EPDM/POLYOLEFIN NANOCOMPOSITES TPVS

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1 Introduction

A versatile way to produce thermoplastic vulcanizates (TPVs) with rubber-like properties and reprocessability is the blending of a rubber with a thermoplastic polymer. These materials become environmentally friendly because they can be recycled [1]. On the contrary, conventional rubber can not be recycled. On the other hand, the main objectives for studying polymer clay nanocomposites are associated with their improved heat distortion temperature and barrier properties, increased modulus and reduced flammability of polymers containing just a small fraction of the clay [2]. Montmorrillonite clay is usually used as filler in the preparation of polymer nanocomposites and can be considered as a natural product. In this article, the effects of adding different types of polyolefins such as low-density polyethylene (LDPE), metallocene polyethylene (mPE) and polypropylene, and their nanocomposites on the mechanical properties of EPDM thermoplastic vulcanizates were investigated.

2 Experimental

2.1 Materials and compounding.

The polymers used in this study were an ethylene-propylene diene terpolymer (EPDM) supplied by Nordel with 70 wt. % of ethylene and 5 wt. % of diene, a low-density polyethylene (LDPE), a metallocene polyethylene (mPE) and an isotactic polypropylene (PP). Maleic anhydride and dicumyl peroxide were used as the functional monomer and initiator in the grafting reactions of mPE and PP, respectively. Sulfur (S), zinc oxide, stearic acid, methyl tuads (TMTD) and dibenzothiazyl disulfide (MBTS) as curatives of EPDM and paraffinic oil were used as received. Montmorillonite clay modified with octadecylamine (OMMT) was employed in two proportions (4 and 10 wt. %) in the preparation of mPE nanocomposites. The characteristics of the polyolefins employed such as density (ρ), melt flow index (MFI) and melting temperature (Tm) are reported in Table 1.

Table 1. Characteristics of the polyolefins.

Polyolefin	ρ (g/cm^3)	MFI (dg/min)	Tm (°C)
mPE	0.87	30	60
PEBD	0.92	2.4	112
PP	0.92	1.4	168

In the TPVs preparation, the EPDM and curatives (except sulfur and oil) were preblended in a Banbury mixer at 75 rpm for 3 minutes. Then this EPDM premix and each polyolefin were blended in a Haake plasticorder where the EPDM was dynamically vulcanized with sulfur and paraffinic oil was used as processing aid. The blends were removed from the mixer and compression molded. In the preparation of mPE nanocomposites, grafted maleic anhydride grafted materials were also used. The nanocomposites with 4 and 10 wt. % of modified montmorillonite (OMMT) and the grafting reactions of mPE and PP were prepared in a Haake plasticorder. The different formulations of EPDM compounds are shown in Table 2.

2.2 Mechanical properties and characterization

The tensile properties and Shore A and Shore D hardness were determined according to ASTM D-412 and ASTM D-2240 standard procedures, respectively. Determinations of the oil resistance were carried out according to ASTM D 474-98 using toluene. Also, the ageing resistance of the materials was measured. The dispersibility of the silicate layers in the mPE and its nanocomposites and their phase morphology were evaluated on the compression molded samples by transmission electron microscopy (TEM). The reprocessability of the composites was obtained by viscoelastic experiments using parallel plates at 150°C for the blends with PEs and 200°C for that with PP.

3 Results and discussion

3.1 Metallocene PE and PP Nanocomposites

TEM was used to study the dispersibility of the clay in the mPE and PP nanocomposites, and their blends with EPDM. Intercalated and tactoid structures were found in the PP nanocomposite with 4 wt. % of OMMT. However, No significant changes in the structure were observed for the EPDM compounds with nanocomposites.

3.2 Effect of the type of polyolefin on TPV mechanical properties

The tensile strength (σ_b) and elongation at break (ε_b) and Shore A and Shore D hardness of the different EPDM formulations are presented in Table 2. The effect of oil as processing aid in EPDM rubber compounds has been studied extensively. An increase in elongation at break and reductions in modulus, tensile strength and Shore A hardness was found [1]. This behavior can be observed for the F2 formulation, EPDM/oil, 30/20.

In all EPDM compounds without clay (F3, F4, F5 and F6), higher elongation at break and tensile strength were obtained than those of EPDM (F1). These results could be related to the different morphology of the blends obtained by TEM and the tensile properties of the polyolefin employed. The metallocene polyethylene because of its high comonomer content has a very low tensile strength and high elongation at break. Then, the EPDM formulations prepared with mPE (F3 and F4) had the highest elongation at break and the lowest tensile strength. Excellent mechanical properties at room temperature were found for the EPDM formulations prepared with PEBD and PP when they are compared with other TPVs prepared with EPDM and PP or PA-6 [1, 3]. However, the ageing resistance of the different formulations was not very high.

No significant improvement in tensile properties for the EPDM /Nanocomposites TPVs (F7, F8 and other EPDM formulations with different OMMT proportions) was obtained. However, an increase in the Young's modulus (not shown here) was found. The tensile properties of the EPDM compounds with mPE nanocomposites were improved only at high temperatures. On the other hand, the different EPDM formulations without clay showed good reprocessing ability.

Table 2. Mechanical properties of the blends.

Material	Shore A ± 1	$\sigma_b \pm 0.3$ (MPa)	ε_b (%)
EPDM (F1)	67	3.2	221 ± 21
EPDM/oil 30/20 (F2)	38	1.6	335 ± 55
mPE/EPDM/oil 40/40/20 (F3)	55	5.0	> 700
mPE/EPDM/oil 50/30/20 (F4)	52	3.4	> 700
PEBD/EPDM/oil 40/40/20 (F5)	68	12.5	682 ± 20
PP/EPDM/oil 50/30/20 (F6)	40*	18.0	328 ± 17
mPE/OMMT (Nano 1, 96/4)	-	3.9	525 ± 67
PP/OMMT (Nano 2, 96/4)	-	28.0	5.8 ± 0.8
Nano 1/EPDM/oil 50/30/20 (F7)	57	4.3	> 700
Nano 2/EPDM/oil 50/30/20 (F8)	37*	11.0	232 ± 17

***Shore D hardness**

4 Conclusions

TPVs with PEBD and PP with excellent mechanical properties were prepared by dynamic vulcanization. The different TPVs without clay showed good reprocessing ability. The tensile properties of the nanocomposites were improved only at high temperatures.

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