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Research paper

Mechanical and rheological properties of nitrile rubber/fluoromica composites

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ABSTRACT

Fluoromica is a clay mineral obtained from chemical modification of talc with Na_2SiF_6. In this study, it was used to prepare clay mineral polymer composites (CPN) based on nitrile rubber. The composites were compounded in a roll mill and it was studied the effect of the fluoromica content as well as the shear ratio employed during the preparation. The composites were assessed based on the mechanical properties, dynamic-mechanical performances, rheological properties, and morphological aspects. The results suggested that the formation of chemical crosslinks was affected with the presence of the clay mineral, moreover, little or no reinforcement effect was achieved most likely to the lack of interaction with the matrix.

1. Introduction

Semi-synthetic swelling micas can be obtained from the thermochemical treatment of talc, and are more crystalline than natural clays (Utracki et al., 2007; Souza et al., 2011). Synthetic mineral clays also have the advantage of a more precise controlled chemical composition, physico-chemical properties, and purity (Souza et al., 2011; Zhu et al., 2015). Fluoromica (trade name Somasif ME100), which is an expandable phyllosilicate, is produced modifying talc with Na_2SiF_6 (Utracki et al., 2007; Souza et al., 2011; Zhu et al., 2015). It possesses similar structure to montmorillonite (Mt), however, with considerable chemical differences (Utracki et al., 2007; Souza et al., 2011), e.g., Mt possesses hydroxyl groups whereas the fluoromica possesses also fluorine groups. Somasif does not have active aluminium ions in the octahedral positions (Souza et al., 2011).

Clay minerals, as well as nanoclay minerals, are used as filler to prepare clay polymer composites (CPN) given their availability, low cost, and lighter weight (Nazir et al., 2016). Once the clays are well dispersed and distributed through the polymer matrix, even at low levels, properties of the CPN are markedly improved, e.g., mechanical properties, impermeability, and thermal resistance (Liu et al., 2006; Galimberti et al., 2015;Galimberti et al., 2017). However, it is only possible to obtain a reinforcement effect when there is a proper interaction between the filler (clays) and the matrix (polymer).

Varghese and Karger-Kocsis (2013) prepared different natural rubber (NR) composites with somasif fluoromica and with bentonite (Bent). The study suggested a reinforcement effect of fluoromica because of a clay mineral network formation and the intercalation/exfoliation of the mica. This reinforcement effect was noted by an increase in stress as a function of strain and in tensile strength at break. Honorato et al. (2016) also studied NR composites with Somasif fluoromica and reported that the crosslink density was affected after incorporation of the clay mineral filler. Other different CPN based on NR are found in the literature reporting some reinforcement effect of different clay minerals (Teh et al., 2004; Sharif et al., 2005; George et al., 2016).

Most of the studies on rubber CPN are limited to natural rubber, therefore there is a lack of literature regarding the use of clay minerals with different rubber, like nitrile rubber. Acrylonitrile-butadiene rubber, most commonly known as nitrile rubber (NBR), and is widely used in oil and gas industry for articles that are in contact with fuel and other non-polar solvents (Varghese et al., 2013; Zhao et al., 2013; Pazur and Cormier, 2014).

This study aimed at assessing the addition of fluoromica Somasif ME100 on the mechanical, and rheological properties on nitrile rubber (NBR) composites. Furthermore, the shear ratio during the preparation of the composites was also evaluated. Clay minerals are not able to fully substitute traditional fillers used in polymer composites, e.g., carbon black and silica (Galimberti et al., 2015), nevertheless, in this study the fluoromica was used as only filler to better understand its behaviour in

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the rubber matrix without further interference of other fillers.

2. Experimental

2.1. Materials

Synthetic fluoromica Somasif ME-100™ was kindly donated by Co-Op Chemical Co.

Nitrile rubber (NBR) samples with 33% of acrylonitrile content and Mooney viscosity 42–52 ML1 + 4 (100 °C) were supplied by Nitriflex S/A Indústria e Comércio. According to ASTM D-1646, Mooney viscosity is a measure of rubber's viscosity determined in a Mooney shearing disk viscometer. The test result is reported as ML 1 + 4(100 °C), where M is Mooney, L is larger rotor, 1 and 4 are, respectively, the times (minute) before and after starting the motor at which the reading is taken, and 100 °C is the temperature of test.

Commercial grades of zinc oxide, stearic acid, sulphur, tetramethylthiuram dissulfide (TMTD), and 2-mercaptobenzothiazol (MBT) were donated by Teadit Indústria e Comércio Ltda.

2.2. Compounding

Rubber formulations were prepared employing a two-level full-factorial design of experiments (DOE) with central point (2^2 + 3) to assess the influence of the factors: fluoromica content and shear ratio employed during the preparation process. The different shear ratios were achieved by changing the speed of the one of the rolls (diameter: 470 mm), while keeping the other at constant speed of 24 rpm (rotations per minute).

For each factor investigated (fluoromica content and shear ratio) two levels were used, coded as −1 and +1. Level 0 (zero) represents the central point, which was replicate three times to measure the experimental error. The coded and actual values for each factor are represented on Table 1. Each composite was labelled as *XX/YY*, which *XX* stands for the amount of fluoromica used, given in phr (parts per hundred parts of rubber), and *YY* stands for the rotation of the fastest roll, given in rpm. The analysis of DOE was performed using *Statistica 8* software and analysis of variance (ANOVA) was carried out at 95% confidence level. The ANOVA gives information regarding the contribution of each factor investigated, and their interaction, on the variable response by value of "*P-values*" generated. *P-value* low than 0.05 means that the respective factor (or interaction) has a significate influence on the variable responses, which in this study were: vulcanization rheometric parameters, crosslink density, complex viscosity, and mechanical properties.

Additionally, an unfilled NBR composition was also prepared to be used as reference (coded as 0/37) employing the same shear ratio as for the central point (1.53). The content of others formulation components were kept constant (nitrile rubber: 100 phr, sulphur: 1.5 phr, zinc oxide: 3 phr, stearic acid: 1 phr, TMDT: 0.5 phr, and MBT: 1 phr).

Table 1
Design of the experiments (2^2 + 3) for the NBR/fluoromica composites.

Experiment code	Factor coded level		Actual factor value	
	Fluoromica	Shear ratio	Fluoromica (phr[a])	Shear ratio fastest roll: lowest roll speed (rpm)
2/34	−1	−1	2	34:24
2/40	−1	1	2	40:24
7/34	1	−1	7	34:24
7/40	1	1	7	40:24
4.5/37(A,B,C)[b]	0	0	4.5	37:24

[a] Parts per hundred parts of rubber.
[b] Central point repeated three times.

The compounds were prepared in a roll mill, at 50 °C ± 5 °C in two steps. During the first part, the fluoromica was mixed with the elastomer for 10 min at the respective shear ratio indicated in Table 1, except for unfilled vulcanized NBR, which was processed without the addition of any filler. On the second part, the procedure was based on the ASTM D3187, in which recommends to add firstly the activator system together (zinc oxide and stearic acid), and after to add the curing system together (in this study: TMTD, MBT, and sulphur). Each composite was vulcanized by compression mold at 160 °C according to their respective optimum cure time.

2.3. Test methods

2.3.1. Particle size distribution of Fluoromica

The Laser analyzer Mastersizer 2000 (Malvern Instruments) was used to determine the number particle size distribution of Fluoromica using accessory Hydro 2000SM.

2.3.2. Vulcanization rheometric parameters

The samples were analyzed in a rubber process analyzer (RPA), RPA 2000 from Alpha Technologies, according to ASTM D5289, for 30 min at 160 °C, to determine the main vulcanization parameters: induction time (t_{s1}), optimum cure time (t_{90}), minimum torque (ML), maximum torque (MH), and cure rate index (CRI).

2.3.3. Crosslink density

The crosslink densities of the composites were estimated from the elastic shear modulus using RPA. First, the uncured sample was preconditioned in the equipment for 2 min at 100 °C with 0.2° strain and 0.5 Hz frequency. Then, elastic modulus was obtained at 100 °C, with 0.25° strain and 5.0 Hz frequency to estimate the physical crosslinks. The sample was, then, vulcanized, in the equipment; at 160 °C using the respective optimum cure time previously obtained. At last, elastic modulus was again obtained at 100 °C, with 0.25° strain and 0.5 Hz frequency to estimate the total crosslinks formed during vulcanization. Chemical crosslinks are generated during vulcanization process, while the physical crosslinks are a contribution of entanglement, constrains or other effects not related to chemical changes (Pechurai et al., 2009). The physical crosslinks $\mu_{(phy)}$, the total crosslinks $\mu_{(total)}$, and the chemical crosslinks $\mu_{(chem)}$ were calculated employing the Eqs. (1), (2), and (3).

$$\mu_{(phy)} = G'_{(5\,Hz)}/2RT \quad (1)$$

$$\mu_{(total)} = G'_{(0.5\,Hz)}/2RT \quad (2)$$

$$\mu_{(chem)} = \mu_{(total)} - \mu_{(phy)} \quad (3)$$

wherein G′(5 *Hz*) is the elastic modulus obtained from the uncured sample, G′(0.5 Hz) is the elastic modulus obtained from the cured sample, R is the gas constant (8.314 J/K.mol), and T is the absolute temperature in Kelvin (K).

However, when some filler is present in the composition, it is necessary to deduct the filler effect on the elastic modulus values, using the Eq. (4), before employing the previous equations.

$$G'_{filled} = G'_{unfilled}(1 + 2.5\varnothing + 14.1\varnothing^2) \quad (4)$$

wherein, G_{filled}' is the elastic modulus obtained from any filled composites, either before or after vulcanization, $G_{unfilled}'$ is the elastic modulus after the adjustment, deducting the volume fraction of filler, either before or after vulcanization, and Ø is the volume fraction of filler (Lee et al., 1994; Pechurai et al., 2009).

2.3.4. Rheological behavior

Rheological properties were investigated before and after vulcanization using RPA and analysis was performed based on ASTM D6601. First, the sample was submitted to a preconditioned step during 2 min