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Effect of montmorillonite intercalant structure on the cure parameters of natural rubber

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ABSTRACT

Two quaternary phosphonium salts (aromatic and aliphatic) have been used as intercalants for Na-montmorillonite and the effect of intercalant structure on clay morphology and natural rubber vulcanization kinetics was investigated. Due to its lower rigid structure the aliphatic salt was easier to intercalate into the clay galleries giving rise to a higher interlayer distance and facilitating the rubber intercalation obtaining an exfoliated structure in the nanocomposite. The vulcanization process was sensibly accelerated by this organoclay and a higher crosslinking degree was observed in the nanocomposite which gave rise to materials with improved processing and physical characteristics.

1. Introduction

Clays and clay minerals such as montmorillonite, saponite, hectorite, etc., were widely used as filler for rubbers and plastics for many years, for saving polymer consumption and reducing the cost [1]. At present, nanocomposites based on polymer matrices and organo-layered silicates represent an interesting opportunity for the design of high characteristic materials mainly from the mechanical properties and thermal stability points of view [2–5].

Two specific characteristics of layered silicates are useful for nanocomposites development. The first one is based on the possibility of these high aspect ratio (L/D relationship) layers [6] to be individually dispersed and the second one on their chemical capacity to be modified through cation exchange reactions [7]. So, not only their reinforcing effect may become apparent but their chemical compatibility with polymer may be considerably improved [8].

The interlayer cations of the montmorillonite can be easily ion-exchanged with other positive charged atoms or organic ions such as quaternary ammonium or phosphonium salts. The introduction of organic ions into the interlayer spacing not only render more organophylic phyllosilicates but also results in a larger interlayer spacing depending on functionality, packing density and length of organic molecule [9]. So, organoclays improve the compatibility with a polymer matrix and the intercalation of the polymer within the galleries. The organic chains into the galleries may lay either parallel to the silicate layers, forming mono or bilayers or to radiate away from the surface, forming mono or even bimolecular "paraffinic" arrangement [10,11], in this case with a higher interlayer spacing.

As above mentioned, quaternary ammonium or phosphonium salts can be used as intercalants for layered silicates. The advantage of using phosphonium instead of ammonium salts is that they give rive to an increase in the degradation temperature of the organoclay from 250–300 to 350 °C [12]. However, only a few references on these phosphonium salts can be found in the literature.

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Okamoto et al. [13] used a saponite organically modified with a commercial quaternary phosphonium salt. Salahuddin and Akelah [14] studied the synthesis of phosphonium salts of styrene–chloromethylstyrene-maleic anhydride terpolymer and their intercalation with montmorillonite. Recently, Arroyo et al. [15] synthesized triphenyl vinylbenzyl phosphonium chloride and described the treatment of a bentonite with this salt and its effect on the bentonite morphology.

On the other hand, rubber nanocomposites based on natural rubber (NR) with layered silicates have received increasing attention in the last years [16–31]. In fact, intercalated and partially exfoliated structures have been successfully prepared by several processing techniques, such as vulcanization curing process [17,28,32–38], solution blending [39,40] or latex compounding [23,27,41–43]. A natural rubber–organoclay nanocomposite with a fully exfoliated structure was firstly reported by López-Manchado et al. [35,36]. The nanocomposite was successfully prepared via vulcanization process. The cure characteristics of pristine natural rubber (NR) were affected by the organoclay. So, the optimum vulcanization time was sharply shortened with the incorporation of the organoclay which was attributed to amine groups coming from the organophilization of the clay. The addition of the organoclay also resulted in a sensible increase in the torque value as compared to the pristine NR which indicates that a higher number of crosslinks were formed. This statement was supported by swelling measurements and DSC isothermal studies.

Having in mind the above, the main goal of this study is to investigate the effect of the organic phosphonium salt structure (aliphatic and aromatic) on the morphology, vulcanization characteristics, thermal stability and tensile properties of natural rubber nanocomposites and to analyze the structure/behavior relationship of the obtained materials.

2. Experimental part

2.1. Materials

Natural rubber was kindly supplied by Malaysian Rubber under the trade name CV-60 (Mooney viscosity: ML (1 + 4), 100 °C: 60). Na-montmorillonite (Na-MMT) with a cation exchange capacity (CEC) of 92 meq/100 g was provided by Southern Clay Products (Gonzalez TX). Triphenyl vinylbenzyl phosphonium chloride (TVBP), synthesized in our laboratories [15] and tetraoctyl phosphonium bromide (TOP) supplied by Aldrich, were used as intercalants.

2.2. Preparation of organoclays

The intercalation of the aliphatic phosphonium salt into the pristine-MMT galleries was carried out through a cationic exchange reaction, following the next procedure: 100 g of Na-MMT were dispersed in 2000 ml hot water, under continuous stirring and maintained over night. Then the suspension was heated at 80 °C and a solution (clay/phosphonium salt molar ratio 1:1.2) of the protonated quaternary phosphonium salt in 500 ml water, previously heated at 80 °C, was added under strong stirring The protonation of the salt was carried out by addition of hydrochloric acid (HCl/quaternary salt molar ratio 1:1). After 2 h at this temperature and under vigorous stirring, the suspension was filtered and washed several times with hot water until complete elimination of chloride anions, as was checked by silver nitrate test. Finally the organoclay was washed with ethanol, filtered and dried at 60 °C overnight. The dried organoclay was grinded in a ball mill. Thermogravimetric analysis showed a 27% b.w. modification of this organoclay named aromatic-MMT.

The modification of the Na-MMT with tetraoctylphosphonium bromide was carried out following the above described procedure. In this case, the phosphonium salt was previously dissolved in ethanol and then added to the Na-MMT suspension under vigorous stirring. Finally, the organoclay was washed several times with water until complete elimination of bromide anions, washed with ethanol, filtered, dried and grinded. Thermogravimetric analysis showed a 31% b.w. modification of this organoclay, named as aliphatic-MMT.

2.3. Preparation of NR/clay nanocomposites

Rubber nanocompounds were prepared in an open two-roll mill, at room temperature. The rolls operated at a speed ratio of 1:1.4. The vulcanization ingredients were incorporated to the rubber before the addition of the clay, and finally, the sulfur was added to the blend. The recipes of the studied compounds are compiled in Table 1.

Vulcanization parameters of the nanocompounds were calculated by means of a Rubber Process Analyzer (RPA2000, Alpha Technologies), at 170 °C. A frequency of 10.49 rad/s and a strain of 2.79% were used.

Vulcanizates were prepared at 170 °C, in a thermofluid heated press. The vulcanization time of the nanocompounds correspond to the optimum cure time (t_{97}) obtained from the curing curves.

2.4. Characterization of the obtained nanocomposites

Wide-angle X-ray diffraction (XRD) was used to characterize the clays and to study the nature and extent of the dispersions of the clays in the composites. XRD patterns were collected using a Phillips Diffractometer at the wave

Table 1
Recipes of the studied rubber compounds

	NR	NR/pristine-MMT	NR/aliphatic-MMT	NR/aromatic-MMT
Natural rubber	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	1	1	1	1
Sulfur	2.5	2.5	2.5	2.5
MBTS[a]	1	1	1	1
PBN[b]	1	1	1	1
Pristine-MMT	–	5	–	–
Aliphatic-MMT	–	–	5	–
Aromatic-MMT	–	–	–	5

[a] Benzothiazyl disulfide.
[b] Phenyl betanaphthylamine.