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Recycling the nanostructured carbon from waste tires

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ABSTRACT

Recycling the core-shell structured carbon nanoparticles from waste tires was investigated at a high temperature of 300 °C and a moderate temperature of 140 °C, respectively. The core-shell carbon black (CSCB) nanoparticles could be selectively separated by the reactive extrusion process or warm aging under the effect of swelling. The microstructures of CSCB were characterized by transmission electron microscopy (TEM). The results indicated that the core of CSCB was composed of the carbon black and the shell was made up of the bound rubber which could not be extracted by solvent. In addition, the reinforcing effect of the CSCB in natural rubber (NR) was studied by tensile test. The results showed that the CSCB had higher interfacial interaction with the rubber chains and a new layer of reinforced bound rubber was formed.

1. Introduction

Over billions of tires are produced worldwide to support the transportation system for the advancement of economy each year. Simultaneously, a large number of waste tires have also been manufactured and the amount is about 17 million tonnes per year according to statistics [1]. Therefore, how to properly deal with waste tires has become a global challenge. The appropriate disposal of waste tires is not only helpful to solve the environmental pollution, but also beneficial to the solution of the shortage of rubber resources.

Generally, preparing high value-added reclaimed rubber is a reasonable way to deal with the discarded tire rubber. At present, the extrusion method under high temperature or high pressure is often utilized to prepare the reclaimed rubber [2]. However, it should be mentioned that although the waste tire rubber can be devulcanized by the twin-screw extrusion technology effectively, the high temperature will also lead to the production of a great deal of harmful gases [3]. In addition, the high energy consumption and equipment investment increase the cost of reclaimed rubber likewise. Therefore, an environmentally friendly, efficient, low-cost degradation method is urgently desired to be discovered as an ideal reclamation technique.

Historically, the ideal reclamation of cross-linked rubber means the destruction of cross-linking bonds (mono-, di-, polysulfide bonds) as much as possible without destroying the main chain of the rubber [4–9]. However, this ideal reclaiming effect can hardly be achieved because of the breakage of main chain is difficult to be avoided in the reclaiming process. Furthermore, destruction of cross-linked network never refers to the breakage of bound rubber among rubber and carbon black. As we know, there are two kinds of crosslinked networks in the rubber filled with carbon black: the cross-linked network formed during the process of sulfur vulcanization; the bound rubber network formed by the physical or chemical interaction between carbon black and rubber [10,11]. Usually, the molecular chain and cross-linking bonds of the tire rubber will suffer a higher degree of damage at the same time during reclaiming process. In this condition, the three-dimensional cross-linked structure of rubber is completely destroyed and the sol fraction is formed. Subsequently, the carbon black can be separated and dispersed in the sol under a high degree of degradation. It must be noted that the recycled carbon black has potential to be reutilized as a useful and economical kind of carbon material. In that case, it is essential for us to obtain separated carbon black during reclaiming process. Meanwhile, how to achieve a high degree of degradation is a prerequisite for separating carbon black from tire rubber.

Plasticizers as high-performance reclaiming aids often play an important role in the reclaiming process [12]. With the addition of plasticizer such as aromatic oil and soybean oil, the three-dimensional network in tire rubber can be swollen and the interaction between rubber chains gets weaken, which enhance scission of cross-linking bonds. In addition, the plasticizer can contribute to the uniform dispersion of other reclaiming aids such as desulfurization agent to promote the reclaiming process.

Currently, tire rubber is one of the typical composite material which has been widely used in industry till now. Unfortunately, the extensive exploitation of tire rubber leaves numerous waste materials annually, causing serious environmental problems. However, there is few studies focusing on the aspect of degradation or recycling of this kind of

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material in nano-scale. In this study, the carbon nanoparticles from waste tires were separated from tire rubber during continuous degradation process at a high temperature of 300 °C and a moderate temperature of 140 °C, respectively. The investigation of the carbon nanoparticles will unveil the micro-structure of rubber-filler interaction by characterizing CSCB, give more insights on the core-shell structured carbon black in rubber, which provide a potential way for recycling tire rubber. An additional part of this work concentrates on the presence of CSCB in the reclaiming rubber, and furthermore the CSCB is applied into the natural rubber to study its reinforcing effect.

2. Experimental

2.1. Materials

Ground tire rubber (GTR) (600–700 μm) is shredded at the ambient temperature from the waste whole truck tire, which is supplied by Jiangsu Anqiang Rubber Co., Ltd. The GTR consists of 8.24 *wt*% soluble material, 41.46 *wt*% natural rubber (NR), 12.09 *wt*% synthetic rubber (SR), 31.59 *wt*% carbon black and 6.62 *wt*% inorganic filler. The aromatic oil is provided by Shanghai Gaoqiao Petrochemical Co., Ltd (Shanghai, China), and the percentage of aromatic hydrocarbon compounds is 65%. The soybean oil is supplied by Shanghai Liangyou Oil Industry Co., Ltd. The natural rubber (NR), with a density of 0.913 g/cm^3, is supplied by Hainan Agronomic Group Co., China. Other additives, such as, sulfur, accelerators, stearic acid and zinc oxide are commercial grades.

2.2. Preparation

2.2.1. Preparation of CSCB

High-temperature degradation: The GTR was reclaimed by using a co-rotating inter-meshed twin screw extruder under air atmosphere (ZE25A from Berstorff GmbH, Germany). The screws had four heating/cooling zones with a L/D ratio of 41 and a diameter of 25 mm. GTR was added through the hopper at a constant flow rate (5 kg h^{-1}). The screw rotation speed was set at 300 rpm and the temperature was set at 300 °C. The products were cooled in room temperature after extrusion. Then the reclaimed rubber was completely dried in an oven at a temperature of 50 °C for 2 h.

Warm-temperature degradation: The samples of GTR were mixed with the aromatic oil or soybean oil in certain proportions ($w_{(GTR)}$:$w_{(oil)}$ = 1:1). Then they were placed in an oven (XMTD-8222, Jinghong Laboratory Instrument, Shanghai) with hot air aging at 140 °C for a short period of time (2–6 h).

Subsequently, in order to remove the low molecular sol and other additives, these two kinds of reclaimed rubber compound were extracted with toluene in a Soxhlet extractor for 72 h at 120 °C. The residual was classified as gel which was dried in a vacuum oven at 70 °C for 4 h, then it was ground into powder and the CSCB was obtained.

2.2.2. Preparation of the NR/CSCB composites

The reclaimed rubber was composed of CSCB, low molecular weight sol fraction and much plasticizers such as aromatic oil or vegetable oil, after removing plasticizers via extraction experiment using acetone and the residues were regarded as a whole to be blended with NR to explore the reinforcing effect of CSCB. The mass percentage of CSCB in reclaiming rubber is 31.59 *wt*% or so according to the GTR components. Because the aromatic oil was hardly removed completely by acetone and its presence will affect the reinforcement of CSCB for NR, the reclaimed rubber degraded by soybean oil was chosen to prepare the NR/CSCB blends. In order to further find out the difference between reclaimed rubber containing CSCB and ordinary reclaimed rubber, the reclaimed rubber degraded with different soybean oil content was studied and the specific ratios were shown in Table 1. The different reclaimed rubber were labeled as $CSCB_{20}$, $CSCB_{60}$ and $CSCB_{100}$, respectively. Afterwards, the reclaimed rubber with different oil-filled ratios was blended with NR by a two-roll mill and the formulation was shown in the Table 2. The samples were compressed in a vulcanizing machine (LP-S-50, Labtech Engineering Co., Ltd., Thailand) at a temperature of 145 °C for 7 min, which was tested by a rubber processing analyzer (RPA 2000, Alpha technologies, USA) at 145 °C with a frequency of 1 HZ and a strain of ± 7% for 30 min.

Table 1
Different ratios between GTR and soybean oil.

Samples	$CSCB_{20}$	$CSCB_{60}$	$CSCB_{100}$
GTR	100	100	100
Soybean oil	20	60	100

Table 2
The formulation of NR/CSCB blends.

Materials	NR	RR	S	CZ	ZnO	SA
Content (phr)	80	20	1.2	0.8	2.5	0.34

RR is the abbreviation of reclaimed rubber and the actual content of CSCB in reclaimed rubber is approximately 6.3 phr.

2.3. Characterization

CSCB samples were ultrasonically dispersed in toluene (0.025 g ml^{-1}) and then dropped onto a carbon grid using a micropipette. The grid was dried under vacuum at 50 °C for 24 h and viewed with transmission electron microscopy (TEM, JEM-2100, JEOL Ltd., Japan).

The samples of NR/CSCB composites were measured on a universal electronic tensile machine (Instron 4465, Instron Corp., USA). The dumbbell shape samples of dimension of 75 × 4 × 1 mm^3 were tested at 500 mm min^{-1}.

Actual and theoretical gel fraction can be calculated by the following equation:

$$\text{Actual gel fraction}(wt\%) = m_1/m_0 \times 100$$
$$\text{Theoretical gel fraction}(wt\%) = \sum (a_i w_i) \times 100.$$

Where m_0 is the mass of the sample before extraction and m_1 is the mass of the dried sample after extraction, where a_i is the gel fraction of the ith components (including the NR and reclaimed rubber) and w_i is the mass fraction of the ith components.

3. Result and discussions

3.1. TEM micrographs of different CSCB

As shown in Fig. 1, several samples of CSCB prepared by high temperature extrusion and warm temperature degradation were observed by TEM. In order to compare the structure of CSCB with that of the commercial carbon black, the N330, which was often used in tire rubber, was chosen as a control sample. The primary N330 particles were about 30 nm in diameter and tended to fuse into carbon black clusters, as shown in Fig. 1(a). A distinct rubber layer was able to be seen on the surface of CSCB prepared by the high temperature extrusion in Fig. 1(b). However, the CSCB still contained more rubber gel and a larger aggregation was formed because of the short time of extrusion.

The core-shell structure of CSCB prepared by aromatic oil can be obviously observed from Fig. 1(c) and the thickness of the shell was about 10 nm. As a green plasticizer, soybean oil was chosen as a swelling agent to degrade GTR under warm temperature. The CSCB prepared by using the soybean oil to achieve a high level of degradation was shown in Fig. 1(d). It was obvious that the surface of the CSCB was similar with that of N330. It could be ascribed to the assumption that