



Core-shell structured carbon nanoparticles derived from light pyrolysis of waste tires



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ABSTRACT

Carbon black nanoparticles (CB_{ip}) were derived from waste tire rubbers via a melt-extrusion pyrolysis process at 300 °C. A polymeric shell was observed on the surface of CB_{ip}, which was formed by bound rubber. The chemical structure and content of the bound rubber shell were characterized and quantified, and compared with the commercial carbon black N330 and pyrolytic carbon black (CB_p). The average particle size of CB_{ip} is about 22 nm, with a rubber shell thickness of 7–12 nm. Functional carboxylic group and ZnO were detected on the surface of CB_{ip} by FTIR and XRD, respectively, which are absent from N330 and CB_p. The core-shell structure of CB_{ip} facilitate the dispersion and interfacial interaction in natural rubber, and lead to a higher reinforcement effect as compared those of N330 and CB_p. The light pyrolysis process provides a facile and clean approach to generate useful carbon nanoparticles out of waste tire rubbers.

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1. Introduction

The ever growing transportation industry has driven the fast development of modern society, but meanwhile induced serious pollution issues to the environment [1]. Waste tire disposal management is one of the major concerns, as about 1.4 billion unit of tires are produced globally every year, and around 800 million tires are discarded [2]. The present methods of disposal of waste tire rubbers include landfill, retreading and pyrolysis [3,4]. Pyrolysis is an economical and environmental-friendly way to deal with waste tire rubbers. It involves a process that heats tires over 400 °C in an oxygen poor or free atmosphere to crack the organic components of rubber, and thus results in pyrolytic carbon black (CB_p) as one of the main products [5–7]. As compared to commercial carbon black (e.g., N330), CB_p generally has lower specific surface area and higher ash content, which gives lower reinforcing efficiency to rubbers. These limitations of CB_p hinder its industrialization and marketability [8–10].

To improve the performance of CB_p, different methods, such as developing high efficient pyrolysis apparatuses, optimizing pyrolysis parameters and improving the chemical activation of CB_p have

been under developing [6,11–13]. For example, microwave irradiation has the advantages of low heating cost, fast and direct heating of any microwave absorbing material. The CB_p produced by microwave irradiation has a small ash content in the range of 5.9–9.5 wt% [14]. Although this method reduces the energy cost in the pyrolysis process, the properties of CB_p still cannot reach the level of commercial carbon black. The properties of CB_p can be adjusted by either varying the pyrolysis pressure [15] or atmosphere [16,11]. The surface chemistry of CB_p obtained at vacuum pressure is close to that of commercial carbon black due to its low ash content. Pyrolytic atmosphere was also adopted to improve the specific surface area of CB_p. With steam and CO₂, the specific surface area of CB_p reached 1000 m² g⁻¹ [11], much larger than that of conventional CB_p, which is in the range of 54–87 m² g⁻¹ [15]. However, the complex procedures and expensive equipment restrict the industrial application of this pyrolytic process.

It is challenging to separate carbon black from chemically crosslinked structures of tire rubbers. Reactive extrusion is regarded as an efficient method to devulcanize the crosslinked rubber, by applying high temperature with shear and chemical force [16–19]. Tzoganakis et al. [20] used supercritical CO₂ to aid continuous devulcanization of waste tire rubber. Shi et al. [21] combined the advantage of twin-screw extrusion with an appropriate amount of desulfurizer to reclaim ground tire rubber (GTR)

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into liquid rubber, which can be further used as a reactive softener for tire rubber. The purpose of the aforementioned studies is to obtain high performance devulcanized rubbers via reactive extrusion. Given the facilely adjustable processing parameters, such as compounding temperature and shearing force, reactive extrusion is a potential technology to disassemble the three-dimensional cross-linked covalent structure of rubbers, and subsequently recover carbon black nanoparticles.

Generally the reinforcement of rubbers with carbon black is largely due to the formation of bound rubber, and the content of bound rubber can directly reflect the interactions between rubber and carbon fillers. Bound rubber is formed by physical and chemical interactions between rubber and carbon black during compounding, and coated firmly as a shell layer on the surface of carbon black [22,23]. The particle size, specific surface area and chemical functional groups of the carbon black determine the formation of bound rubber. To enhance the bound rubber content, many techniques, such as oxygen plasma treatment [23], graft modification and surface coating, have been adopted to treat the surface of carbon black, in order to increase the content of functional groups and reduce the particle size [24–27]. Wu et al. [23] used the high-energy electron beam to irradiate carbon black to increase oxygen content and reduce particle sizes. However, the aforementioned methods are mostly suitable for original carbon black, and involve complex and costly processes. If the bound rubber can be preserved in the process of pyrolysis, the carbon black with bound rubber separated from recycled waste tires would be a new carbon material with some special properties.

The aim of this study is to separate lightly pyrolytic carbon black (CB_{lp}) from GTR by using a mild twin-extrusion process. A layer of bound rubber is preserved on the surface of CB_{lp} after melt-extrusion and solvent extraction process, which is detected by using FTIR and TGA. The structure, morphology and reinforcement properties of CB_{lp} were characterized by using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), transmission electron microscopy (TEM) and dynamic light scattering (DLS), and also compared with commercial carbon black (N330) and pyrolytic carbon black (CB_p).

2. Experimental

2.1. Materials

The GTR (600–700 μm) is shredded and ground at the ambient temperature from whole used truck tire rubber. The GTR (Jiangsu Anqiang Rubber Co., Ltd) consists of 6.97 wt% soluble material, 40.25 wt% natural rubber, 14.64 wt% synthetic rubber, 30.44 wt% carbon black and 7.70 wt% inorganic filler. The content of acetone extract is 16.3% and toluene extract is 36.4%, and the left is defined as light pyrolytic carbon black. Commercial carbon black (N330) with primary particle size of 26–45 nm is provided by Shanghai Cabot Carbon Black Co., Ltd. Pyrolytic carbon black (CB_p) produced by high temperature (500–600 °C) pyrolysis, is supplied by Shandong Jintai Co., Ltd.

Natural rubber (SCR WF) is supplied by Hainan Agribusiness Group Co., China. The compounding ingredients, such as sulfur (S), zinc oxide (ZnO), and the accelerator tetramethylthiuram disulfide and N-Cyclohexyl-2-benzothiazolesulfenamide were industry grades.

2.2. Preparation

2.2.1. Preparation of CB_{lp}

CB_{lp} was prepared in two steps. Firstly, GTR was melt-compounded through a reactive extrusion process by using an

inter-meshed twin-screw extruder (ZE25A from Berstorff GmbH, Germany). The screws have 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 throughput (5 kg h⁻¹). The screw rotation was set constant at 300 rpm and the temperature was set at 300 °C for the four zones. The pyrolytic rubber compound was completely dried in an oven at a temperature of 50 °C for 2 h.

Secondly, 2 g of the pyrolytic rubber compound were extracted with acetone in a Soxhlet apparatus for 48 h to remove polar and low molecular weight fraction such as accelerator and plasticizer from the rubber. Subsequently, nonpolar components such as soluble rubber were extracted with toluene for 72 h. The residual CB_{lp} was dried in a vacuum oven at 50 °C for 1 h.

2.3. Characterization and measurement

2.3.1. Characterization

Carbon blacks samples N330, CB_{lp} and CB_p were characterized by using FTIR Spectrum 100, Perkin Elmer, Inc. (USA), in the wavenumber range from 4000 to 350 cm⁻¹. A thermo-gravimetric analysis (TGA, Q5000IR, TA Instruments, USA) was used to study the thermal degradation behavior of N330, CB_p and CB_{lp} in the temperature range from room temperature to 700 °C at a heating rate of 10 °C min⁻¹. Particle size analysis of N330, CB_{lp} and CB_p were performed with particle size analyzer ZS90 (Malvern Instruments Ltd., UK) at 25 °C. To prepare the suspension (0.02 g l⁻¹), carbon black particles were dispersed into toluene under ultrasonication for 30 min. The Brunauer-Emmett-Teller (BET) surface area of the three carbon blacks were tested by using ASAP 2010 M + C (Micromeritics Instrument Corp., USA) with nitrogen as the adsorbate at 100 °C. Transmission electron microscopy (TEM) was conducted by using a JEM-2100 (JEOL Ltd., Japan). X-ray photoelectron spectroscopy (XPS) analysis was carried out on an AXIS Ultra DLD (Shimadzu, Japan). X-ray diffraction (XRD) analysis of the samples was performed with a D8 Advance (Bruker Corporation, Germany). The patterns were scanned between 0° and 90° at a scanning rate of 2° s⁻¹.

2.3.2. Bound rubber extraction

Natural rubber compounds with carbon black samples were prepared according to the formulation: NR 100 phr (parts-per-hundred rubber), carbon black 30 phr, ZnO 5 phr, S 2 phr, stearic acid 1 phr, TMTD 0.5 phr, CZ 0.5 phr. The mixing was carried out in toluene and dried, and was further mixed by a S(X)K-160A Two-Roll mill from Shanghai light industry machinery Co., Ltd (China). The compounds were vulcanized for 330 s (t_{c90}) in a hydraulic press (LP-S-50, Labtech Thailand) at 143 °C and 10400 kPa into 1 mm thick sheets.

Total bound rubber contents of the rubber compounds of NR/N330, NR/CB_{lp} and NR/CB_p compounds were determined by extracting the unbound rubber with toluene at ambient temperature for 7 days and then dried at 50 °C for 24 h. The content of bound rubber was calculated according to Eq. (1),

$$R_b(\%) = (W_A - W_{CB}) / (W_B - W_{CB}) \cdot 100 \quad (1)$$

Where R_b is the contents of bound rubber, W_A is the weight of compounds after extraction, W_{CB} is the weight of carbon black, W_B the weight of compounds before extraction [28].

2.3.3. Mechanical testing of NR/carbon black composites

Tensile testing was conducted using universal mechanical tester (Instron 4465, Instron Corp., USA) at room temperature. For each sample, six dumbbell shape specimens of dimension of 75 × 4 × 1 mm³ were tested at 200 mm min⁻¹, and average results

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