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Test Method

Stepwise exfoliation of bound rubber from carbon black nanoparticles and the structure characterization

Pan Song[a], Chaoying Wan[b], Yanling Xie[a], Zhen Zhang[a], Shifeng Wang[a,c,*]

[a] Department of Polymer Science and Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China
[b] International Institute for Nanocomposites Manufacturing (IINM), WMG, University of Warwick, CV4 7AL, UK
[c] Key Laboratory of Polymer Processing Engineering (South China University of Technology), Ministry of Education, China

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ABSTRACT

The covalently crosslinking structure between rubber matrix and carbon black (CB) fillers present a significant challenge to analyze the structure and properties of bound rubber in vulcanizate. This work provides a layered exfoliation method to destruct cross-linked network and separate bound rubber encapsulated CB particles out of vulcanizate. A layer of loosely bound rubber was observed by using transmission electron microscopy (TEM), and the existence of tightly bound rubber layer was proved by thermogravimetric analyzer (TGA), atomic force microscopic (AFM) and dispersion experiment. The chemical components of studied layers were further analyzed by using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), where the detection of S, N and Zn elements indicated the vulcanization reaction occurred in it, and the content of polysulfide and disulfide bonds was higher than that of monosulfide. The existence of oxygenic groups is resulted from the occurrence of oxidative scission reaction.

1. Introduction

Rubber materials are widely used in different industrial fields due to its outstanding elasticity and insulation properties. To enhance the mechanical properties of raw rubbers, reinforcing fillers such as carbon black (CB) are commonly incorporated to rubbers in industry [1]. The reinforcement mechanism of CB has been ascribed to its physical structure, dimension and surface functionalities [2–9], which form strong physical and chemical interactions between the particle surface and the rubber molecular chains.

The bound rubber theory has been often used to explain the reinforcement mechanism of CB to rubbers [3]. A layer of bound rubber is formed on the surface of CB through strong physical adsorption and chemical interaction, which is stable and hard to be disrupted by extraction with a good solvent of rubber. The existence of this layer of bound rubber leads to reinforcing effect to rubber matrix. According to this theory, rubber reinforced by carbon black includes three components [8,10,11]: (1) a layer of tightly bound rubber, where the rubber chains are tightened on the surface of carbon black by strong physical and chemical interactions, and with low mobility; (2) A layer of loosely bound rubber, where part of rubber chains physically interact with the tightly bound rubber, and the rubber chains have limited spatial scale mobility and can be extracted by solvent extraction; (3) unbound rubber, which can be removed from the CB-filled rubber compound by a good solvent of rubber.

To study the formation and properties of bound rubber on the surface of CB, a great deal of work have been conducted to explore the effects of type and content of carbon black [8,12–14], structure and type of rubber [15–17]. Most of the studies have applied an extraction process with boiling solvents to separate the bound rubber from the unbound rubber and loosely bound rubber. It is found that the content of bound rubber slightly decreased with gradual increase of temperature below 70 °C, and there was a significant decrease of it when the temperature increased above 80 °C [18,19]. This phenomenon was caused by gradual removal of unbound rubber with free molecular chains. In order to thoroughly remove bound rubber from the CB surface, Hoshikawa et al. treated CB-filled SBR composites with toluene at 150 °C in an autoclave vessel [14]. The experimental results showed that most of loosely bound rubber was removed and the residual rubber fraction was still remained as 2.1 wt%. This further suggests that the residual rubber is tightly bound rubber which is permanently combined with CB by strong chemical interaction. Therefore, the content of bound rubber on CB surface can be controlled effectively *via* different experimental methods, which laying a foundation for further study of chemical structure and composition of bound rubber.

So far, most studies focus on analysis of bound rubber associated

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* Corresponding author. Department of Polymer Science and Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China.
E-mail address: shfwang@sjtu.edu.cn (S. Wang).

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with CB, and few work reports the analysis of bound rubber in vulcanizates. For vulcanizates, unbound rubber with free molecular chains is cross-linked by sulfur and thus it is difficult to be separated by solvent extraction [10]. As a result, both the 'original' bound rubber and the unbound rubber that is chemically cross-linked are strongly tightened with CB particles in vulcanizates, which raise a new challenge in structure analysis and recycling of the rubber products. Understanding the composition and structure of bound rubber in vulcanized rubber reinforced by CB has become a key topic in rubber industry. In previous research work, plenty of softener was used to fully swell the cross-linked network of vulcanizates in order to facilitate the oxidative decomposition of the cross-linked network. The vulcanized rubber as thus could be decomposed into sol with low molecular weight, as a result, the cross-linked unbound rubber was separated from the loosely bound rubber out of the vulcanizate, a high degradation degree was achieved [20–22].

In this work, a mild separation process is applied to isolate the bound rubber from CB reinforced natural rubber (NR) vulcanizates. Soybean oil is used as the softener due to its advantages of large output, low cost and renewable origin [23,24]. The linear molecular chains of soybean oil can easily penetrate into the cross-linked network of vulcanizate to achieve a better swelling effect, which make it decomposed easily. The NR vulcanizates are firstly swollen with soybean oil and NR then heat-treated at 150 °C. The samples were subjected to an extraction process to isolate the sol fraction and residual rubber fraction. The chemical composition and structure of the residual gel are analyzed by TGA, TEM, XPS, XRD and AFM to differentiate loosely bound rubber and tightly bound rubber.

2. Experimental

2.1. Materials

Natural rubber (NR), with a density of 0.913 g/cm^3, was provided by Hainan Agronomic Group Co., China. Commercial carbon black (N330) with primary particle size of 26–45 nm is supplied by Shanghai Cabot Carbon Black Co., Ltd. Soybean oil was provided by the Shanghai Liangyou Oil Industry Co., Ltd. Rubber additives for vulcanization, such as sulfur, accelerator N-Cyclohexyl-2-benzothiazolesulfenamide (CBS), stearic acid and zinc oxide, are commercial grades.

2.2. Preparation of CB-filled NR compound and vulcanizate

Carbon black (N330) was blended with NR in a batch lab mixer (HAAKE Polylab OS, Thermo Electron Gmbh, Germany) at 70 °C for 10 min with a rotor speed of 60 rpm. Subsequently, rubber additives were added into CB-filled NR compound by a two-roll mill (LRMR-S-150/EW, Labtech Engineering, Thailand) according to the formulation shown in Table 1 and the CB-filled NR compound was obtained. In order to prepare vulcanizates, the compound was vulcanized at a temperature of 150 °C using a temperature-controlled hydraulic press (LP-S-50, Labtech, Thailand) and curing times were tested by a rubber processing analyzer (RPA 2000, Alpha technologies, USA).

2.3. Decomposition of vulcanizate

Vulcanized NR sheet was ground into small particles (less than 2 mm, approximately 10–15 meshes) by two-roll mill with 0.1 mm roller space and then it was mixed homogeneously with soybean oil. According to previous work, optimal decomposition effect is achieved when the ratio between ground vulcanizates and soybean oil was 1 to 1 and decomposition temperature was set at 150 °C [20,21]. Therefore, the blends with optimal ratio were decomposed in a hot-air oven (XMTD-8222, Jinghong Laboratory Instrument, Shanghai) at 150 °C and decomposition time was in the range of 1/3 h–4 h. The NR compound and vulcanizate treated for 1 h was labeled as NC-1 and NV-1, respectively.

Table 1
Formulation of the CB-filled NR blends.

Material	NR	N330	S	CBS	ZnO	SA
Content (phr)	100	50	1.9	1.6	5	3

Sulfur (S): cross-linked agent; N-Cyclohexyl-2-benzothiazolesulfenamide (CBS): accelerator. Zinc Oxide (ZnO) and Stearic Acid (SA): activator.

2.4. Measurement of sol fraction and residual rubber fraction

The decomposed sample with a certain weight was wrapped by filter paper and then it was extracted with toluene for 72 h by a Soxhlet extractor to remove low molecular weight components, such as broken chains of NR, soybean oil and rubber additives. The gel part composed of carbon black and residual rubber were dried in a vacuum oven at 60 °C for 4 h until constant weight. The gel was tested by thermogravimetric analyzer (TGA) to obtain residual rubber fraction. The sol fraction and residual rubber fraction were calculated by equation (1) and equation (2), respectively.

$$S_f = \frac{m_0 - 2 \times (m_1 + m_a)}{m_0} \times 100 \tag{1}$$

$$S_r = \frac{m_1 \times w}{m_0 \times 0.31} \times 100 \tag{2}$$

Where S_f is sol fraction of samples and S_r is residual rubber fraction of sample, m_0 is mass of samples before extraction and m_1 is mass of the dried samples after extraction. The m_a is mass of rubber additives in samples and w is rubber fraction in dried sample. Because the fraction of pure rubber in vulcanizate is 62% (100 divided by 161.5 according to the NR compound formulation) and the decomposed sample (m_0) contains only half of vulcanizate (it is prepared with the ratio of 1 to 1 between NR vulcanizate and soybean oil), so the pure rubber content in decomposed sample is $m_0 \times 0.31$ ($m_0 \times 0.62 \times 0.5$).

2.5. Characterization

The thermal decomposition behavior of sample after extraction was tested by thermogravimetric analyzer (TGA, Q5000IR, TA Instruments, USA). The samples were heated from 50 °C to 550 °C under a nitrogen atmosphere and from 550 °C to 700 °C under an oxygen atmosphere with a heating rate of 10 °C/min.

The sample after extraction containing carbon black and residual rubber was ground into powder and ultrasonically dispersed into toluene (0.025 g/ml). Then it was placed onto a carbon grid by a micropipette and dried in a vacuum oven at 50 °C for 24 h, the microstructure of carbon black was observed by transmission electron microscopy (TEM, JEM-2100, JEOL Ltd., Japan). And the sample dispersed into toluene was placed onto a mica sheet and dried, then the surface roughness analysis of carbon black was conducted by Atomic Force Microscopy (AFM, Dimension Icon & FastScan Bio, USA) in tapping mode under ambient conditions.

The analysis of element content on CB surface was characterized by X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Shimadzu, Japan) using a monochromatic Al Ka radiation ($h\nu = 1486.6$ eV). X-ray diffraction (XRD) pattern was measured on a BRUKER D8 ADVANCE using Cu Kα radiation ($\lambda = 1.54$ Å).

3. Results and discussion

3.1. Analysis of sol fraction and residual rubber fraction

The sol fractions after decomposing for various periods of time are