Tribology International 69 (2014) 141–149

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Dependence of abrasion behavior on cross-linked heterogeneity in unfilled nitrile rubber ☆

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ARTICLE INFO

Article history:
Received 24 April 2013
Received in revised form
9 August 2013
Accepted 15 September 2013
Available online 23 September 2013

Keywords:
Cross-linked heterogeneity
Abrasion behavior
Nitrile rubber
Cross-linking density

ABSTRACT

Four unfilled nitrile rubber specimens with different sulfur contents were prepared, from 1.0 to 1.7 phr. The friction energy density, morphology of abraded surface, cross-linking density and fracture energy of NBR specimens were studied. Additionally, the dissipated energy by tapping mode atomic force microscopy was determined to investigate cross-linked heterogeneity of the network. It was found that the cross-linked heterogeneity plays a critical role in abrasion performance of NBR. Then a model of network was proposed. The simulation results indicate that the higher level of cross-linked heterogeneity would increase the probability of network failure and lead to inferior abrasion resistance, which are accordant with the results of experiments.

1. Introduction

Nitrile rubber (NBR), a synthetic copolymer of acrylonitrile and butadiene, is widely used as a sealing material due to its excellent physical properties, outstanding gas permeability and good resistance to oil [1]. Even so, the wear of NBR is still unavoidable when the seal assemblies are used under rough conditions. The wear accounts for 60%–80% of application failures, leading to enormous economic loss [2]. Thus, the abrasion behavior of NBR has attracted increasing attention and many studies have been carried out. In addition to the influences of operating conditions, e.g. applied load [3], sliding speed [4], temperature [5] and type of medium [6], it is well known that the abrasion behavior of vulcanized NBR is also dependent on itself structure factors, including acrylonitrile content [7], cross-linking density (molecular weight between cross-links) [8], and interfacial combination of reinforcing filler/rubber matrix [9], etc. Among those factors, the cross-linking density plays an important role for physical properties of polymer [10], and optimization of this factor provides a practical way to enhance the abrasion performance of NBR. Cho et al. studied the effect of molecular weight between cross-links on the abrasion behavior of rubber by a blade type abrader. It was found that the abrasion rate and mechanism were closely related to the critical frictional input work [11]. Jurkowska et al. reported that K95, a fluorine-containing lubricant, participated in forming strong physical junctions of NR/BR rubber and reduced molecular weight between junctions of thermally stable network by which an increase in the abrasion resistance of rubber compound was observed [12]. Generally, the abrasion rate of elastomer is directly proportional to the molecular weight between cross-links. On the other hand, there are many evidences to support the existence of the cross-linked heterogeneity in the network structure [13–15], even in polymer gels [16]. The uneven distribution of cross-links in polymer network usually reduces the mechanical strength, deformability [17], and abrasion resistance. Bhuyan et al. reported that the nonuniform cross-linked structure in soybean oil-based polymers results in softer and weaker regions where the cutting or plowing of the surface by diamond is apt to take place [18].

The tapping mode atomic force microscopy (TMAFM) is suitable to characterize microscale properties of the polymer surface because of the minimal lateral and shear forces. Note that the dissipated energy (E_{dis}), a function of phase shift and amplitude setpoint, is sensitive to the surface deformation [19], and the curve shape of E_{dis} can highlight the compositional contrast on the heterogeneous surfaces [20]. Dietz et al. mapped the local surface of crystalline and amorphous regions of elastomeric polypropylene through the E_{dis} values [21]. Garcia et al. characterized the hybrid surfaces of polystyrene/polybutadiene blend by dynamic dissipation curves [19]. And Bar et al. investigated the butadiene/styrene-co-butadiene rubber blends and concluded that the phase shift increases almost linearly with the increasing of energy dissipation [22].

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0301-679X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.triboint.2013.09.011

In this paper, the effect of cross-linked heterogeneity on abrasion behavior of unfilled NBR vulcanizates is discussed. NBR specimens with different contents of sulfur were well prepared. The corresponding friction energy density, cross-linking density and distribution of cross-links were obtained using a conventional ball-on-flat tribometer, equilibrium swelling method and TMAFM, respectively. Then, a model of cross-linked network was proposed. The results of numerical simulation are well consistent with the findings in the experiments.

2. Experiments and methods

2.1. Materials and specimen preparation

The NBR (N215SL, acrylonitrile content of 48%) was purchased from JSR company (Japan). Sulfur with purity of 99.5%, as the curing agent, was supplied by Kezhan Chemical company (China) and the content of sulfur was varied from 1.0 to 1.7 phr. Other ingredients were obtained as commercial grade chemicals and used without further treatment. The formulas of these four specimens are shown in Table 1, denoted as S1.0, S1.2, S1.5, and S1.7. Unfilled NBR vulcanizates were well prepared with two-roll laboratory mill and then cured in hydraulic press under a pressure of 20 MPa at 155 °C. The optimal cure time was determined by the Moving Die Rheometer (GoTech-M2000A, China).

2.2. Cross-linking density measurement

The average molecular weight between cross-links (M_c) was determined through the equilibrium swelling method using dichloromethane as a solvent. Test piece, 30 mm in diameter and 2 mm thick, was weighed and then immersed to equilibrium into solvent at 25 °C, which process took around 72 h. Then the value of M_c was calculated using the Flory–Rehner equation [23].

$$M_c = \frac{-\rho_p V_S \Phi^{(1/3)}}{[\ln(1-\Phi)+\Phi+\chi\Phi^2]} \quad (1)$$

$$\gamma = \frac{\rho_p}{M_c} \quad (2)$$

where ρ_p, V_s, Φ, χ, and γ are the density of polymer, molar volume of solvent, volume fraction of polymer, interaction parameter and cross-linking density, respectively. The χ value was adopted as 0.31 [24].

2.3. Mechanical properties testing

The uniaxial tensile test was carried out using a universal test machine (WDTII-20, China) according to ISO 37:1994. Crosshead displacement rate was set at 500 mm/min, and the initial separation distance between two clamp holders was 36 mm. To determine the fracture energy (G_c) of NBR specimen, unnicked angle tearing test was conducted using the same universal test machine at a speed of 5 mm/min. The G_c value was calculated using the following equation [11].

$$G_c = \frac{2F}{t} \quad (3)$$

where F is the tear force and t is the thickness of test piece.

Table 1
The formulas of testing NBR specimens.

Ingredient (phr)	Informal code			
	S1.0	S1.2	S1.5	S1.7
Nitrile butadiene rubber	100	100	100	100
Stearic acid	1	1	1	1
Zinc oxide	5	5	5	5
CBS	1.5	1.5	1.5	1.5
TMTD	0.2	0.2	0.2	0.2
Sulfur	1.0	1.2	1.5	1.7

2.4. Wear testing

The wear experiment was carried out using a ball-on-flat tribometer (HT600, China). A stainless steel ball with diameter of 5 mm was chosen as counterpart sliding against NBR specimen. The surface of the steel ball with an arithmetic average roughness of around 0.8 μm was ultrasonically cleaned with acetone and then thoroughly dried before use. The NBR vulcanizate was prepared as plate that was 70 mm long, 40 mm wide and 2 mm thick. And it was bonded on the steel disc during curing process. The wear experiment was conducted at a speed of 0.37 m/s and a constant load of 3.5 N, which lasted for 3 h at 25 °C and a relative humidity of 20 ± 5%. During the experiment, the frictional force and coefficient of friction were monitored continuously by strain gauges. Each testing result was averaged from five tests. High resolution images of the worn surface on the NBR specimen were obtained using a Scanning Electron Microscope (FEI Quanta 200 F). All specimens were sputter-coated with gold before observations.

2.5. Energy dissipation measurement

The TMAFM measurement of the cross-linked heterogeneity was performed on a Nanoscope (IIIa) instrument for NBR specimen. Before measurement, the NBR vulcanizate was cryogenically cut by a Lecia EM FC6 instrument at −90 °C. The resonance frequency (ω_0) of the cantilever was 218 kHz. And the force constant (k), free amplitude (A_0) and quality factor of the cantilever (Q) were 4.0 N/m, 100 nm and 130, respectively. Both phase and amplitude images were recorded simultaneously at the amplitude set-point ratio (A/A_0) of 0.4. Then the data of phase shifts and amplitudes were used to calculate the dissipated energy (E_{dis}) by the following equation [19].

$$E_{dis} = E_{ext} - E_{med} = \frac{\pi k A}{Q}\left(A_0 \sin \Phi - \frac{A\omega}{\omega_0}\right) \quad (4)$$

where E_{ext}, E_{med}, Φ, and ω are excitation energy, energy dissipated into the medium, phase shift and excitation frequency, respectively.

3. Results and discussion

3.1. Physical properties of NBR specimens

Fig. 1 shows the uniaxial tension stress–strain curves of NBR vulcanizates. All specimens display a similar tensile behavior until the strain reached 200%. Within the strain range from 200% to 450% the stress value increases with the sulfur contents, while the elongation at break shows the opposite trend. The tightness of the polymer network depends on the cross-linker concentration which can reduce the molecular mobility of chains between the cross-linked junctions [25]. According to previous work, uniaxial deformation of cured NBR would have no influence on the chemical nature of the chain and cross-linking density of the network [24]. Thus the cross-linking density is an essential factor to gain a better understanding of mechanical properties.

Then the average molecular weight between cross-links (M_c) of NBR specimen was calculated according to the Flory–Rehner equation. Fig. 2 displays a decrease tendency of M_c with the incease of sulfur contents. The Mooney–Rivlin constants were also determined according to the uniaxial tension curves over the range: $1 < \text{extension ratio} < 2$.