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Research paper

Stress relaxation of nitrile rubber composites filled with a hybrid metakaolin/carbon black filler under tensile and compressive forces

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ABSTRACT

Stress relaxation of nitrile rubber composites filled with metakaolin and carbon black under tensile and compressive loading was assessed to determine the effect of the hybrid-system filler on the relaxation process. Nitrile rubber-filled formulations were designed with 50 parts of filler per hundred parts of rubber (phr), using carbon black-to-metakaolin ratios of 50:0, 35:15, 25:25, 15:35, and 0:50 phr. In addition, one unfilled vulcanized nitrile rubber (NBR) composite was prepared as reference. The results demonstrated that, although the presence of either filler system composition accelerated the relaxation process compared to the unfilled compound, the substitution of carbon black by metakaolin decreases the relaxation process for both the tensile and compressive tests. The lower stress relaxation caused by metakaolin in hybrid-system filler was ascribed to the reduction of filler-filler network and filler shape. Moreover, metakaolin imposed some constraints on the rubber chain movements when the load was applied in the tensile mode, but the opposite behavior was observed under compressive force.

1. Introduction

Rubber is arguably one of the most versatile engineering materials due to its elasticity and resilience. Rubber materials also exhibit notable sealability, as well as damping, mechanical and fatigue strength, making them suitable for a wide range of applications (Litvinov et al., 2011; Österlöf et al., 2015). In the oil and gas industry, for example, rubber is used in a multiplicity of plants, equipment and operating environments, at extremes temperatures and pressures, in addition to being exposed to different classes of fluids and chemicals, including corrosion inhibitors, biocides and hydrate inhibitors. Nitrile rubber (NBR), an important material in the oil and gas industry is widely used in seals, plugs, hoses, packers, and other products (Mitra et al., 2006; Slay and Webber, 2011; Varghese et al., 2013).

The design or specification of rubber materials for high-performance applications requires intensive investigation of their properties, which must meet rigorous criteria, such as fluid compatibility, extrusion resistance, fatigue strength, rapid gas decompression, sealability, creep, and stress relaxation. For instance, sealing devices such as O-rings are made from rubber composites and, in order for the seal to perform satisfactorily, it must be deformed to achieve contact stress (higher than the fluid pressure) between the seal-gland surfaces and O-ring. However, if the sealing contact stress of the rubber composite decreases (stress relaxation) to a level at which it can no longer resist the fluid pressure, the O-ring will fail, causing leakage (Slay and Webber, 2011; Guidani et al., 2016; Yang et al., 2017).

Stress relaxation is a viscoelastic property, which can be defined as the decrease in stress that occurs when fixed strain is applied to a rubber (Mitra et al., 2006; Maria et al., 2014). Despite the importance of stress relaxation in the performance of rubber composites (Fernandes and De Focattis, 2014), only a few recent studies have investigated the contribution of fillers to stress relaxation in rubber composites. Meera et al. (2009) reported that stress relaxation is filler loading-dependent for both silica and titanium dioxide-filled natural rubber (NR) composites, that is, the rate of stress relaxation rose as filler loading increased. Furthermore, the author observed greater stress relaxation for silica-filled NR when compared to titanium oxide-filled NR, attributing this finding to the degree of agglomeration in silica. Wang and Han (2013)

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reported similar behavior for the effect of filler content on compressive relaxation in silicone rubber/carbon nanotube composites. Furthermore, when comparing the stress behavior of natural/nitrile rubber nanocomposites filled with two concentrations of organically modified clay, Maria et al. (2014) found that the polarity of the filler drives its location in the blend. Another explanation for the high relaxation rates was the decrease in interaction between the nanoclay mineral and rubber.

Filler reinforcement of rubber products improves their final properties and performance, with the most widely used fillers being carbon black and silica (Rattanasom and Prasertsria, 2012; Senthivel et al., 2015; Ivanoska-Dacikj et al., 2017). However, rubber composites in products such as pump stators, seals, and oilfield production packers require a large amount of carbon black and may exhibit high heat build-up, filler dispersion difficulties, and cure retardation, in addition to causing environmental pollution (Lin et al., 2016). The partial replacement of carbon black with other fillers in rubber formulations (hybrid-system filler) has recently emerged as a valuable technological alternative in material design, owing to the synergistic effects of multiphase filler systems (Liu et al., 2010; Rattanasom and Prasertsria, 2012; Varghese et al., 2013; Senthivel et al., 2015; Lin et al., 2016; Vijay et al., 2016; Ivanoska-Dacikj et al., 2017).

Metakaolin (MK) is obtained by calcining kaolinite at temperatures ranging from ~450 to ~750 °C to remove water and transform it into metakaolinite (Gamelas et al., 2014). Although several industries apply metakaolin as filler, there is little research on its use in hybrid-systems filler with rubber composites, especially nitrile rubber. Thimmaiah and Siddaramaiah (2012) reported that metakaolin acts as non-reinforcing filler in natural rubber (NR) composites and that a maximum of 10 parts per hundred resin (phr) of carbon black can be replaced with metakaolin. Rattanasom and Prasertsri (2012) compared the partial replacement of carbon black with metakaolin or china clay in carbon NR vulcanizates and found that metakaolin produced vulcanizates with higher crosslink density, modulus, and tear strength, but lower gas barrier properties, rebound resilience, scorch and cure times. Ahmed and El-Sabba (2014) prepared metakaolin and kaolin styrene–butadiene rubber (SBR) composites using different filler loadings and reported that metakaolin produced SBR composites with better rheological, mechanical, and thermal properties than the kaolin/SBR composites.

Thus, given the lack of studies on metakaolin in NBR composites, the importance of stress relaxation in the application of rubber materials, and motivated by the possibility of designing a new material using a hybrid filler in rubber composites, the present study aimed to assess the stress relaxation behavior of metakaolin/carbon black-filled NBR composites under tensile and compressive forces. The Payne effect and filler dispersion in the rubber matrix were also evaluated to substantiate the analysis of relaxation behavior.

2. Materials and methods

2.1. Materials

Nitrile Rubber (NBR) (acrylonitrile content: 45%, Mooney viscosity: MML1 + 4 at 100 °C: 50–70) was provided by Nitriflex S/A Indústria e Comércio.

Metakaolin (MK) (specific surface area, BET: 8 m^2/g, specific gravity: 2.6, Si/Al atomic percentage ratio: 1.06), with chemical composition of SiO_2 53.95%, Al_2O_3 43.08%, TiO_2 1.67%, Na_2O 0.30% (as well as other oxides below the detection limit) was supplied by KaMin Performance Minerals. Morphology assessed by scanning electron microscopy (SEM) and particle size distribution of metakaolin are shown in Fig. 1. According to the photomicrographs (Fig. 1a-b), the metakaolin particles exhibit a platy structure, seemingly round edges, and irregular sizes. Fine sheet particles and agglomerates are also evident.

Carbon black (CB) (iodine adsorption number: 27.5 g/kg, oil absorption number: 119 mL/100 g, specific gravity: 1.8) was supplied by the Cabot Corporation. Carbon black morphology assessed by SEM revealed the presence of CB agglomerates, as shown in Fig. 2. According to the literature (Fröhlich et al., 2005), elementary spherical nanoparticles cluster during carbon black production to form three dimensional branched clusters, known as aggregates. Similarly, these aggregates also combine into huge assemblies, denominated agglomerates.

Zinc oxide (ZnO), magnesium oxide (MgO), stearic acid, *N*-Cyclohexyl-2-benzothiazolesulfenamide (CBS), tetramethyl thiuram disulfide (TMTD), dipentamethylene thiuram hexasulfide (DPTH), and 2,2,4-trimethyl-1,2-dihydroquinoline (antioxidant) were commercial grade and obtained from local rubber industries.

2.2. Composite preparation

The NBR composite formulations are presented in Table 1. The rubber composites were designed using a hybrid-system filling with a total of 50 phr (parts per hundred rubber). In addition to the hybrid-system filler composites, three additional composites were prepared: NBR filled with carbon black alone, NBR filled with metakaolin alone, and unfilled NBR, to determine the presence or not of synergism between the two fillers. The experimental nomenclature was defined as *XX*CB/*YY*MK, where *XX* and *YY* are the amounts (phr) of carbon black and metakaolin, respectively.

All the composites were prepared in a laboratory using a two-roll mixing mill (Luxor, model BML 150) at a friction ratio of 1:1.4 and temperature of 50 ± 5 °C. The mixing sequence was in accordance with ASTM D3187. Metakaolin and carbon black were added simultaneously. Total mixing time was 25 min. After mixing, the rubber composites were allowed to rest for 24 h at 25 °C. Next, each composite was vulcanized in sheet format using a hydraulic press at 180 kgf/cm^2 of pressure and temperature of 160 °C according to its respective vulcanization time (t90), which was previously obtained at 160 °C with a rubber process analyzer (RPA 2000, Alpha Technologies), in line with ASTM D5289.

2.3. Characterization

2.3.1. Morphological analysis

The morphology of MK, CB, and the hybrid-system filler NBR composites was analyzed by scanning electron microscopy (SEM) in a JEOL JSM-6510LV microscope, in order to assess filler dispersion in the rubber matrix. MK dispersion was assessed, using energy dispersive spectroscopy (EDS). The NBR composite specimens were prepared by cryogenic fracture in liquid nitrogen and then gold-coated after being fixed on metal stubs using carbon tape.

2.3.2. Payne effect

The Payne effect was assessed based on complex modulus (G*) data, obtained with a rubber process analyzer (RPA 2000, Alpha Technologies). The test procedure was based on ASTM D6601. Initially, the sample was pre-conditioned (1 Hz, 2.8%, 60 °C) for 2 min and then vulcanized into RPA at 160 °C during the vulcanization time (t90), followed by strain sweeping (1 Hz, 60 °C) with a range of 0.7 to 90%. The Payne effect (ΔG*) was calculated by subtracting the values of complex modulus at 0.7 and 11.5% of strain, as per Eq. (1).

$$\Delta G^* = G^*_{0.7\%} - G^*_{11.5\%} \quad (1)$$

2.3.3. Stress relaxation under tensile and compressive forces

Stress relaxation tests were carried out using a universal testing machine (EMIC, DL2000). These tests typically involve applying specific strain to a specimen and monitoring the force required to maintain constant strain during the test. Two different methods were used, namely tensile and compressive stress relaxation tests.