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Interfacial interaction between the epoxidized natural rubber and silica in natural rubber/silica composites

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ABSTRACT

The epoxidized natural rubber (ENR) as an interfacial modifier was used to improve the mechanical and dynamical mechanical properties of NR/silica composites. In order to reveal the interaction mechanism between ENR and silica, the ENR/Silica model compound was prepared by using an open mill and the interfacial interaction of ENR with silica was investigated by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), X-ray diffraction (XRD) and stress–strain testing. The results indicated that the ring-opening reaction occurs between the epoxy groups of ENR chains and Si-OH groups on the silica surfaces and the covalent bonds are formed between two phases, which can improve the dispersion of silica in the rubber matrix and enhance the interfacial combination between rubber and silica. The ring-opening reaction occurs not only in vulcanization process but also in mixing process, meanwhile, the latter seems to be more important due to the simultaneous effects of mechanical force and temperature.

1. Introduction

Silica (SiO_2) is one of the important reinforcing fillers in rubber industry. Since the beginning of the 90s of last century, silica was increasingly used in tires as the rise and development of "green tire". The application of highly dispersible silica together with some special rubbers such as solution polymerized styrene-butadiene rubber (SSBR) in tires leads to the best improvement of rolling resistance and wet traction without any compromises in tread wear [1]. The silica in green tire was usually used together with some silane coupling agents such as bis(triethoxysilylpropyl)tetrasulfane (TESPT).

It is well known that epoxidized natural rubber (ENR) is a modified rubber prepared by the epoxidized reaction of natural rubber (NR) in peracid conditions [2,3]. ENR possesses some new properties except the normal characteristics of NR, such as oil resistance, gas tightness [4,5], low rolling resistance and high wet skid resistance. These properties are useful in tires and other rubber products. It was shown that the comprehensive properties of silica-reinforced vulcanizate can be substantially improved by adding ENR as a compatilizer [6]. In addition, ENR can be applied in composites reinforced with other fillers, such as organoclay [7,8] and halloysite nanotubes [9], also some other blends and composites [10–14]. The authors [15] reported morphology and properties of styrene-butadiene rubber/silica (SBR/SiO_2) composites modified by ENR. The results showed that the addition of a small amount of ENR could improve the dispersion of silica in rubber matrix. The modulus, tensile strength, tear strength and wear resistance of the vulcanized composites were enhanced and the compression fatigue temperature rising was reduced when ENR amounts varied from 0 to 8 phr, also the wet skid resistance was improved evidently without increasing the rolling resistance.

There are a mass of active Si-OH groups on the surfaces of silica particles that can be chemically modified [16]. The research showed that the interaction [17–19] between ENR and silica might be induced by chemical bond, hydrogen bond, physical adsorption or something else [20–23], but till now there is not a definite concept of the interaction mechanism between ENR and silica.

In this article, ENR as an interfacial modifier was used to improve the mechanical and dynamical mechanical properties of NR/silica composites. To investigate the interfacial interaction mechanism between ENR and silica, ENR/silica model compound was prepared by mixing method on the mill and characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM) and mechanical properties determination. The results showed that the properties improvement of NR/silica composites can be attributed to the ring-opening reaction between the epoxy

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groups of ENR chains and Si-OH groups on the surfaces of silica particles, which can improve the dispersion of silica in the rubber matrix and enhance the interfacial interaction between rubber and silica. The ring-opening reaction happens not only in vulcanization process but also in mixing process, and that the latter seems to be more important due to the dual effects of mechanical force and temperature.

2. Experimental

2.1. Materials

Epoxidized natural rubber is supplied by Agricultural Product Processing Research Institute, Chinese Academy of Tropical Agriculture Sciences (Zhanjiang, China) and its epoxidized degrees are 40% (ENR-40) and 25% (ENR-25), respectively. Natural rubber (NR) is Thailand 3# smoked sheet. Precipitated silica (type 518) is produced by Wanzai Huiming Chemical Limited Company (Jiangxi, China). Trichloromethane ($CHCl_3$, AR) is supplied by Jin Mao Tai Chemical Limited Company, Shanghai, China. Toluene (AR) is provided by Kaixin Chemical Reagent Limited Company (Hengyang, China). Other rubber additives are industrial grade and used as received.

2.2. Preparation of ENR/silica model compound

To shed light on the interfacial reaction between ENR and silica more clearly, ENR-40 (40% epoxy groups in natural rubber molecular chain) was employed to prepare the ENR/silica model compound. In the model, the ENR and silica with the mass ratio of 100/50 were mixed by LRMR-S-150/0 two-roll open mill (Lab Tech Engineering Company LTD.) at different temperatures for 10 min. No other rubber additives were added into the compound in the whole process. After that, the ENR/silica compounds were divided into two parts. The one at the mixing temperature of 70 °C was extracted with trichloromethane ($CHCl_3$) in Soxhlet extractor for 72 h to remove the physical adsorbed ENR from silica. The dried residuum of extraction was then subjected to characterize by FTIR, XPS, XRD, and TEM. The other part was compressed into 2 mm thick sheets by flat vulcanizing machine (KSH R100, Shanghai China) at different temperatures for 15 min, then the sheets were used for stress–strain test.

2.3. Preparation of NR/silica composites modified by ENR-25 as an interfacial modifier

NR was firstly compounded with ENR, then SiO_2 and other additives were added into the NR/ENR blends and compounded on the X(S)K-160 two-roll open mill (Zhanjiang China). The compounds were compression molded at 143 °C for optimum curing time T_{90} determined by a rheometer. The compositions of NR/silica composites are showed in Table 1. In the preparation of NR/silica composites, considering that ENR-40 has strong polar and poorer compatibility with NR, we employed ENR-25 with less oxygen groups to modify silica instead of ENR-40.

2.4. Testing and characterization

2.4.1. Mechanical properties

Tensile tests were performed following ISO 37-2005 at 25 °C using U-CAN UT-2060 tensile instrument (Taiwan). The stress–strain curves were obtained from tensile tests.

Dynamical mechanical analysis (DMA) was carried on by an EPLEXOR 500N dynamical mechanical spectrometer (GABO, Germany). The samples were scanned from −80 °C to 100 °C with a heating rate of 5 °C/min. The tensile mode was adopted, and the frequency was fixed at 10 Hz.

Compression heat-up performance was determined by an UD-3801 compression fatigue tester according GB/T 1687–1993. The testing conditions: die cavity temperature 50 °C ± 1, dynamic strain 5.71 mm, static load 245 N, compression frequency 1800 r m^{-1}, determination time 25 min.

Table 1
Composition of NR/silica composites (mass ratio) .

Sample code	1	2	3	4
NR	100	97	94	91
Silica	30	30	30	30
ENR-25	0	3.0	6.0	9.0
Zinc oxide	4	4	4	4
Stearic acid	2	2	2	2
Accelerator CZ[a]	1.5	1.5	1.5	1.5
Accelerator DM[b]	0.5	0.5	0.5	0.5
Sulphur	1.5	1.5	1.5	1.5
Antioxidant 4010NA[c]	1.0	1.0	1.0	1.0

[a] N-cyclohexyl-2-benzothiazolesulfenamide.
[b] 2,2′-Dibenzothiazoledisulfde.
[c] N-isopropyl-N′-phenyl-p-phenylenediamine.

2.4.2. Fourier transformation infrared spectroscopy (FTIR)

FTIR analysis of ENR/Silica model compound after extraction was taken by using a Bruker VERTEX 70 infrared spectrometer. The samples were compressed into platelets with KBr. To make sure the change of epoxy ring content in the processing process, the compound sheets of different stages of processing were investigated by Attenuated Total Reflection-Flourier transformed Infrared Spectroscopy (ATR-FTIR).

2.4.3. X-ray photoelectron spectroscopy (XPS)

XPS spectra of ENR/silica model compound after extraction was recorded by using a X-ray photoelectron spectrometer (Kratos Axis Ultra DLD). Operating voltage and electric current were 15 kV and 10 mA, respectively. The vacuum degree of analysis room was 10^{-8} to 10^{-7} Pa and analysis area was 0.7 mm × 0.3 mm. The treatments of high-resolution survey of the samples were performed with XPS Peak 4.1 software [24,25].

2.4.4. X-ray diffraction (XRD)

The XRD analysis was performed by using a D8 ADVANCE X-ray diffractometer (Bruker, Germany) with CuKα radiation and Lynx-Exe array detector. Accelerating voltage and electric current were 40 kV and 40 mA, respectively. The samples were scanned from 5° to 90° with a step length of 0.02° at the scanning speed of 17.7 s per step.

2.4.5. Transmission electron microscopy (TEM)

The ENR/silica model compound after extraction was diluted by ethanol and dispersed with KQ3200 ultrasonic dispersion apparatus for 2 h, then the suspension was dropped into copper net for observation. A Hitach-7650 TEM machine was used to observe the morphology of the samples at the accelerating voltage of 80 kV.

2.4.6. Field emission scanning electron microscopy (SEM)

The vulcanizates of NR/silica composites, with ENR-25 as a modifier, were made into the shape (15 mm × 6 mm × 1 mm) and then got the brittle fracture in liquid nitrogen. The morphology of fractured sections that sprayed by platinum were achieved by using the ZEISS Merlin SEM (German) machine at the acceleration voltage of 5 kV.