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PP-EPDM-NBR blends - The influence of added phenolic resin on processing and mechanical properties

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Summary

Polypropylene (PP), ethylene-propylene-diene terpolymer (EPDM) and acrylonitrile rubber (NBR) in different proportions were mixed in a Haake Rheocord Mixer. To these mixtures phenolic resin was added in various concentrations, during processing, and the effects of this addition on processing and mechanical properties of the resulting blends were investigated.

Introduction

Polymer blending is a well known strategy used to modify physical properties, without the need to synthetize new materials. Thus, thermoplastic elastomers (TPEs) have been recognized as economically and technologically important. The great majority of TPEs are heterogeneous in their morphology, constituted by hard domains and soft ones which give the material its elastomeric characteristics (1,2). As a consequence, they show short mixing and processing cycle as well as low energy consumption. In addition, the scrap can be recycled and properties can be adjusted by changing the components ratio (3,4). This fact explains the large number of studies on TPEs being reported (5-7).

It is also known that higher strength, high-temperature mechanical properties, hot oil and solvent resistance are better achieved when the rubber phase in these materials is vulcanized. This is usually accomplished by dynamic vulcanization, first described by Fisher (8) and also reported by Coran (1) for various elastomer-plastic blends (1,4,9). This technique differs from static vulcanization in that it occurs during mixing of the composition, without affecting processability if enough of the thermoplastic is present in the molten state (1).

The aim of this work is to investigate the effect of the addition of a commercial phenolic resin as a curative in PP-EPDM-NBR blends as well as the behavior of these blends as for processing and mechanical properties when NBR is present in different amounts.

Experimental

Materials

Materials were used as received and are listed in Table 1.

Blending

Polymer blends based on PP, EPDM and NBR were prepared by melt mixing in a HAAKE Rheocord Mixer 9000, coupled with a mixer chamber (Cam rotors), in proportions of 60:10:30, 50:10:40 and 40:10:50/PP:EPDM:NBR. These mixtures were processed in the presence or absence of both commercial phenolic resin SP-1045 and stannous chloride, at different concentrations.

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Table 1- Materials and their Characteristics.

Materials	Properties	Source
Polypropylene (PP)	• density: 0.905 g/cm^3 • melt flow index: 15.4 g/10min	Polibrasil S.A.
Acrylonitrile rubber (NBR)	• density: 0.908 g/cm^3 • nitrile content: 33%	Nitriflex S. A.
Ethylene-propylene-diene terpolymer (EPDM)	• density: 0.810 g/cm^3 • ethylene/propylene ratio: 73/27 • Iodine Index: 15%	Nitriflex S. A.
Dimethylol phenolic derivative (SP-1045)	• density: 1.27 g/ cm^3	Schenectady do Brasil LTDA.
Stannous chloride	• density: 3.45 g/ cm^3	Vetec Química Fina LTDA.

Processing conditions: Rotor speed - 80 rpm
Time of processing - 12 min
Temperature of processing - 185°C

Testing procedure:

The energy necessary to process the blends and their processing parameters were calculated by using Haake Rheometer data. The torque ratio (Tr) between the rubber phase and the matrix and also the specific energy from each blend had to be evaluated in order to calculate the processing parameter (Pp), according to the following equations (10, 11):

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

The specific energy required to process the materials at a given temperature at a given shear rate was obtained by multiplying the integral of the area under the blending torque curve as a function of time by the mixing speed per unit mass of the blend ingredients. The processing parameter (Pp) relates the torque ratio to the specific energy input during melt blending (10-12), as:

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

The samples for mechanical property measurements were prepared in a hydraulic press (Carver - model C) by compression-molding at 190°C, at 30 Kgf/cm^2 for 7 minutes. Tensile tests were carried out on a Instron Tensile Tester - Series IX - automated machine (model 4204). The crosshead speed was 1 mm/min, following ASTM D1708-93. Hardness was measured on a Shore D Hardness Durometer, according to ASTM D2240-86. Impact tests were carried out on a H.20 Plastics Impact Machine (Charpy-type) by Monsanto, according to ASTM D 256-93a.

Results and discussion

The influence of the addition of a commercial phenolic resin and the variation in the relative amounts of PP and NBR on the processing of the melt blended PP-EPDM-NBR mixtures can be seen from the results in Table 2.

It is possible to observe that the increasing addition of the commercial phenolic resin leads to increasing specific energy and processing parameter for the blends with 50% of NBR, up to a resin content of 8%. This indicates that the phenolic resin effectively promotes crosslinking of the rubber phase, making processing more and more difficult. Once the rubber has been completely consumed in the vulcanization step, the excess resin starts to act as a plasticizer and, as a result, processing becomes easier. For the blends with 30% of NBR, the elastomeric component will be dispersed in a larger amount of PP so, by adding resin, chances are that some of it will actually crosslink the dispersed rubber. However, as the rubber content is rather small, most of the resin will probably be spread over the PP phase. Thus, to impart effective crosslinking of NBR in the blends, higher amounts of resin are needed. Even so, the resulting increments in both specific energy and processing parameter are gradual, all lying below values obtained for blends with 50% of NBR, in spite of the higher content of rubber in these blends.

For the blends with 40% of NBR, the influence of the increasing commercial phenolic resin concentration on the specific energy and processing parameter is not clear.

Table 2- Processing characteristics of PP-EPDM-NBR blends with different contents of commercial phenolic resin and NBR.

ratio PP:EPDM:NBR	phenolic resin (%)	steady-state torque (Nm)	specific energy (J/g)	processing parameter (J/g)
40:10:50	0	3.75	331.37	45.00
	4	7.11	460.06	68.66
	6	7.51	524.69	78.31
	8	7.84	551.27	82.28
	10	7.86	469.13	70.02
50:10:40	0	3.40	321.14	48.36
	4	5.97	447.71	67.42
	6	6.33	437.56	65.89
	8	6.62	427.16	64.33
	10	7.03	468.82	70.60
60:10:30	0	2.74	305.15	52.07
	4	4.66	376.42	64.24
	6	5.04	380.25	64.86
	8	5.38	397.20	67.78
	10	5.73	405.20	69.15

Table 3- Mechanical properties of PP-EPDM-NBR blends with different contents of commercial phenolic resin and NBR.

ratio PP:EPDM:NBR	phenolic resin (%)	hardness (Shore D)	stress at yield (MPa)	strain at yield (%)	impact strength (J/m)
40:10:50	0	18	5.40	38.02	36.22
	4	20	5.09	10.69	23.98
	6	19	5.34	17.30	29.89
	8	20	5.68	29.85	22.97
	10	21	5.70	24.94	19.24
50:10:40	0	21	7.58	24.85	32.12
	4	18	7.09	11.33	35.82
	6	20	7.26	31.50	21.91
	8	20	7.02	28.65	25.00
	10	21	7.47	15.64	18.81
60:10:30	0	20	11.00	14.69	21.19
	4	23	10.15	10.14	27.09
	6	20	9.69	19.04	19.92
	8	21	9.83	37.78	19.40
	10	22	10.04	21.82	15.11

The influence of the phenolic resin added and of the amount of NBR on the mechanical properties of PP-EPDM-NBR blends is shown in Table 3.

Within each set of blends, the increasing addition of resin does not promote significant variations of hardness or stress. The influence of increasing resin concentration on strain is nevertheless not clear.

For all compositions, it is possible to observe a decrease in the impact strength when phenolic resin is added, which suggests the presence of a vulcanized rubber phase. It is known that vulcanization decreases molecular mobility and decreases the impact strength (13). Moreover, we could verify that as the amount of NBR increases, the compositions become less plastic-like and more rubber-like: the hardness decreases somewhat while the stress decreases significantly.

Comparing the blends with 30, 40 and 50% of NBR without commercial phenolic resin, an increase in the amount of rubber increases the strain and the impact strength. All these effects arise from cristallinity reduction which occurred with the addition of an amorphous phase.

Conclusion

The presence of commercial phenolic resin in each composition influences the processing properties, indicating that this component is effective as a curative. This fact is supported by scanning electron microscopy of the blends (to be presented in a future paper), which shows that the rubber phase is vulcanized.

Although not very clear, the effects of the commercial phenolic resin on the mechanical properties are significant and will be studied in detail in the future.

Finally, the influence of the amount of NBR on the processing and mechanical properties met our preliminary expectations, which can be considered as a consequence of the cristallinity reduction in the compositions.

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