Composites Part B 107 (2016) 106–112

Contents lists available at ScienceDirect

Composites Part B

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

Morphology and performance of NR/NBR/ENR ternary rubber composites

Xiuying Zhao [a], Kaijing Niu [a], Yong Xu [a], Zheng Peng [b, *], Li Jia [c], David Hui [d], Liqun Zhang [a, **]

[a] State Key Laboratory of Organic Inorganic Composites, Beijing University of Chemical Technology, Beijing, 100029, China
[b] Institute of Agricultural Products Processing, Chinese Academy of Tropical Agricultural Sciences, Zhanjiang, 524001, China
[c] Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA
[d] Department of Mechanical Engineering, University of New Orleans, New Orleans, LA 70148, USA

ARTICLE INFO

Article history:
Received 1 April 2016
Received in revised form
5 September 2016
Accepted 5 September 2016
Available online 28 September 2016

Keywords:
Natural rubber
Nitrile butadiene rubber
Epoxidized natural rubber
Ternary composites
Compatibilizer
Tread material

ABSTRACT

Epoxidized natural rubber (ENR) was used as a compatibilizer to prepare ternary composites with natural rubber (NR) and nitrile butadiene rubber (NBR). The morphological, structural, and mechanical properties of the NR/NBR/ENR ternary composites were systematically investigated by using SEM, AFM, TEM, DSC, DMTA, and tensile testing. The NR matrix was the continuous phase, and NBR was the dispersed phase with a size of several micrometers. ENR reduced the aggregation of the NBR phase and improved the compatibility between NR and NBR. According to the rule of "like dissolves like", with increasing polarity, ENR migrated from the NR matrix and was dispersed into the NBR phase or gathered at the interface between NR and NBR. Compared with pure NR, the ternary composites had a higher tan δ at 0 °C and lower tan δ at 60 °C, related to the wet grip and rolling resistance of tread materials, respectively. The results also indicated that the prepared NR/NBR/ENR ternary composites exhibited improved tensile strength and tear strength because of the strain-induced crystallization of NR. Therefore, the NR/NBR/ENR ternary composites are promising high-performance tire tread materials.

1. Introduction

Pneumatic tires, which not only can provide traction between the vehicle and the road, but also can provide a flexible cushion that absorbs shock, are used widely on many types of vehicles, including cars, bicycles, motorcycles, trucks, and aircrafts [1]. With the development of modern vehicles with high speed, security, energy savings, and comfort, the demands for high-performance tires have increased year after year. Therefore, the tire tread should have the characteristics of low rolling resistance, good wet-skid resistance, and excellent wear resistance. It is difficult to improve all three properties at the same time; the improvement of one or two properties usually leads to the degradation of the other property [2]. The tread wear resistance of tires has increased significantly because of the adoption of the radial-ply tire structure, and researchers have mainly focused on the tire rolling loss and wet grip for improving the safety of the vehicle, especially on rainy and snowy days [3]. Rolling resistance correlates directly with tan δ in the temperature range of 50–70 °C: the lower the value of tan δ, the lower the rolling resistance. Reducing the tan δ value in this temperature range, however, also reduces the tan δ value at lower temperatures. But good wet grip corresponds to a high tan δ value at lower temperatures (near 0 °C). Thus, it's hard to achieve good wet grip and rolling resistance at the same time [4].

Natural rubber (NR) is an indispensable material for industrial applications, such as pneumatic tires for heavy-duty uses, due to its excellent tensile properties and good crack growth resistance, which derives from its prominent ability to crystallize under tensile deformation [5,6]. Although NR has many excellent properties, it cannot completely fulfill the industrial need for high-performance tires. A NR tire tread has low rolling resistance, but its wet-skid resistance is poor. Blending is a good and traditional way to improve the performance of individual polymer [7]. Polymer blend is prepared to meet performance requirement that cannot be satisfied by the current available commodity polymer or properties

* Corresponding author.
** Corresponding author.
E-mail addresses: zhanglq@mail.buct.edu.cn (Z. Peng), zpengcatas@126.com (L. Zhang).

http://dx.doi.org/10.1016/j.compositesb.2016.09.073
1359-8368/

lacking in the component polymers [8,9]. NR has been blended with acrylonitrile-butadiene rubber (NBR) with the propose of improving the damping property at 0 °C [10–13]. But NR/NBR blends have deficiencies, such as the delamination of the vulcanizates, due to the poor compatibility and difference in polarity between NR and NBR [14–17].

There have been many reports on the use of epoxidized natural rubber (ENR) as a potential compatibilizer for rubber blends [18–22]. ENR is a relatively new rubber material, though the epoxidation of natural rubber is not a new idea [23,24]. Known since 1922, ENR only became commercially available in the past decade. ENR is a random copolymer made of isoprene and epoxidized isoprene units, generating from the reaction of formic acid or hydrogen peroxide on the natural rubber latex [25–29]. It imparts high polarity and is miscible with other polar polymers, but is still compatible with non-polar rubbers [30–32]. ENR shows such attractive properties as oil resistance, reduced air permeability, damping, and wet grip, comparable to those of synthetic specialty rubbers. It also exhibits superior mechanical properties because of its strain-induced crystallization, a property inherited from natural rubber [33–35]. The aim of this study was to prepare and characterize NR/NBR/ENR composites, in which NR is the matrix and provides the general mechanical properties, NBR improves the damping property at 0 °C, and the third component ENR acts as a compatibilizer to improve the compatibility between the NR matrix and NBR dispersed phase. Thus, these NR/NBR/ENR composites are expected to be good tire tread materials. Atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscope in the back-scattered electron mode (SEM-BSE), differential scanning calorimetry (DSC), dynamic mechanical thermal analyzer (DMTA), tensile tester were used to investigate the microstructure, damping properties, and mechanical properties of the NR/NBR/ENR composites and the effect of the degree of epoxidation of ENR on the properties the NR/NBR/ENR composites.

2. Experimental

2.1. Materials

NR (ribbed smoked sheet No.1) was obtained from Nanjing Shengdong Chemical Co., Ltd. (Nanjing, China). NBR (N220S) with an acrylonitrile mass fraction of 41% was provided by Japan Synthetic Rubber Co., Ltd. (Tokyo, Japan). ENRs, denoted by ENR25, ENR40, and ENR50, with degrees of epoxidation of 25%, 40%, and 50%, respectively, were provided by Chinese Academy of Tropical Agricultural Sciences (Zhanjiang, China). Other chemicals and ingredients were purchased in China. All materials were used without further purification.

2.2. Sample preparation

1. **NBR compound:** The as-received NBR was kneaded on a Φ 152.4 mm two-roll mill at room temperature for 2 min and then blended with compounding and crosslinking additives, including 5.0 phr of zinc oxide, 2.0 phr of stearic acid, 0.5 phr of accelerant D (diphenyl guanidine), 0.5 phr of accelerant DM (dibenzothiazole disulfide), 0.4 phr of accelerant TMTD (tetramethylthiuram disulfide), and 1.5 phr of sulfur. The mixture was then kneaded on the two-roll mill at room temperature for 5 min to form the NBR compound.
2. **NR/ENR compounds:** The as-received NR and each of ENR25, ENR40, and ENR50 were mixed in the mass ratios of 70/0, 70/5, 70/10 on a Φ 152.4 mm two-roll mill at room temperature for 2 min. Then each compound was blended with compounding and crosslinking additives, including 3.0 phr of zinc oxide, 1.0 phr of stearic acid, 0.5 phr of accelerant D, 0.5 phr of accelerant DM, 2 phr of antioxident N-isopropyl-N'-phenyl-p-phenylene diamine (4010NA), and 1.5 phr of sulfur. Each compound was then kneaded on the two-roll mill at room temperature for 5 min.
3. **NR/NBR/ENR composites:** The NBR compound and NR/ENR compounds were kneaded with mass ratios of 30/70, 30/75, 30/80, 30/85, 30/90 to form the NR/NBR/ENR (70/30/0), NR/NBR/ENR (70/30/5), NR/NBR/ENR (70/30/10), composites on a Φ 152.4 mm two-roll mill at room temperature for 5 min. These mixtures were then hot pressed and vulcanized at 143 °C under a pressure of 15 MPa for various periods of time as determined by a disc rheometer (P355C2, Huanfeng Chemical Technology and Experimental Machine Co., Beijing, China). The NR/NBR/ENR composites were obtained by naturally cooling the vulcanizates down to room temperature.

2.3. Characterization

The morphological, structural, and mechanical properties of the NR/NBR/ENR composites were systematically characterized/evaluated if there is no difference between by using SEM, AFM, TEM, DSC, DMTA, and tensile testing. The morphologies of the NR/NBR/ENR composites were observed under a scanning electron microscopy (SEM, S-4700, Hitachi Co., Japan) used in the back-scattered electron (BSE) mode. Before the observations, the samples were polished at −130 °C by using a cryo-ultramicrotome (Leica EM UC7, Germany). An atomic force microscopy (AFM, Multimode 8, Bruker Co., Germany) was used in the tapping mode to measure surfaces of the composites. The samples were polished in the same way as the SEM samples. An AFM measurement provided the modulus of the surface depicted as height images. Transmission electron microscopy (TEM, Tecnai G2 20 S-TWIN, FEI Co., Hong Kong) was employed to examine the morphology of the NR/ENR/NBR composites. The samples for TEM observations were cryogenically cut with a glass knife on a Reichert-Jung Ultracut microtome (Leica Camera AG, Germany) and then stained by OsO_4 for 10 min. Differential scanning calorimetry (DSC) measurements were performed on a DSC 204F1 calorimeter made by Netzsch Co. in Germany. The DSC curves were recorded from −100 °C to 100 °C at a heating rate of 10 °C/min. Dynamic viscoelasticity measurements were carried out on a dynamic mechanical thermal analyzer (DMTA VA3000) made by 01 dB-Metravib Co., Ltd. in France. The samples were cut into a rectangular shape with dimensions of 20 × 6 × 2 mm^3. The temperature dependence of the dynamic tensile modulus was measured in the temperature range −100 °C to 100 °C at a frequency of 10 Hz and a heating rate of 3 °C/min. Tensile tests of the NR/NBR/ENR composites were performed according to ASTM D412 (dumbbell-shaped) and tear tests were conducted according to ASTM D624 (Type C) on a tensile tester made by Sans, Ltd., in China.

In order to assess the compatibility between NR, NBR, and ENR, the solubility parameters (δ_s) of the ENRs with different degrees of epoxidation were calculated by the swelling method, which is based on an evaluation of the maximum in swelling from a series of solvents with different, but known solubility parameters. The swelling ratio (Q) can be expressed by the following equation:

$$Q = \frac{V_s}{V_r} = \frac{(W_2 - W_1)/\rho_s}{W_1/\rho_r} \quad (1)$$

where V_s is the volume of solvent absorbed by the rubber during swelling, V_r is the volume of the rubber before swelling, W_2 and W_1 are the masses of the rubber before and after swelling, respectively,