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Material properties

Investigation of aging behavior and mechanism of nitrile-butadiene rubber (NBR) in the accelerated thermal aging environment

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ABSTRACT

Nitrile-butadiene rubber (NBR) was exposed to an accelerated thermal aging environment produced by an air-circulating oven for different time periods. NBR aging was evaluated by morphology, crosslink density, mechanical properties, chemical changes and thermal stability. The results showed that the surface damage of NBR turned severe and inhomogeneous, and the aging degree was most serious on the edge region of voids. Crosslinking reactions mainly occurred in the aging process. The tensile strength increased with increase in crosslink density up to a maximum value and thereafter decreased with further increase in crosslink density. X-ray Photoelectron Spectroscopy (XPS) and Pyrolysis Gas Chromatography-Mass Spectrometry (Py-GC/MS) analysis demonstrated that hydroxyl groups were formed and the additives migrated from inner to surface of NBR samples. In addition, the thermogravimetric analysis (TGA) indicated that the thermal stability of NBR did not significantly change in the accelerated thermal aging environment.

1. Introduction

Nitrile-butadiene rubber (NBR) has been widely used in industry over the years [1–5]. NBR has great potential in seals industry because of its low cost, excellent resistance to oil, fuels and greases, low abrasion rate, and good processability [1,2]. However, the aging resistance of NBR is sensitive to environmental factors because of the presence of unsaturated back-bone of the butadiene part. A degrading environment, such as one characterized by high temperature, high humidity, strong light, low temperature, or a mechanical load, can have a profound effect on durability of NBR [3–9]. For instance, in oxygen containing environments, the hardness, morphology and mechanical properties of NBR rubber can be greatly affected by oxidation, especially at relatively high temperatures [10–14]. In fact, the process of rubber degradation is very slow in an actual working environment, so it takes a long time to obtain rubber with degradation behaviors. Thus, accelerated aging tests are typically used to study the degradation of rubbers in a comparatively short time [15].

Thermal aging of the NBR rubber in air is an extremely complex process that involving several reactions that proceed in oxygen and without it. Thermal oxidation research of NBR has been carried out for decades. In the previous works [16–20], the effects of thermo-oxidation on the physical properties of NBR were investigated, and the volatile components and oxidative degradation products changes during thermal aging of NBR were analyzed. During the thermal aging, mainly three changes occurred successively: (1) migration and loss of additives such as plasticizers, stabilizers; (2) extra crosslinking of the rubber network; and (3) oxidation of macromolecular chains [21,22]. Although there are many studies [16–20,23–24] on the accelerated thermal aging behavior of NBR rubber up to now, the thermal aging mechanism of nitrile-butadiene rubber (NBR) still need to be studied further.

The objective of the present work was to investigate the aging behavior and mechanism of nitrile-butadiene rubber (NBR) in the accelerated thermal aging environment. The change of morphology was monitored by Scanning Electron Microscope (SEM). Crosslink density of NBR specimens was measured by the solvent swell method. Mechanical properties were monitored by computer-controlled universal tensile testing. The surface chemical changes were detected by Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR), X-ray Photoelectron Spectroscopy (XPS) and Pyrolysis Gas Chromatography-Mass Spectrometry (Py-GC/MS). The thermal stability was evaluated by

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Thermogravimetric Analysis (TGA).

2. Experimental

2.1. Materials

The sulfur vulcanized NBR sheets with thickness of 2 mm were supplied by Changjiang Rubber Manufacturing Limited Company of China. The nitrile content is around 32%. In addition to NBR, carbon black, ZnO, Dibutyl Sebacate plasticizer, DCP curing package and antioxidant D were included in the composition of the sheets. To improve the aging resistance of NBR, a certain percentage of Neoprene was also added into NBR. The specific compounds formulation and technological process were not disclosed because of commercial reasons. The samples were cut into dumbbells and strips according to the standard ASTM D412-2006 for mechanical properties measurements.

2.2. Thermal aging

Accelerated thermal aging studies were carried out in an air-circulating oven (Electro-mag with sensitivity of ±1 °C) equipped with thermocouples connected to continuous recorders. The test temperature was selected at 65 °C for up to 90 days in this work.

2.3. Surface morphology and component analysis

The surface morphology of the samples was studied by using Quanta 200 Scanning Electron Microscope (SEM) (Quanta 200, FEI Inc, Netherlands) operating at an accelerating voltage of 20 kV. All the samples for SEM tests were not stained. The surface component analysis was carried out by an INCA Energy Dispersion Spectroscopy (EDS) (Oxford Instrument, UK) accompanied with SEM.

2.4. Crosslink density

The volume fraction of rubber in swollen network of the vulcanizates V_r, was determined by means of equilibrium swelling in acetone laboratory grade at 23 °C. The equilibrium swelling was used to calculate the crosslink density, which was the number of network chain density by applying the Flory-Rehner equation [25] as follow:

$$V_e = -\frac{1}{V}\left[\frac{\ln(1-V_r)+V_r+\mu V_r^2}{V_r^{1/3}-V_r/2}\right] \tag{1}$$

where V_e was crosslink density; μ was polymer-solvent interaction parameter; V was molar volume of solvent; V_r was volume fraction of rubber in the swollen gel.

2.5. Evaluation of mechanical properties

The mechanical properties were evaluated by tensile tests. The tensile specimens were tested according to ISO 37: 2011 at room temperature (23 °C) with a crosshead speed of 500 mm min^{-1} using a computer-controlled universal testing machine (INSTRON 5565, USA) equipped with pneumatic grips. At least five samples were tested in order to get a reliable result.

2.6. Attenuated total reflection-fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR spectra of the samples were taken at room temperature using a Nicolet 470 Instrument (Nicolet Inc, USA) in the range 700–4000 cm^{-1} with 32 scans at a resolution of 4 cm^{-1}. The infrared radiation (IR) penetrates the surfaces of samples to approximately 1 μm. The average of three scans for each sample was taken for peak identification, with diamond as the ATR crystal.

2.7. X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed using a ESCALAB 250 analyzer (Thermo Inc, USA) equipped with an achromatic Al Kα X-ray source. The pressure during the analysis was 6.7×10^{-8} Pa and the take off angle was 45°. The survey spectra in the range of 0–1200 eV were recorded in 1 eV step for each sample. Atomic concentrations of each element were carried out by determining the relevant integral peak intensities. High-resolution scans with step size 0.1 eV for C 1s and O 1s were recorded. The binding energies were corrected by referencing to the hydrocarbon component at 284.8 eV.

2.8. Pyrolysis gas chromatography-mass spectrometry (Py-GC/MS)

Py-GC/MS analysis were carried out using an EGA/PY-3030D multi-shot pyrolyzer (Frontier Laboratories Ltd., JPN) coupled to a Trace GC Ultra gas chromatograph equipped with a TSQ Quantum XLS mass spectrometer (AGILENT Inc, USA). The sample (about 1.0 mg) was preheated at 300 °C for 3 min and pyrolyzed at 450 °C for 1 min under a helium (He) atmosphere. The volatiles were carried by carrier gas He through a HP-5MS capillary column (30.0 m, i.d. 0.32 mm × 1.0 μm stationary phase thickness) and the mixture was separated. The GC oven temperature program was as follows: 70 °C (held for 2 min) to 230 °C at 20 °C/min (held for 16 min). The interface temperature of GC to MS was 250 °C. Electron ionization (70 eV) was used to ionize the pyrolysis products. The MS source temperature was 230 °C.

2.9. Thermogravimetric analysis (TGA)

The thermogravimetric analysis of NBR was carried out using a TG/DTA Q600 system (TA Inc, USA). Specimens weighing 10–15 mg were heated to 550 °C in nitrogen at a feed speed of 60 ml/min, and the heating rates was 10 °C/min. Nitrogen flow (80 ml/min) was employed in order to remove all corrosive gases involved in the degraded materials and to avoid thermo-oxidative degradation.

3. Results and discussion

3.1. Surface morphology and component analysis

The morphology changes on the surface of samples before and after thermal aging for different times were obtained by Scanning Electron Microscopy (SEM) as shown in Fig. 1. Apparently, the surface of the unaged NBR samples was relatively homogeneous and smooth and with no obvious defects appeared. With increasing aging time, small voids appeared. When the aging time reached 90 days, the surface turned rougher, the size of the voids became greater and more white spots can be observed. The appearance of white spots on the NBR samples was related to precipitation of some additives [26–29], and this phenomenon would be demonstrated below.

In order to analyze the degree of thermal aging of NBR samples after 90 days conveniently, the components of oxygen and carbon on the NBR surface were analyzed by Energy Dispersion Spectroscopy (EDS) microanalysis system. Three different regions were selected in Fig. 2, which respectively corresponded to the bottom of one void (Spectrum 1), the edge of voids (Spectrum 2) and the relatively smooth region (Spectrum 3). The atomic weight proportion of oxygen and carbon (O/C) was adopted to determine the