussion

The effect of shear rate on the viscosity of pure polypropylene and its blends with SBS dynamically vulcanized with sulphur, at different compositions is shown in Figure 1. As the rubber content in the blend increases, the blend viscosity is also increased [7,8,10,11]. The thermoplastic/rubber blends can be considered as viscous emulsions where the elastomer, in droplets form, is dispersed into the plastic matrix. As the elastomer content increases, the volumetric fraction of the rigid phase also increases, obtaining a system of greater viscosity [12]. Further, a high % of SBS leads to a bigger rubber particle size, which makes it difficult for the material to flow and hence the viscosity increases. Wilhelm et al[13] observe that the domain size increases with increased elastomer concentration for PP/SBS blends as a consequence of the coalescence of the dispersed elastomer particles. In the case of dynamically vulcanized blends there is a network structure and disruption of overlapping chains is restricted especially at low flow rates, resulting in a slow decrease of melt viscosity with shear rate. The shear induced droplet breaks up and intermolecular slippage becomes predominant at higher shear rates, which further depends on the degree of crosslinking. As the degree of crosslinking increases with increasing SBS content, so is the critical shear rate at which the rapid decrease in melt viscosity takes place.

The next step of this rheological research was based on PP/SBS 80/20 vulcanized blends, since it was the minimum composition where significant changes on viscosity values were obtained. Inoue[14] used similar composition blends for PP/unsaturated elastomers with other crosslinking agents.

Table 2 lists MFI values for dynamically vulcanized blends with different extrusion speeds. It can be observed that system I (S) presents the following behavior: low extrusion speeds give low MFI, being all values in the same magnitude order. When screw speed is low, the residence time of polymer within the extruder is longer, permitting the polymer to cure and increase viscosity. Concerning system II (DCP) there is no precise tendency on MFI values. It seems that two opposite behaviors are in compromise with this type of curing agent. First, the mechanochemical degradation of PP and second, the crosslinking of the SBS phase by means of the peroxide; being the degradation effect more representative since all MFI values are higher than the values obtained for the sulphur blends.
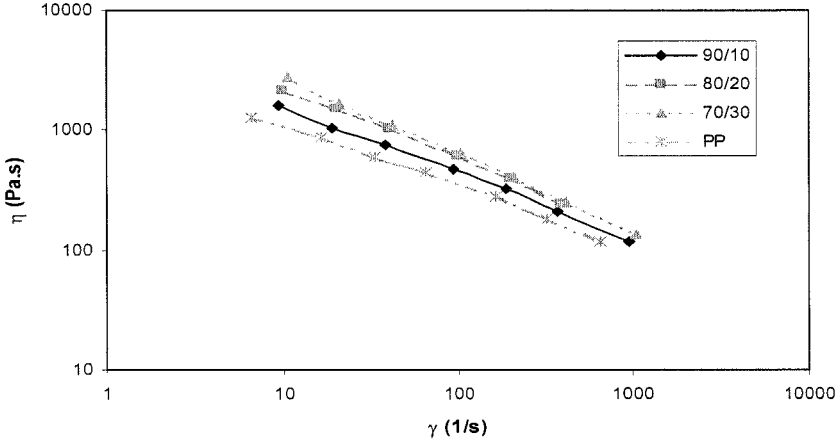
Figure 1. Effect of shear rate on the melt viscosity of PP/SBS blends dynamically cured with S.

Table 2. Melt Flow Index values for dynamically vulcanized PP/SBS (80/20) blends with different curing agents and screw speeds

| Screw speed (rpm)	MFI (g /10min)	
	System I (S)	System II (DCP)
60	0.8	19.8
75	1.5	11.2
90	1.7	21.9

Figure 2 shows the effect of different extrusion rates on melt viscosity for a sulphur cured PP/SBS 80/20 blend. There is a slight increase on viscosity values at low shear rates when decreasing extrusion rates; however, at high shear rates, not much effect on the melt viscosity is observed since all flow curves have a converging behavior. These results show that the dynamically vulcanized samples can be processed like thermoplastics by extrusion or injection molding techniques. In addition, the higher viscosity values obtained for the blends compared to pure PP indicate that a crosslinking reaction took place at all extrusion speeds.

In the case of the peroxide curing system the dynamically vulcanized blends at all extrusion speeds showed a drop in viscosity values as observed in Figure 3. The reported viscosity behavior may be attributed to the accelerated degradation of polypropylene in the presence of peroxide during the dynamic curing. Similar results were obtained by Ha et al.[15] for PP/EPDM blends. They found that the reduction in viscosity with increasing shear intensity could be due to mechanical degradation of polypropylene molecules in the blend, along with the oxidative degradation of PP induced by the presence of peroxide. Figure 3 also shows that the curve corresponding to 75 rpm gives the highest viscosity values compared to other extrusion speeds, thus indicating that the degradative effect of peroxide is less pronounced at that extrusion rate. This result is in accordance to MFI values reported on Table 2.

The rheological behavior of PP/SBS (80/20) blends with SBS content statically cured can be seen from Figure 4. The curves corresponding to system I (S) show scarce differences all along the shear rates tested for both curing times (2 min and 4 min), attributing this behavior to the similar crosslinking degrees obtained (Table 4).
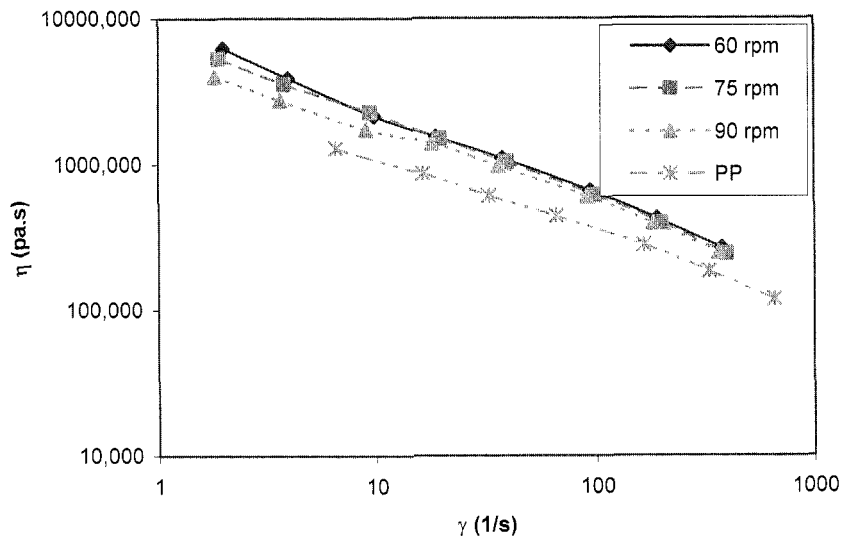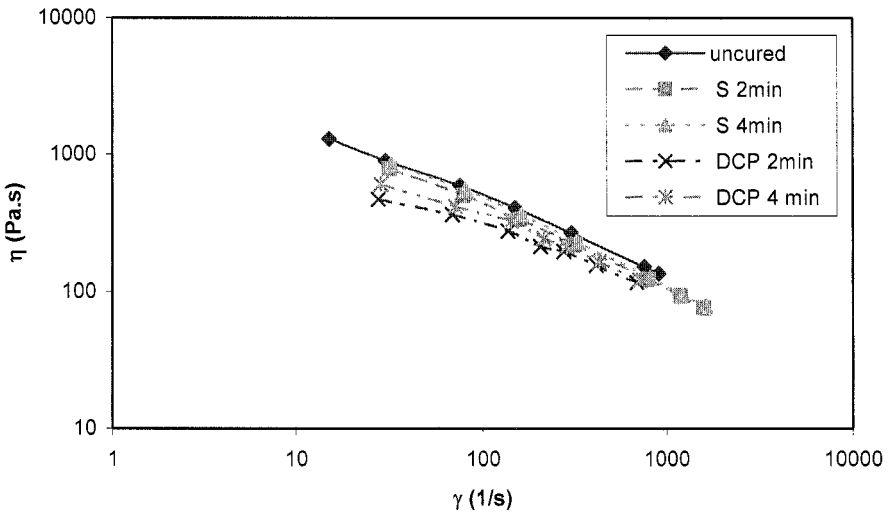

Figure 2. Effect of shear rate on the melt viscosity of PP/SBS (80/20) blends dynamically cured with S at different extrusion rates
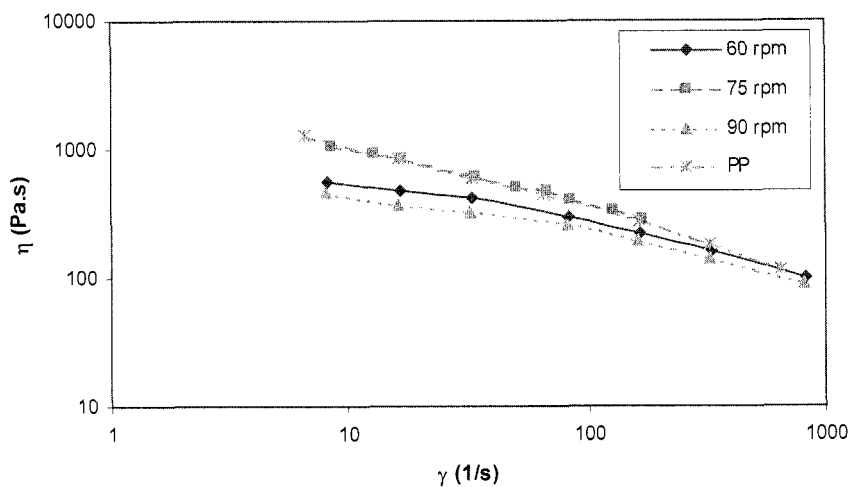
Figure 3. Effect of shear rate on the melt viscosity of PP/SBS (80/20) blends dynamically cured with DCP at different extrusion rates

On the other hand, when using peroxide viscosity values vary if curing times rises. Blends obtained with SBS vulcanized at 2 min and 4 min show melt viscosities lower than corresponding values for blend with uncured SBS being this difference more noticeable for the lower curing time (2 min). This behavior may be consequence of two opposite factors. Firstly, the accelerated mechanochemical degradation of polypropylene in the presence of peroxide during the blending step which gives rise to PP chain scission, thus decreasing melt viscosity. Scott[16] reported that the effect of peroxide on PP was primarily to increase the rate of formation of hydrogens attached to the tertiary carbons within the chain of polypropylene which could lower molecular weight (M_w), hence decreasing melt viscosity. Secondly, the crosslinking degree obtained for the rubbery phase when increasing curing time to 4 min, decreases remarkably the probability of scission mechanisms of PP chains during blending[10].

Figure 4. Effect of shear rate on the melt viscosity of PP/SBS (80/20) blends with SBS statically cured with S and DCP.

If melt viscosity of the dynamically and statically cured blends is compared at 75 rpm (Figures 2, 3 and 4), it can be seen that the value corresponding to the blend dynamically crosslinked with sulphur is superior to all other blends. This effect can be attributed to a high degree of crosslinking attained by the SBS and to the interlocked morphology of the PP/SBS blend that makes the mixture more resistant to flow because of the interactions between the PP and SBS phases (Figure 5-b). The flow behavior index (n) obtained for this blend confirm such result, as it is shown in Table 4. Flow index values decreased for the dynamically cured blends with both curing agents and for the statically cured with S, when compared to the uncured system. Kuriakose et al.[6] obtained similar results in PP/NR blends where the rise on the degree of crosslinking of the rubbery phase was directly related to the decrease on "n" values. For the DCP statically cured systems, the substantial increase on "n" values indicates, once again, a decrease on the molecular weight of the thermoplastic matrix due to the degradative process induced by the peroxide, being this effect more noticeable than the crosslinking reaction of the SBS phase.

Concerning mechanical properties, optimum toughening is related to the degree of dispersion of rubber in the blends. Particle size of the rubber-rich phase and the degree of phase mixing between the two-phase boundaries are two primary factors for improving mechanical strength and adhesion properties of multicomponent systems, the blend with the smaller particle size showing the best performance[17]. Figure 5 presents the morphology of PP/SBS blends with different curing systems. From these microphotographs it is possible to observe a better interaction between both phases when the blends are dynamically cured. López[18] observes the same behavior for PP/EPDM blends cured with sulphur. The increased adhesion in dynamically vulcanized systems can be explained on the basis of a smaller size of the dispersed rubber particles. Further, as been suggested in the literature[14,19] there can be a chemical graft formation or interlinking between SBS and PP during melt mixing and vulcanization that increases the interfacial adhesion and results in improvement in mechanical properties. This better compatibility and greater interfacial adhesion are responsible for the higher degree of elongation attained by the blend dynamically cured with S. An increase on interfacial adhesion supresses production of voids or flaws in the PP matrix, which can grow into cracks.

a)   b)   c)
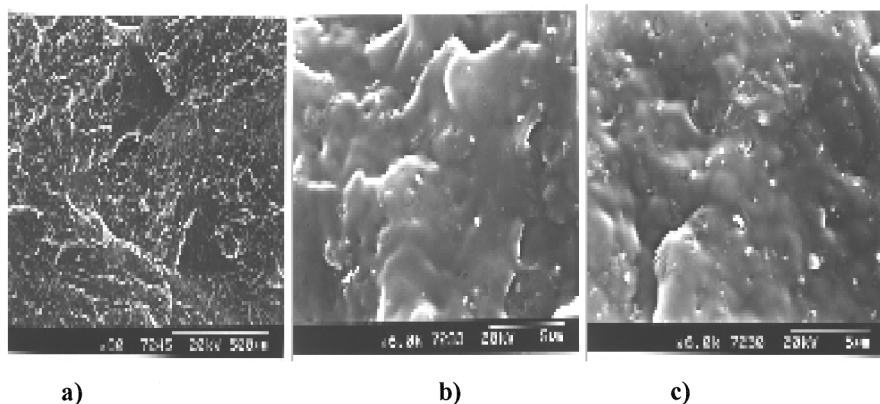
Figure 5. Microphotographs of PP/SBS (80/20) blends. a) Statically vulcanized with S; b) Dynamically vulcanized with S; c) Dynamically vulcanized with DCP

Table 4. Mechanical properties of pure PP and PP/SBS (80/20) blends

Blend	Flow Index (n)	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Toughness (MPa)	Gel Content (%)
Uncured	0.45	1028	21	299	37	< 1.0
Dynamically cured with S	0.39	965	19	440	87	16.0
Dynamically cured with DCP	0.40	958	12	108	19	14.0
Statically cured with S (2 min)	0.40	1077	23	13	2	*13.0
Statically cured with S (4 min)	0.38	1096	23	12	2	*19.0
Statically cured with DCP (2 min)	0.56	922	20	11	2	* 9.0
Statically cured with DCP(4 min)	0.51	988	21	11	2	*19.0
PP	0.46	1417	19	116	23	---

*Gel content was measured for the SBS phase[10] and extrapolated to the PP/SBS blend

For the dynamically vulcanized systems with DCP, tensile strength and elongation at break values are lower if compared with the uncured mixture, due to the loss on properties of the PP matrix.

On the other hand, when statically cured blends are studied, one can observe a rise on Modulus for system I (2 and 4 min), which may be a consequence of the SBS phase acting as a rigid filler. While for system II, the probability of scission mechanisms of PP chains is the predominant factor, hence decreasing Modulus, particularly for a curing time of 2 min where the free peroxide concentration is high enough for affecting PP[10].

Regarding gel content lectures, Table 4 shows that even though the crosslinking degree for system I statically cured (4 min) blends is higher than the one for the dynamic blends, a cavitation phenomenon is likely to occur with the production of voids at the rubber-rigid polymer interface[20] (Figure 5-a), thus decreasing substantially elongation at break. Similar behavior occurred with system II (DCP).

Conclusions

Rheological behavior of isotactic polypropylene (PP) and Styrene-Butadiene-Styrene block copolymer (SBS) blends was investigated. It was found that pseudoplastic behavior of blends was favored by increasing rubber content. The incorporation of the elastomer caused an increase on viscosity and toughness of the blends. Concerning the influence of extrusion rates, there was a slight increase on viscosity values at low shear rates for the sulphur curing systems when decreasing screw speed; however, at high shear rates, not much effect on melt viscosity was observed. The vulcanization type affected the rheological and mechanical behavior of the blends, resulting materials of higher stiffness but less elongation at break and with a behavior nearly Newtonian when statically cured with peroxide. Dynamic vulcanization with sulphur produced blends of higher toughness that can be easily processed by conventional methods.

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