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Effect of direct fluorination on the mechanical and scratch performance of nitrile butadiene rubber

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ABSTRACT

To explore the possibility of direct fluorination to enhance the scratch performance of rubber materials, the effect of direct fluorination on the mechanical and surface properties and scratch performance of nitrile butadiene rubber (NBR) was studied. The bulk mechanical performance of NBR showed no apparent change after fluorination except the fair alteration of the type B tear strength, while the surface properties experienced substantial variations. The surface of the fluorinated samples appears to be cleaner, accompanied with the decreased surface roughness. The friction coefficient decreased substantially with fluorination treatment for only 30 minutes. Obvious changes were observed for the surface modulus and surface energy of the fluorinated NBR. The onset of the scratch groove was significantly delayed under certain fluorination conditions. However, the surface whitening did not show significant improvement. The correlations between the scratch resistance and the bulk mechanical and surface properties were analyzed systematically. The findings demonstrated the surface fluorination can be an efficient method to enhance the rubber's resistance to scratch groove.

1. Introduction

For rubber products such as tires or sealing rings, the scratch on their surface is unpleasant because it not only harms the aesthetics, but also severely damages the functionalities. The stress concentration at the region of scratches may even cause premature failure of the rubber components. Therefore, excellent scratch resistance is critical for the normal use and properties sustaining of rubber products.

The surface scratch behaviors of polymeric materials have been studied by various researchers [1–3]. For rubber materials, scratch tests have been performed on natural rubber (NR) [4–6], styrene butadiene rubber (SBR) [7] and hydrogenated nitrile butadiene rubber (HNBR) etc [8]. under different loading modes. The pioneering work by Schallamach studied the needle friction on NR in a single pass and demonstrated that the lateral tears on the sample were produced by the tensile stress in the sample behind the needle [4–6]. Briscoe et al. displayed severe scratch damages of the NR, SBR and butadiene rubber (BR) resulted from the decreasing of the cone angle of the scratch tip [7,9]. Low et al. found out that the scratch damage of ethylene propylene diene monomer rubber (EPDM), neoprene and SBR was aggravated with the increasing scratch velocity while reinforcing the rubber materials with carbon black could enhance their scratch performance [10]. Zhu et al. observed two distinct scratch damage modes, namely flake peeling and the helical-form damage, for HNBR, under a linearly increasing scratch depth. They found a strong correlation exists between the bulk tear strengths and the scratch resistance [8].

Recently, the surface fluorination was used to modify the surface properties of rubbers due to its high efficiency, simple treatment process and low costs. For example, the surface modulus of wiper blade can be increased by fluorination to obstacle the possibility of forming high friction on wet surfaces [11]. By treating the rubbers either with F2, namely direct fluorination, or fluoride, the fluorine element can be attached onto the rubber surface with the formation of -CF, -CF2 or -CF3 groups by addition reactions occurring at the C=C bounds or substitutions of hydrogen atoms [12–14]. The work by Fan demonstrated that the direct fluorination can be used as an effective way to substantially increase the crosslinking density of the fluoroelastomer film by extending fluorination time at 100 °C atmosphere [12]. Systematical works by Kharitonov et al. demonstrated that direct fluorination with F2 remarkably improved the chemical resistance and adhesive property of polymers meanwhile reduced their electrostatic charging and the friction coefficient [13,16,17]. Nazarov et al. experimentally found the wear properties during a repeated abrasion of rubbers were enhanced by direct fluorination [18]. Schlögl et al. observed that direct fluorination decreased the wettability

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and the surface tension of NR films, however the oxy-fluorination led to an increase of hydrophilicity and increased the surface tension [14]. Gao et al. detected a great increase of the contact angle and a remarkable reduction of surface roughness and friction coefficient of fluoroelastomer after fluorination at 50 °C for 2 hours [22]. With the alteration of the surface properties, the scratch performance of rubber materials was expected to be amended. Therefore, there's a considerable probability to use direct fluorination as a surface modification method to enhance the scratch resistance of rubber materials. However, few studies have addressed this issue.

In the present paper, the influence of direct fluorination on the bulk and surface properties of the nitrile butadiene rubber (NBR) was studied experimentally. Then how the direct fluorination influencing the scratch behavior of NBR was discussed. The results demonstrated that the direct fluorination can be an efficient method to enhance the scratch performance of the rubbery materials.

2. Experiment

2.1. Material and fluorination experiments

The nitrile butadiene rubber (NBR) plates in thickness of 2 and 6mm were provided by Kaidi Northwest Rubber Co., Ltd. Rubber plates in 2 mm thickness were adopted for the tensile and tear tests following ASTM D412-06A (2013) [23] and ASTM D624-00 (2012) [24]. To prevent accident penetration, plates in 6 mm thickness were used for scratch tests. The samples containing 29% acrylonitrile were reinforced with 60 fast extruding furnace black (FEF). The mixed treatment gas containing 10 vol% fluorine (99.99% in purity) diluted with 90 vol% nitrogen was provided by Sichuan Juhe Technology Co., Ltd. The direct fluorination was performed in a closed reaction chamber, which was evacuated at first and then filled with the F_2/N_2 mixture gas until the pressure in the vessel reached 30kPa. The rubber samples were hung in the reaction chamber to allow the air well circulated. The fluorination treatment was conducted at room temperature (25 °C ± 2 °C) and 45 °C respectively and the reaction duration was set at either 0.5 or 1.0 hour.

2.2. Surface properties measurements

The surface morphology of the virgin and fluorinated samples was observed by a super depth digital microscope (VHX-1000, Keyence). The surface roughness Ra of the samples was calculated from the 3D height profile obtained with a confocal laser scanning microscopy (VK-9700, Keyence) according to ISO 25178-2 (2012) [25] within an analyzed area of 2 mm × 2 mm.

The friction coefficients of the virgin and fluorinated samples were measured using a home-made scratch equipment (detail information about the scratcher can be found in [9]) under the ambient temperature. A squared flat stainless steel smooth counterpart with dimensions of 10 mm × 10 mm was used. A constant normal load of 10N was applied over a distance of 100 mm at a speed of 25 mm/s. The tangential friction force was recorded simultaneously.

The contact angle measurements were carried out using a drop shape analysis system (DSA 100, Krüss). Deionized-water and diiodomethane were used as the test liquids. The contact angles were determined at 10 locations on the same specimen surface then the average was recorded. The surface energy was then estimated based on the data of the contact angle according to the conventional Owens method [26].

The Young's modulus of the local surface layer of the samples was measured using an atomic force microscope (MultiMode-8 h, Bruker) with Peak Force Quantitative Nanomechanical Mapping (PFQNM) mode. A spring constant of 6N/m and a resonance frequency of 105 kHz were used for measuring in air. The calibration was conducted on the PDMS-SOFT-2-12M standard surface (3.5 MPa) before the surface modulus measurements. The modulus was calculated from the force-separation curve using the DMT model.

2.3. Bulk mechanical properties measurements

Uniaxial tensile tests were conducted using an electronic universal testing machine (AGS-J, SHIMADZU) under the ambient temperature (about 25 °C). A 500mm/min loading rate was used following the requirement of ASTM D412-06a (2013) [23] to measure the tensile strength and the fracture strain (also known as elongation-at-break) of the samples before and after fluorination.

A universal testing machine (AGS-J, SHIMADZU) was utilized to conduct the tearing tests at about 25 °C. The tear strengths of the type T and type B specimens were measured with a crosshead speed of 50 mm/min and 500 mm/min respectively according to ASTM D624-00 (2012) [24].

2.4. Scratch tests

The scratch tests were carried out using a home-made scratch equipment same as mentioned in Section 2.2 under the ambient temperature. The stainless steel indenter used in this work was conical (half cone angle: 22.5°) with a spherical indenter tip (diameter: ≈0.3 mm). The scratch depth (D) was increased linearly from 0 to 3 mm on a 100 mm scratch length with a constant scratch speed of 25 mm/s. At least three duplicated scratch tests were performed on the samples with same fluorination degree. The overall surface morphology of the samples was scanned using a high resolution (2400 × 2400 dpi) optical scanner (LiDE 210, Canon). The detailed topology of the scratches was observed using a super depth digital microscope (VHX-1000, Keyence). The in-situ depth d at a given scratch distance x can be calculated using the following equation:

$$d = Dx/L \tag{1}$$

where D ($D = 3$ mm) is the final depth of the scratch process and L ($L = 100$ mm) is the scratch length. The residual depth can be obtained from the 3D height profile obtained with a super depth digital microscope. In the present paper, the depth of the scratch damage was the in-situ depth.

3. Results and discussion

3.1. Effect of direct fluorination on surface properties

The surface morphology of the NBR samples fluorinated under various conditions is shown in Fig. 1. Since the impurities on the virgin sample surface were etched by the fluorine, cleaner sample surfaces were observed after fluorination. The density of the surface layer is substantially increased due to the attachment of fluorine groups. The resulted difference between the densities of fluorinated surface layer and that of untouched substrate layer would lead to an uneven shrinkage of the rubber material which causes larger but shallower pits and furrows [14,15]. A more homogeneous sample surface was gradually formed with the shoaling of the pits and furrows. The evolution of the surface morphology was accompanied with the change of surface roughness. A decline of the surface roughness from 6.47 μm to 5.61 μm and 5.86 μm was observed for the sample fluorinated under room