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Effect of phenolic resin on processing and mechanical properties of PP-NBR blends

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Summary

Polymer mixtures based on polypropylene (PP) and acrylonitrile rubber (NBR) were prepared in a Haake Rheocord Mixer model 9000, coupled with a mixer chamber (cam rotors), in a proportion of 60:40/PP:NBR. These mixtures were processed in the presence either of phenolic resin SP-1045 or a phenolic derivative synthesized with cashew nut shell liquid (CNSL) distillate, in different concentrations. The influence of this component, as well as its concentration were evaluated by some processing data and through mechanical tests.

Introduction

In recent years, rubber-plastic blends have become technologically interesting for their use as Thermoplastic Elastomers. These materials present the excellent processing characteristics of thermoplastic materials at high temperature, the rubbery behavior at service temperature and the advantage of being turned directly into finished goods (1-2).
Coran and Patel (3-5) have published a series of articles on rubber/thermoplastic blends and have reported on compositions containing a particular thermoplastic and vulcanized rubber particles. According to these authors, one technique used to produce these materials consists basically in creating a multicomponent system with vulcanized rubber particle in a melt processable plastic matrix through a method called dynamic vulcanization. In this method the elastomeric phase is vulcanized during the mixing process (1-5).
In this work the effect of different phenolic resins on the processability and mechanical properties of polymer blends based on polypropylene (PP) and acrylonitrile rubber (NBR) was evaluated.

Experimental

Materials

Polypropylene (PP) of density 0.905g/cm^3 and melt flow index of 15.0 g/10min from Polibrasil S. A. Indústria e Comércio. Acrylonitrile rubber (NBR) of density 0.98g/cm^3 and 33% nitrile content from Nitriflex S. A. Indústria e Comércio. Dimethylol phenolic derivative (SP-1045) of density 1.27g/cm^3 from Schenectady Brasil Ltda. Phenolic resin from the distillate of cashew nut shell liquid (CNSL) of density 1.16 g/cm^3. Stannous chloride of density 3.95 g/cm^3 from Vetec Química Fina Ltda.

Resole prepolymer preparation

The resole prepolymer was prepared in a stirred reactor fitted with a reflux condenser. A 40.01g (1 mol) sample of the distillate of CNSL was placed in a three necked

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flask, then 5g of 10% aqueous NaOH were added. After mixing, 4.80g (0.41 mol) of paraformaldehyde were introduced.The mixture was heated at 90°C under reflux for 2 hr with continuous stirring. After the given reaction time, water was removed by distillation under reduced pressure for 4 hr (6). The resin was removed then transferred to a flask under nitrogen atmosphere and kept at 4°C until use. The molecular weight estimated by size exclusion chromatography (SEC) was 7700 g/mol.

Blending

Polymer blends based of PP and NBR were prepared by melt mixing in a Haake Rheocord Mixer 9000 (Cam rotors) in a proportion of 60:40/PP:NBR, in the presence or absence of each phenolic derivative and stannous chloride, in different concentrations. In the preparation of these blends the way of introducing the phenolic derivative (PD) was varied. In the first case the PD was added in a single step, after complete mixing of PP and NBR. In the second case, the PD was added in two steps as follows: 50% after melting of PP and another 50% after the introduction of NBR. In the third and last case, the resin was previously incorporated into the elastomeric phase in a roll mixer, and this mixture was then added to the melted PP. This last technique was not employed in the preparation of blends with the cashew nut shell liquid derivative. Table 1 presents the mixing parameters used to prepare the different blends.

Testing procedure

Through Haake Torque Rheometer data some properties of the blends were studied, such as the energy necessary to process pure polymers and blends, and their processing parameters. To calculate the processing parameter, the torque ratio (Tr) between the rubber phase and the matrix, and the specific energy for each resin in different concentrations was also evaluated (7,8).

$$\mathrm{Tr} = \frac{\text{steady-state torque of rubber}}{\text{steady-state torque of matrix}} \qquad \text{Eq. 1}$$

The specific energy input was obtained by multiplying the integral of the area under the blending torque curve, as a function of time by the mixing rate per unit mass of blend ingredients. The processing parameter (Pp) relates the torque ratio to the specific energy input during melt blending (7,8).

$$\mathrm{Pp} = \frac{\text{specific energy input}}{\text{torque ratio}} \qquad \text{Eq. 2}$$

The samples for mechanical property measurements were prepared by compression-molding at 190°C in a hydraulic press (Carver - model C) at 30 Kgf/cm^2 for 7 min. Tensile property measurements were carried out on a Materials Testing System - Instron Series IX automated machine (model 4204) at a crosshead speed of 1mm/min, in accord with ASTM 1708-93. Hardness was measured by using a Shore D Hardness Durometer, based on ASTM D 2240-86.

Table 1: Parameters used to prepare the blends

Parameter	Blends with resin from CNSL	Blends with Commercial resin
Processing Parameters	185° - 80rpm - 12min.	185° - 80rpm - 12min.
Technique used	One step	One step
	Two steps	Two steps
	-	With previous incorporation of phenolic derivative
Phenolic derivative concentration (%)	-	4
	6	6
	8	8
	10	10

Results and Discussion

From torque vs time data it was possible to observe the influence of phenolic resin concentration on the processing characteristics. Table 2 shows the effect of commercial phenolic resin and its concentrations on processing properties of PP-NBR blends.

Different behaviors were observed in the presence of the commercial resin, depending on the addition technique used. For blends prepared in one step, the increase in the resin concentration produced a decrease in the Pp, which means that for these blends, by increasing the concentration of this component, an improvement in the blend processing is achieved. The opposite was found for blends obtained by using the other two techniques. Table 3 shows the effect of the resin from CNSL and its concentration on rheometric properties of PP-NBR blends.

Table 2 - Processing properties of PP-NBR blends with commercial phenolic resin in different concentrations

Preparation technique	Phenolic resin concentration (%)	Steady-state torque (Nm)	Processing energy (J/g)	Processing parameter (J/g)
One step	4	5.98	360.97	69.02
	6	6.02	343.26	65.63
	8	5.80	325.61	62.26
	10	6.27	306.22	58.55
Two steps	4	4.88	284.18	54.34
	6	5.25	331.39	63.36
	8	5.88	378.34	72.34
	10	6.07	361.14	69.05
Previous incorporation	4	5.34	286.08	54.70
	6	5.11	342.42	65.47
	8	5.25	368.10	70.38
	10	5.62	377.16	72.11

Table 3 - Processing properties of PP-NBR blends with phenolic resin derivated from CNSL in different concentrations

Preparation technique	Phenolic resin concentration (%)	Steady-state torque (Nm)	Processing energy (J/g)	Processing parameter (J/g)
1 step	6	3.47	263.34	50.35
	8	3.42	260.91	49.89
	10	3.92	277.83	53.12
2 steps	6	3.83	326.59	62.44
	8	3.98	317.60	60.73
	10	4.67	358.55	68.56

In the blends with the CNSL resin (Table 3), a clear tendency of the Pp with increasing amounts of this third component was not evident for any of the techniques used. However, comparing the data obtained by each technique, the addition of resin in one step gives lower values thus suggesting that by this method the material is more easily processed. Effects of commercial resin and its concentration on the mechanical properties of PP-NBR blends can be seen in Table 4.

Table 5 shows the effect of resin derived from CNSL and its concentration on mechanical properties of PP-NBR blends.

The data in Tables 4 and 5 show no significant variations in the stress at yield values, neither in relation to the addition technique, nor in relation to the resin type.

The previous incorporation of commercial resin in the elastomeric phase gave rise to mixtures with elongation slightly lower than those obtained by the other two addition techniques, probably due to a higher degree of rubber vulcanization.

Table 4 - Mechanical properties of PP-NBR blends with commercial phenolic resin in different concentrations

Preparation technique	Phenolic resin concentration (%)	Stress at Yield (MPa)	Strain at Yield (%)	Hardness Shore D
1 step	4	9.29 ± 0.10	9.2 ± 1.4	24
	6	9.28 ± 0.08	7.9 ± 0.4	22
	8	9.42 ± 0.24	8.3 ± 0.3	21
	10	9.62 ± 0.15	8.4 ± 0.4	21
2 steps	4	10.17 ±0.31	10.8 ± 0.5	24
	6	10.11 ± 0.45	10.5 ± 0.9	22
	8	9.38 ± 1.62	10.0 ± 1.1	23
	10	9.37 ± 0.33	8.3 ± 0.7	21
Previously incorporation	4	8.74 ± 0.28	5.6 ± 0.4	27
	6	8.59 ± 0.31	5.7 ± 0.4	22
	8	8.58 ± 0.27	7.1 ± 0.1	22
	10	8.53 ± 0.32	7.4 ± 0.2	22

Table 5 - Mechanical properties of PP-NBR blends with phenolic resin derived from CNSL in different concentrations

Preparation technique	Phenolic resin concentration (%)	Stress at Yield (MPa)	Strain at Yield (%)	Hardness Shore D
1 step	6	9.67 ± 0.43	12.5 ± 0.8	27
	8	8.73 ± 0.17	15.6 ± 0.2	30
	10	8.13 ± 0.24	16.0 ± 0.9	30
2 steps	6	8.52 ± 0.17	13.7 ± 2.5	30
	8	8.92 ± 0.21	11.0 ± 0.9	29
	10	9.18 ± 0.46	10.9 ± 0.6	27

The elongations independent of the technique, were inferior to values obtained for the mixtures with CNSL resin. This can be attributed to an efficient plasticizing effect of this resin. Considering the mechanical properties, the largest differences appear in the hardness. The presence of the CNSL resin, no matter the addition technique, gives rise to harder materials.

Conclusion

In relation to pure PP-NBR mixture, the presence of neither the commercial resin nor the CNSL resin influence greatly the stress or the elongation at yield, but it renders processing easier. This means that materials with comparable mechanical properties can be preferentially prepared with the addition of any of these resins, especially the CNSL resin. This resin together with good processability characteristics gives rise to mixtures with improved hardness.

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