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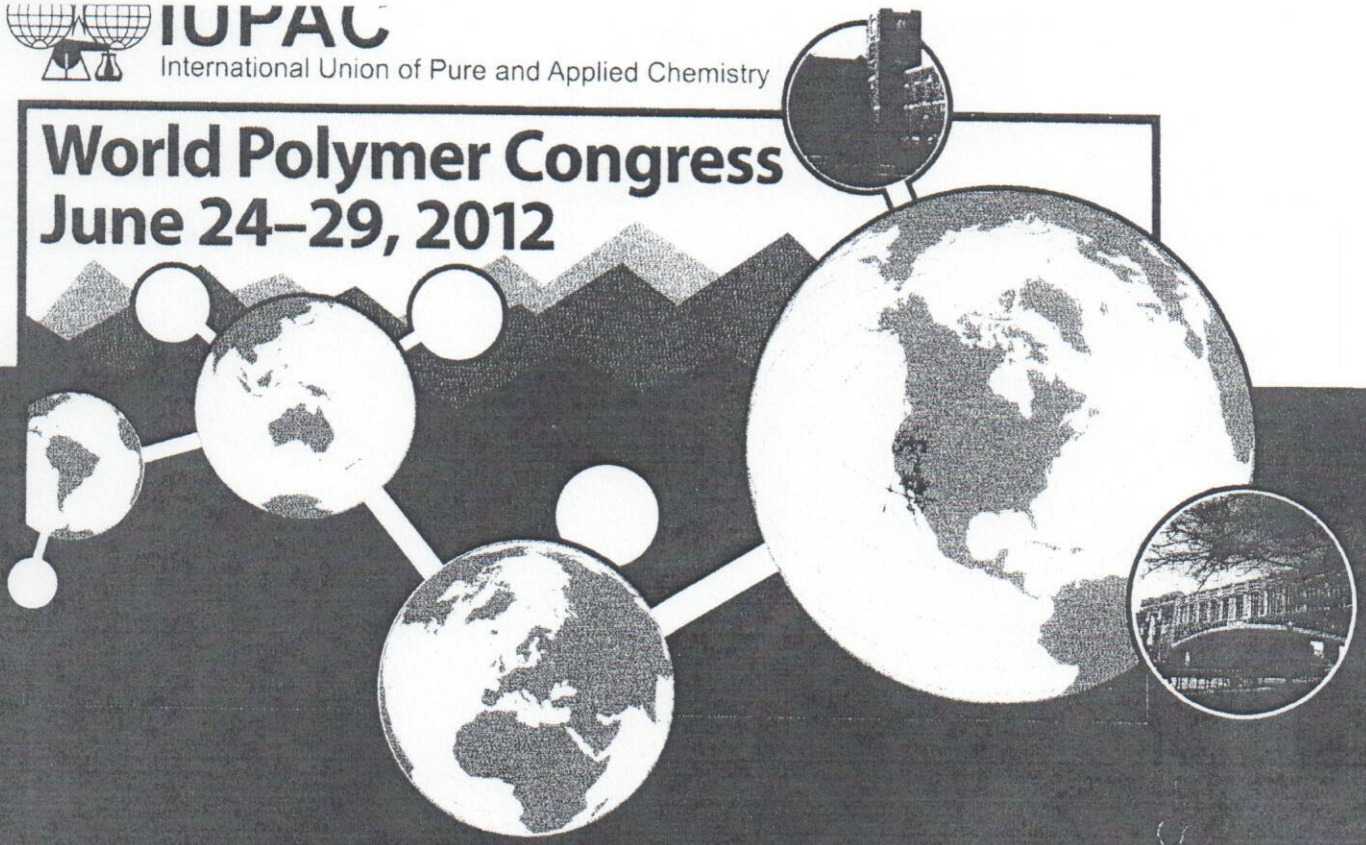

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EFFECT OF IMIDAZOLIUM IONIC LIQUID ON VULCANIZATION PROPERTIES OF NBR/CLAY

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Introduction

Ionic liquids (ILs) have called recent attention from the scientific population due to its unique and detachable properties, such as negligible vapor pressure and inflammability and good thermal and chemical stability (1). ILs have been widely studied as substitutes for regular organic and aromatic solvents, reason why they are characterized as green solvents (2). In polymer area, its effect on elastomers hybrids processing can be analyzed through the use of these materials as clay co-organophilizing agents combined with an ammonium salt (CTAB). Previous studies have shown a thermal stability gain on the organoclays with CTAB/IL when compared to the one modified only with CTAB. NBR/organoclay hybrids (NBR/clay-CTAB; NBR/clay-CTAB-IL) were prepared with a 5 phr amount of clay and the IL was (1-methyl-3-octyl)-imidazolium bis(trifluoromethanesulfonyl) imide (3).

Rubber composites have a great variety of properties that are mostly derivate from their low glass transition and the manipulation of this characteristic by vulcanization (4). In this perspective, this work aims to study and explore the influence of IL on vulcanization properties of NBR/clay hybrids.

Experimental

Clay Organophilization. Sodic montmorillonite (MMTNa) clay was previously modified with a quaternary ammonium salt (hexadecyltrimethylamonium bromide) in a proportion of 1:0,5 based on clay CEC. This clay has been subjected to treatment with (1-methyl-3-octyl)-imidazolium bis(trifluoromethanesulfonyl) imide (OMIm) in proportions of 8, 15, 26, 35 and 45% by weight and denominated OMMT-05-OMIm-8/15/26/35/45, respectively. The modified clays were characterized thermal, structural and morphologically.

Hybrids Processing. The hybrid materials (NBR/OMMT-n) were prepared with five organoclays (OMMT-05-OMIm-8/15/26/35/45) in proportion of 5 phr (parts per hundred parts of rubber). The hybrids were put in the mixing chamber of a Haake torque rheometer with roller rotors at 150 ° C and 70 rpm for 6 minutes. With the chamber at 100 ° C it was added the vulcanizing agents, at 50 rpm, in sequence: 5 phr of ZnO, 3 phr of stearic acid 2 phr of sulfur and 1 phr of MBTS (2-mercaptobenzothiazole). After the mixture was removed from the chamber, passed under roll mill and put in a Rubber Process Analyzer (RPA2000) for rheometric evaluation. Vulcanized hybrids were also characterized by DSC, XDR, SEM and swelling in methylethylketone (MEK).

Results and Discussion

IL organoclays show an increase on Tonset for higher amounts of IL. This indicates higher thermal stability with IL addition. Moreover, d001 are also higher as the amount of OMIm increases, contributing for a better dispersion of the clay in NBR matrix. These results are presented on Table 1.

NBR/Organoclays morphology by SEM indicates that IL induces reduction of organoclays particle size in the rubber with its addition, Fig. 1 (a-c). Besides, it's noticed a better interaction between clay and matrix at the materials interface and spindles formations responsible for size decrease and dispersion on rubber matrix, Fig. 1 (d).

Tests developed on RPA at 160 °C, it's verified that IL addition causes a decrease on MH (maximum torque) values and an increase on T_{90} (time in which 90% of the material is vulcanized). The lowest T_{90} value is 18 for NBR/OMMT-05 and the highest is 34, attributed to OMMT-0.5-OMIm-45, Table 1. This increase is dependent on IL amount increase. It indicates that besides IL contribution to a better thermal stability of clays and increase interlayer space, it also interferes on curing reaction and its addition on clay modifies hybrids' curing kinetics. Posterior studies are going to be prepared to corroborate these arguments.

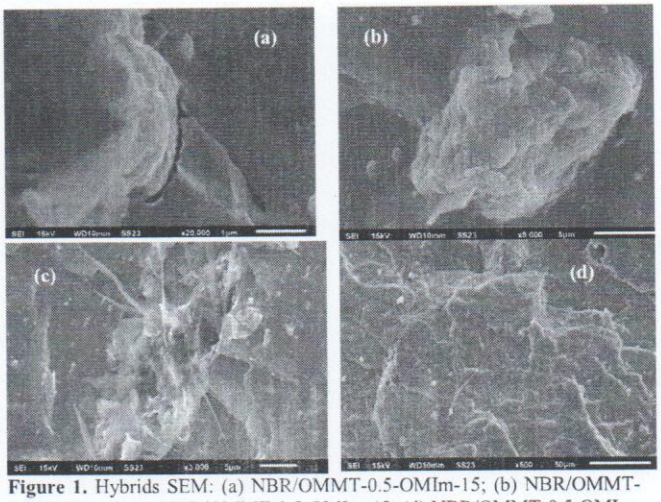

Figure 1. Hybrids SEM: (a) NBR/OMMT-0.5-OMIm-15; (b) NBR/OMMT-0.5-OMIm-35; (c) NBR/OMMT-0.5-OMIm-45; (d) NBR/OMMT-0.5-OMIm-45.

Swelling tests in MEK show an increase on gel fraction in hybrids with higher amounts of IL, which indicates a lower crosslinking degree for these materials corroborating with rheometric studies.

Table 1. Organoclays Characteristics and Hybrids' Curing Evaluation

Clay Samples	T_{onset} (°C)	d_{001} (nm)	Gel Fraction (%)	T_{90} (min)
OMMT-5	241	1.72	---	18
OMMT-05-OMIm-8	310	3.49	99.3	23
OMMT-05-OMIm-15	336	4.90	96.2	25
OMMT-05-OMIm-26	345	3.56	94.9	29
OMMT-05-OMIm-35	351	3.87	96.6	32
OMMT-05-OMIm-45	355	3.92	91.4	34

Conclusions

OMIm IL has proved to be a promising clay organophilizing agent due to its efficiency in both thermal stability and dispersion and interaction with matrix, in a composite preparation perspective. IL influences the hybrids T_{90} by increasing it and also interferes on curing reaction and its addition on clay modifies hybrids' curing kinetics. Hybrids with higher amounts of IL presented inferior crosslinking degree, that is, a lower curing percentage.

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