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

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Abstract

Carbon black nanoparticles (CB_{lp}) were derived from waste tire rubbers via a melt-extrusion pyrolysis process at 300 ^{o}C. A polymeric shell was observed on the surface of CB_{lp}, 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_{lp} 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_{lp} by FTIR and XRD, respectively, which are absent from N330 and CB_p. The core-shell structure of CB_{lp} 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.

Keywords: waste tire rubber; light pyrolysis; carbon black; core-shell structure

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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 CO_2, the specific surface area of CB_p reached 1000 $m^2 g^{-1}$ [11], much larger than that of conventional CB_p, which is in the range of 54-87 $m^2 g^{-1}$ [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 CO_2 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) 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 dissemble the three-dimensional crosslinked 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 microscope (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 pyrolyzed 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 a S(X)K-160A Two-Roll mill from Shanghai light industry machinery Co., Ltd (China). The compounds were vulcanized for 330 s ($t_{c,90}$) 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,

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

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 x 4 x 1 mm^3 were tested at 200 mm min^{-1}, and average results were obtained for comparison.

3. Results and discussion

3.1 Characterization of carbon blacks

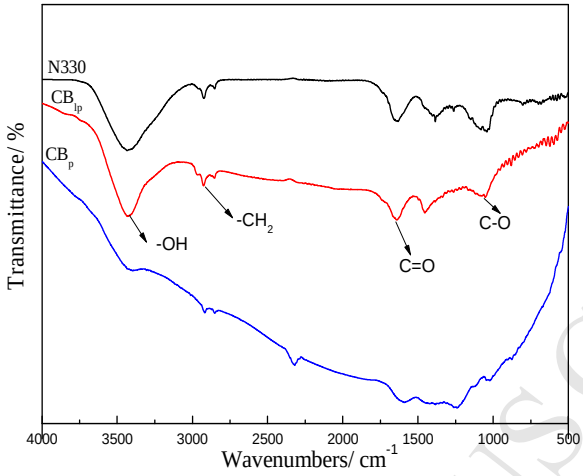


Fig. 1. FTIR spectra of N330, CB_{lp} and CB_p

The derived CBlp was characterized by FTIR and in comparison with commercial N330 and CBp. As shown in Fig. 1, the three spectra are baseline corrected and normalized to the $-CH_3$ deformation vibration peak at 1375 cm^{-1} [31]. CB_{lp} shows similar absorption peaks as N330, but with weaker intensities for peaks at around 3435 and 1084 cm^{-1}, which are attributed to the stretching vibration of -OH and -C-O, respectively [32]. This can be caused by the reactions of CB_{lp} with rubbers during the compounding process, which consumes parts of the functional groups on the CB_{lp} surface [22,33,34]. The peak around 2923 cm^{-1} is attributed to the stretching vibration of $-CH_2$ [35,36], it was observed on both surface of CB_{lp} and N330, indicating some organic matter left on the surface of CB_{lp} and N330. The peak around 1632 cm^{-1} is attributed to the stretching vibration of -C=O [35,36]. Some free radicals can be generated in the process of pyrolysis of GTR rubbers, and further react with -CH=CH group of the carbon chains[37,38], the oxidization of the free radicals may form the -C=O group on the surface of CB_{lp}. The characteristic peaks of -C=C and -C=O of CB_{lp} overlap together, which enhances the intensity of -C=O of CB_{lp}. Moreover, the intensities of functional groups of -OH, C-O, $-CH_2$, and -C=O of CB_{lp} are stronger than

those of CB_p. This may be due to the destruction of functional groups of CB_p is more severe than CB_{lp} under the higher processing temperature (500 °C), or the deposit of ash on the surface of CB_p [8].

Different pyrolytic processes of tire rubber will lead to different structures of carbon black. To understand the composition of N330, CB_p and CB_{lp} the thermal degradation behavior was examined by TGA. As shown in Fig. 2, CB_p and N330 have a similar decomposition behavior when temperature is below 600 °C. N330 decomposes completely at above 700 °C, while CB_p has about 16 wt% residues, which should be ascribed to its ash constituent. CB_{lp} starts to degrade from 350 °C, followed with a distinct weight loss of 18 wt% between 350 °C and 550 °C, which corresponds to the decomposition of the bound rubber layer.

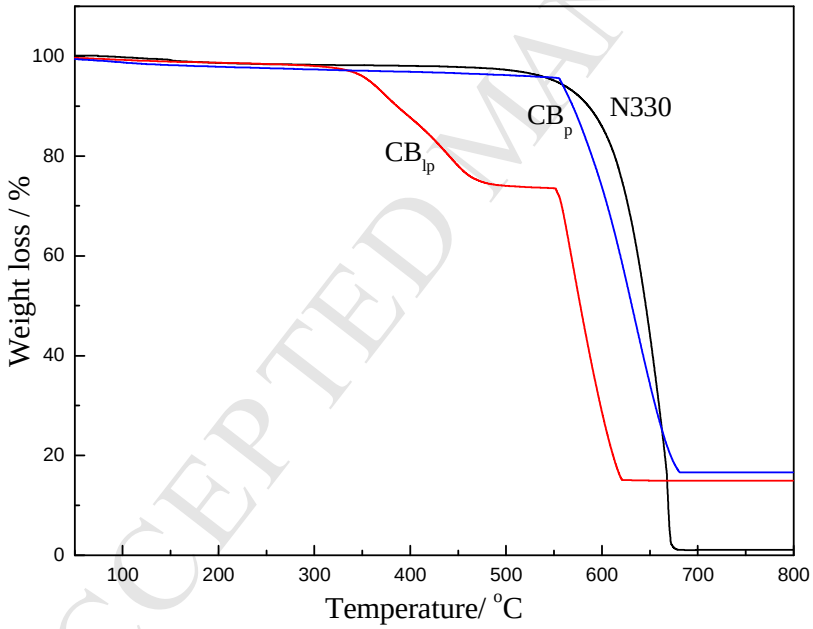


Fig. 2. TGA results of CB_p, CB_{lp} and N330

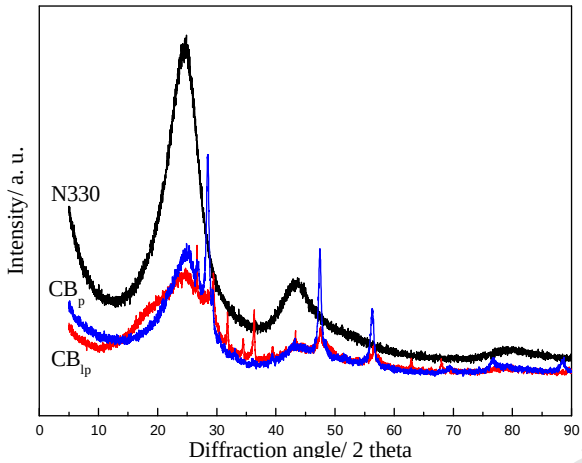


Fig. 3. X-ray diffraction patterns of N330, CB_{lp} and CB_p

As shown in Fig. 3, the three carbon black particles N330, CBlp and CBp show different diffraction patterns. The diffraction peak at 25.5 ° is attributed to the more crystalline/ordered phase characteristic of carbon black [39]. The peaks at 31.80 °, 34.40 °, 36.28 °, 47.58 °, 56.62 ° and 62.92 ° are corresponding to the ZnO [40,41], while 27.10 °, 28.20 °, 31.00 °, 39.20 °, 47.58 °, 51.80 °, 55.70 °, 56.62 ° and 57.80 ° are ascribable to the ZnS [40]. The broad bands at 34.40°, 36.28° and 62.92° reflect the characteristic peaks of ZnO which can only be observed in CB_{lp}, this indicates that most ZnO was transformed into ZnS in CB_p, while some ZnO is still exist in CB_{lp} .

As characterized by TEM, primary N330 particles are about 22 nm in diameter, and are aggregated together (Fig. 4ab). The aggregates of CB_{lp} and CB_p are filled or covered by bound rubber or ash (Fig. 4c-e). As shown in Fig. 4d, there is a layer of bound rubber with a thickness of about 7~12 nm on the surface of CB_{lp}, which can be well-preserved in the condition of light pyrolysis due to the strong interactions between the carbon black and rubber [23,42].

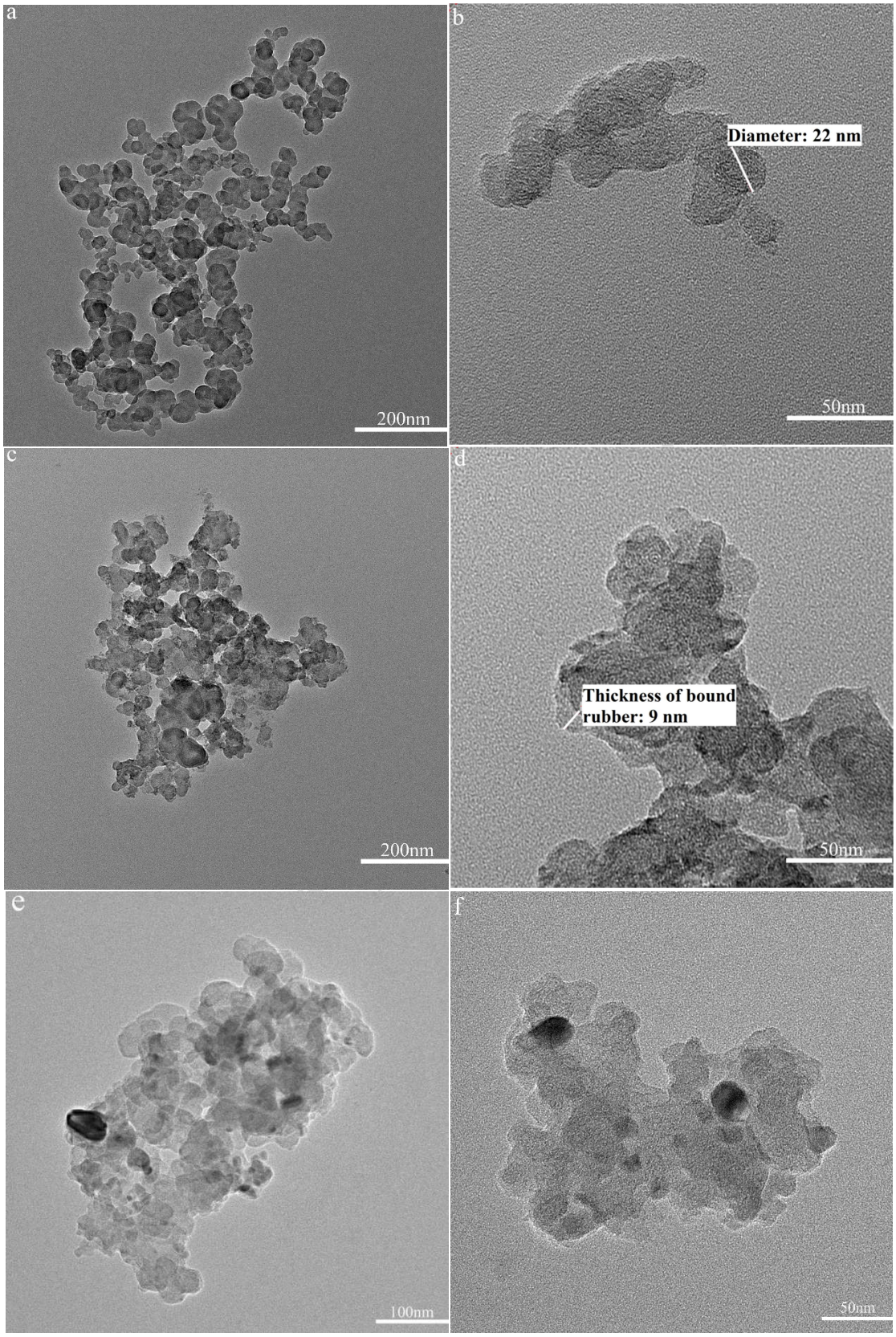


Fig. 4. TEM micrographs of (a-b)N330, (c-d)CB_{lp} and (e-f) CB_p

In comparsion, the surface of CB_p is covered with a layer of ash, which is mainly derived from the deposition of inorganic filler during the pyrolysis of waste tire rubber at high temperature[8]. In this situation, the carbon black particles act as seed, to allow inorganic fillers to absorb and deposit onto it surface, which is shown as black dots in Fig.4 e-f [43,44]. The surface chemical structure of the different carbon black particles was further characterised by XPS, in order to elucidate the composition of the shell materials.

The elemental composition on the surface of N330, CB_{lp} and CB_p are presented in Table 1. The contents of elements C, N and S on the surface of CB_{lp} are higher than that of N330, while the contents of O is lower than N330, indicating an organic layer was attached on the surface of CB_{lp}, also in agreement with the result of FTIR (Fig.1). The bound rubber on the surface of CB_{lp}. suppresses the expression of O element, while the presence of crosslink agent and accelerator in bound rubber provide the elements of S and N. In the high temperature pyrolysis of tire rubber, gases like H_2S and NH_3 are released [43,45], and left lower content of N and S on the surface of CB_p. In comparison, the light pyrolysis of tire rubber will give higher concentration of N and S on the surface of CB_{lp}.

Table 1 surface compositions of N330, CB_{lp} and CB_p tested by XPS

Carbon black	Surface composition /wt%			
	C	N	O	S
N330	88.38	0	11.46	0.16
CB_{lp}	91.22	1.27	5.43	2.09
CB_p	92.39	0.83	5.64	1.14

The curve fitting of C_{1s} photo peaks of XPS spectrum are shown in Fig.5 (a). The XPS spectrum of C_{1s} for N330, CB_{lp} and CB_p are fitted to four peaks: C-C or C-H (C_1, BE=284.8 eV), C-O (C_2, BE=285.5 eV), C=O (C_3, BE=286.7 eV), and COOH (C_4, BE=289.0 eV) [23,41,46]. The results of the curve-fitting of the C_{1s} spectrum are

summarized in Table 2.

Table 2 Area of the C_{1s} peaks of carbon black N330, CB_{lp} and CB_p

Compound	Area of C_{1s} peaks /at%			
	C_1(C-H or C-C)	C_2(C-O)	C_3（C=O）	C_4（COOH）
N330	45.99	28.67	12.85	12.49
CB_{lp}	69.37	17.90	5.29	7.44
CB_p	51.62	33.39	14.99	0

As shown in the Table 2, CB_{lp} has the highest content of C-C or C-H among the three samples, indicating a rubber shell coated on the surface of CB_{lp}. The peak of COOH is not observed in the spectrum of CB_p, which should be destroyed in the process of pyrolysis at high temperature [41]. The existence of COOH functional groups will make CB_{lp} more reactive than CB_p.

As shown in Fig. 5 (b) , the O_{1s} spectra are fitted to four peaks: a peak with a binding energy of 531.0 eV (O_1) assigned to oxide oxygen, peaks at 532.5 eV(O_2), 533.5 eV(O_3) and 535.8 eV(O_4) are assigned to the C=O, C-O groups and a shake-up peak, respectively [41]. The results of the curve-fitting of the O_{1s} spectra are shown in Table 3.

Table 3 Area of the O_{1s} of carbon black N330, CB_{lp} and CB_p

Compound	Area of O_{1s} peaks /at%			
	O_1	O_2（C=O）	O_3（C-O）	O_4
N330	0	43.12	56.88	0
CB_{lp}	1.84	51.61	46.55	0
CB_p	0	53.27	33.87	12.86

It is interesting to see that the oxide peak is only found in CB_{lp}, and absent in both N330 and CB_p. The intensity of C=O in CB_p is the highest among the three samples because of the oxidation of pyrolytic carbon. The ratio of C=O to C-O on the surface of

CB_{lp} is higher than N330. Moreover, the shake-up peak is not observed in the spectrum of N330 and CB_{lp}, showing that there is no free oxygen molecules existing in or close to the aromatic system on the surface of N330 and CB_{lp} [41]. This phenomenon also proves that the chemical structure of CB_{lp} is more similar to N330 rather than CB_p.

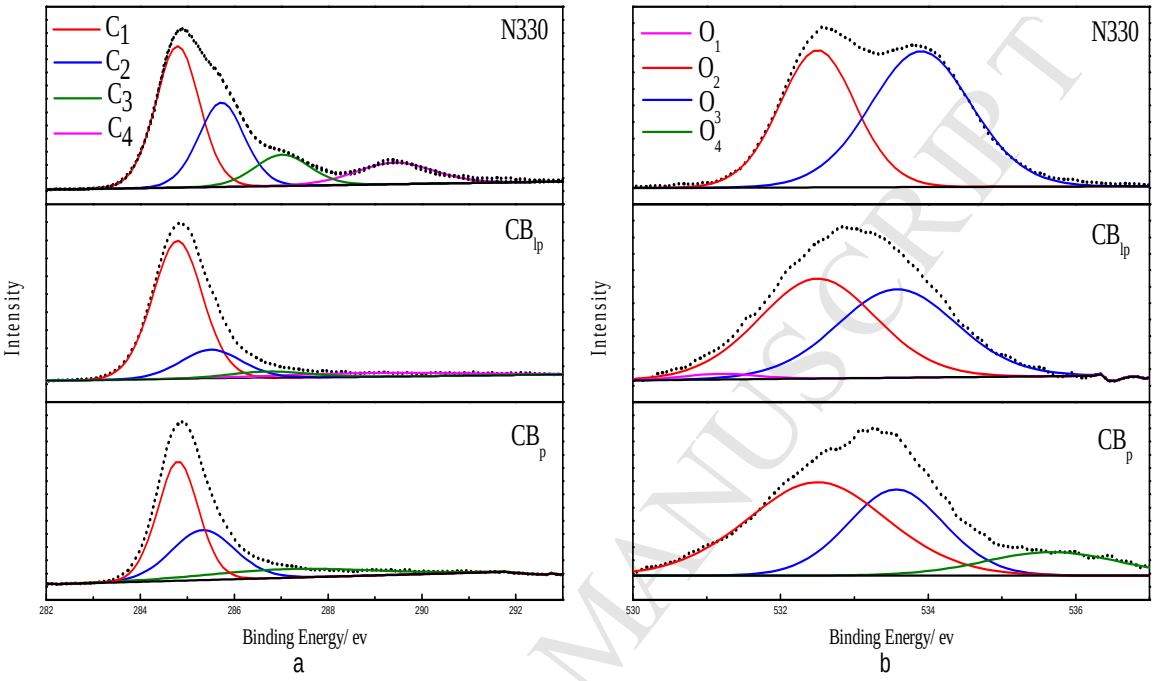


Fig. 5. (a) C_{1s} XPS spectrum of carbon black N330, CB_{lp} and CB_p; and (b) O_{1s} XPS spectrum of carbon black N330, CB_{lp} and CB_p.

The average primary particle size of N330 is estimated to be 21 nm (also shown in TEM, Fig.4), and the smaller size results in higher specific surface area, as shown in the Table 4. The existence of bound rubber on the surface of CB_{lp} increases the particle size to about 29 nm. The particle size and Polydispersity Index (PDI) of CB_p is higher than that of N330 and CB_{lp} because some organic volatiles were released during the pyrolysis of GTR, and transformed into ash and absorbed on the surface of CB_p [43,45](Fig. 6). The Brunauer-Emmett-Teller (BET) surface area of CBlp is lower than CB_p due to the coverage of the rubber on the surface(Table 4).

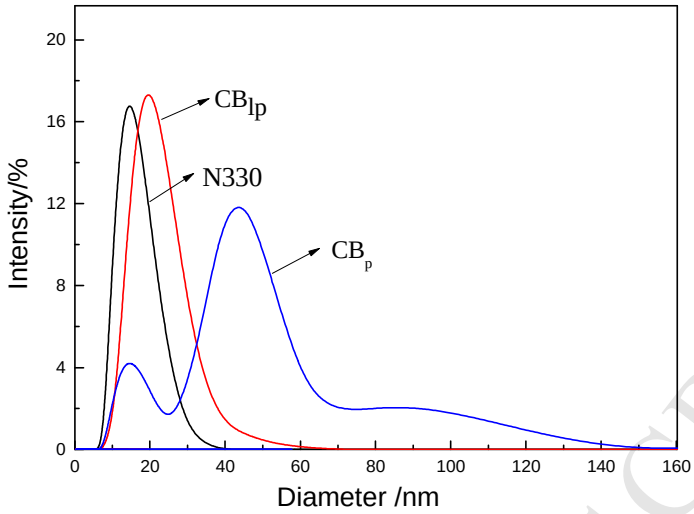
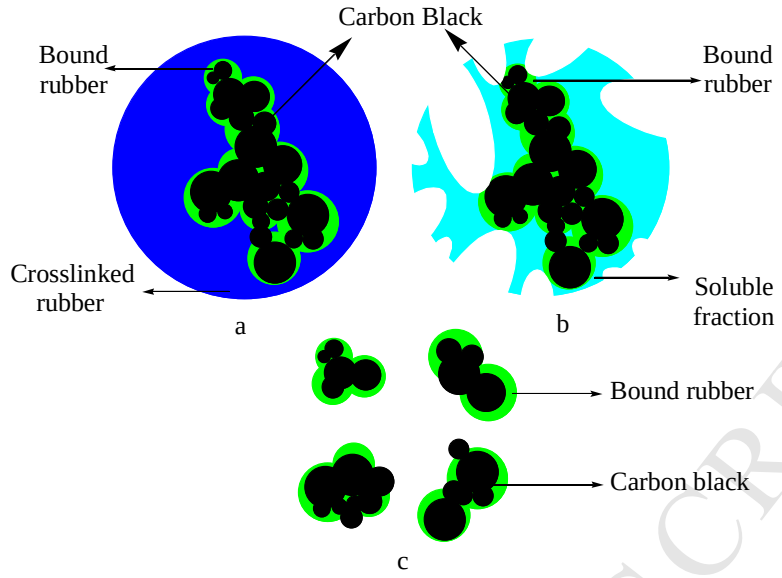


Fig. 6. Particle size distribution of N330, CB_{lp} and CB_p

Table 4 Particle size distribution and BET of N330, CB_{lp} and CB_p

Carbon black	Z-Average (r.nm)	PDI	BET surface area /m^2g^{-1}
N330	21	0.247	64
CB_{lp}	29	0.290	16
CB_p	86	0.606	38

According to the analysis above, the separation process of carbon black (CB_{lp}) out of lightly pyrolyzed GTR rubber is proposed and shown in Scheme 1. The chemical network is firstly degraded and destroyed in the pyrolysis process of crosslinked rubber. The interfacial interactions between rubber chains and carbon blacks could induce a layer of bound rubber at the interface [29,30], and can be further reinforced during vulcanization reactions. The highly crosslinked bound rubber layers are thermally stable that can stand the light pyrolysis (up to 300 ^oC) treatment, as well as chemically robust during solvent extration process, which are confirmed by the characterisation results of FTIR, TGA, TEM and XPS.



Scheme 1. The separation process of carbon black and rubber in light pyrolysis (a, GTR; b, lightly pyrolytic rubber; c, CB_{lp})

3.2 Mechanical properties

Natural rubber containing N330, CB_{lp} and CB_p are studied to evaluate the reinforcement effects of the different carbon black particles. The stress-strain curves of NR/N330, NR/CB_{lp} and NR/CB_p compounds are presented in Fig. 7. NR/CB_{lp} compounds show higher content of bound rubber, tensile strength and elongation at break than NR/N330 and NR/CB_p compounds (Table 5). The presence of bound rubber layer on CB_{lp} surface helps the dispersion and interfacial interactions with natural rubber, which critically affects the mechanical properties of the filled rubber compounds [30].

Table 5 Mechanical properties of N330/NR, CB_{lp}/NR and CB_p/NR compounds

Carbon Black	Content of bound rubber /wt%	Elongation at break /%	Tensile Strength /MPa
N330/NR	49.8	275±5	6.1±0.2
CB_{lp}/NR	64.3	394±3	7.5±0.3
CB_p/NR	39.3	350±5	5.2±0.2

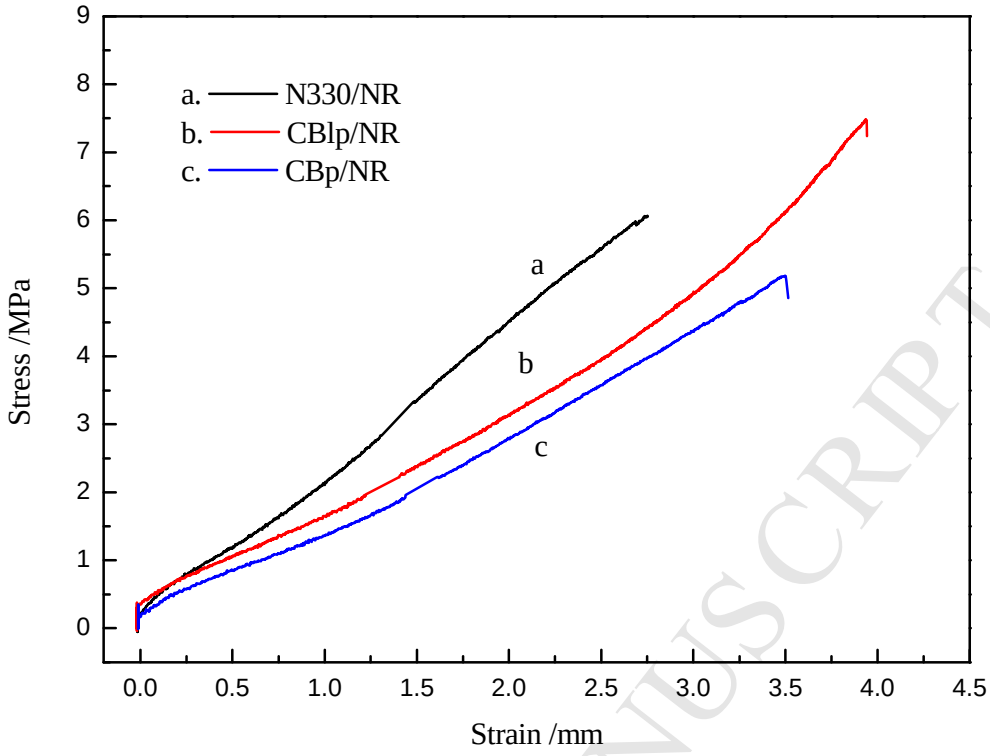


Fig. 7. Stress-strain curves of N330/NR, CB_{lp}/NR and CB_p/NR compounds

4. Conclusions

Core-shell structured CB_{lp} particles were derived from waste tire rubber by reactive melt-extrusion. The bound rubber layer on the surface of CB_{lp} was preserved during the light pyrolysis and toluene-extraction processes. The sulfur bond, filler and chemical additives in bound rubber have an influence on the chemical structure and morphological characteristics of CB_{lp}. The bound rubber increased the contents of N, S and functional group of $-CH_2$, while reduced the oxygenic functional groups on the surface of CB_{lp}. More functional groups and ZnO were preserved on the CB_{lp} surface than CB_p due to the mild pyrolysis process. As a consequence, the CB_{lp} showed higher reinforcement effect than CB_p due to the existence of bound rubber. The light pyrolysis is proven to be an environmental-friendly and efficient method for waste tire rubber disposal and a promising technique for producing core-shell structured carbon nanofillers.

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