

Upgrading pyrolytic carbon-blacks (CBp) from end-of-life tires: Characteristics and modification methodologies

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HIGHLIGHTS

- Modification methodologies of upgrading CBp from ELTs were reviewed.
- Surface microstructures and physiochemical properties of CBp were analyzed.
- Future perspectives of ELTs pyrolysis industries were suggested.

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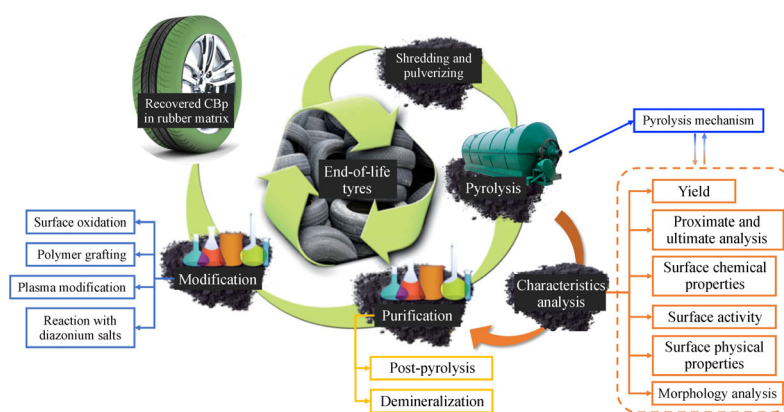
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GRAPHIC ABSTRACT



ABSTRACT

Over 1 billion end-of-life tires (ELTs) are generating annually, and 4 billion ELTs are currently abandoned in landfills and stockpiles worldwide, according to the statistics, leading to the environmental and health risks. To circumvent these issues, pyrolysis, as an attractive thermochemical process, has been addressed to tackle the ELTs' problem to reduce the risks as well as increase the material recycling. However, due to the lack of systematic characteristic analysis and modification methods, poor quality of CBp limits the improvement of ELTs pyrolysis in industry applications, which plays a crucial role in the economic feasibility of pyrolysis process. In this review, we have summarized the state-of-the-art characteristics and modification methodologies of the upgrading of CBp, to in-depth understand the surface microstructures and physiochemical properties of CBp for the foundation for modification afterwards. By virtue of the proper selection of modification methods and modifying agents, the new generation of multifunctional carbon materials with desired properties can be instead of the traditional materials of CB, promising broader and various application fields.

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1 Introduction

In recent years, automobile industry has developed rapidly, especially with the fast growth of the global economy. After 2010, China has replaced the USA and Europe as the world's biggest automobile market, with an increasing rate of 24% per year between 2005 and 2011. Moreover, it is

predicted by McKinsey, a world-renowned management and consulting firm, that the amount of new vehicles in China will reach 22 million by 2020 (Wang, 2012). However, booming of the automobile market has also induced a global issue of the ELTs recovery. According to the statistics released by European Tire and Rubber manufacturers' association, ELTs arisings have been reached up to 2.88 million tones in 31 countries (EU28 plus Norway, Switzerland and Turkey) in 2013 (Association, 2015). And it is also estimated that ELTs have been

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generated over 1 billion per year globally (WBCSD, 2008; Thomas and Gupta, 2016) and discarded in landfills and stockpiles almost 4 billion (WBCSD, 2008), where more than 50% of them remain untreated before discarded (Subulan et al., 2015). Due to its incompressibility, ELTs have occupied ample space in landfills and became the breeding grounds for mosquitoes and rodents. Moreover, the variety of chemical leakage induced by ELTs after excessive rain washing and sun exposure lead to the pollution of soil and air, which will finally add risks to the environment and human health (Sun et al., 2016).

Tyres are made of three dimensional chemically cross-linked rubber (such as natural rubber, styrene-butadiene rubber, polybutadiene rubber, etc.) networks, steel, polymer fiber, CB and other organic (accelerator, antioxidant)/inorganic compounds (sulfur, zinc oxide). In the past 40 years, many research institutions and enterprises around the world have employed various methods to treat ELTs, including recycling, recovered fuel, energy recovery and pyrolysis (as shown in Fig. 1).

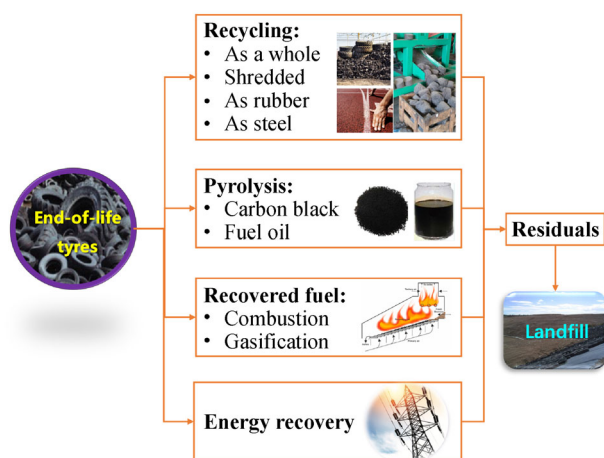


Fig. 1 Conventional approaches in ELTs management.

In these kaleidoscope methods, pyrolysis has been addressed as an attractive thermochemical process to tackle the problem of ELTs while allowing energy recovery, exhibiting a decomposition and separation process under non-oxidative conditions (inert atmosphere or vacuum) usually between 400°C–700°C to allow the breakage of chemical bonds in ELTs (Sugatri et al., 2018). For example, recent research of a wider range of pyrolysis temperature of 400°C–1050°C was conducted by Yazdani et al. (2019). Besides some experiments also conducted in laboratory, recent researches put more attentions on the pyrolysis process in semi-industrial plants (Antoniou and Zabaniotou, 2018; Martínez et al., 2019). CBp and volatile matter composed of condensable and non-condensable compounds mostly from rubber are two major products in this process (CBp refers to the solid fraction that have

difficulty separating from each other). However, the surface activity of CBp is rather weak due to the high content of inorganic ash and carbonaceous deposits (Li et al., 2018), limiting its practical application because of its low commercial value. Although untreated CBp can be often applied as reinforcing filler for directly combusted as fuel, the combustion suffers obvious adverse factor which is that the ash in CBp will act as anti-flaming materials. In addition, the easy-agglomerate property of CBp caused by its small particle size and large specific surface area makes it difficult to disperse uniformly in the polymer matrix, which weakens its reinforcing effect (Cardona et al., 2018; Pazat et al., 2018).

In this paper, recent research progresses about the characteristics and modification methods of CBp are reviewed. We summarize the physiochemical properties of CBp in detail, and further understanding the pyrolysis mechanism and exploring the optimal conditions. The process of demineralization and surface modification to overcome the limitations of origin CB are also discussed to improve the performance of rubber composites. We believe that the economic feasibility of ELTs pyrolysis industries will be significantly improved if the CBp could be upgraded into high-quality value-added products through the modification process.

2 Recycling CBp from pyrolysis of ELTs

Pyrolysis is widely used for treating organic materials, containing the irreversible changes in chemical compounds that large molecules breakdown into smaller parts at elevated temperatures. Generally, there are two main products directly generated from the process: Volatile matter composed of condensable and non-condensable compounds, and carbon enriched materials named char. As for ELTs, the content and quality of gas-solid two-phase products are significantly depended on the type of tires and pyrolysis conditions. Most volatile fraction is generated from the pyrolysis of rubber molecules, which can be divided into oil and gas after condensation while the solid fraction is composed of CB and organic/inorganic fillers of the tire (as shown in Fig. 2). The ratio of two phases is corresponding to the raw material in tire production, in which rubber occupying 60%, fillers occupying 40% (30% of CB plus 10% of other organic/inorganic fillers).

The composition of CBp depends on the tire composition as well as pyrolysis conditions, and its quality and yield greatly influence the ELTs pyrolysis economic feasibility. Therefore, widespread attention has been forced on optimizing the quality of CBp to improve its commercial value, solving the pyrolysis problems of ELTs. To optimize pyrolysis condition for desired CBp, the mechanism of tire pyrolysis and physiochemical properties of CBp are discussed in details.

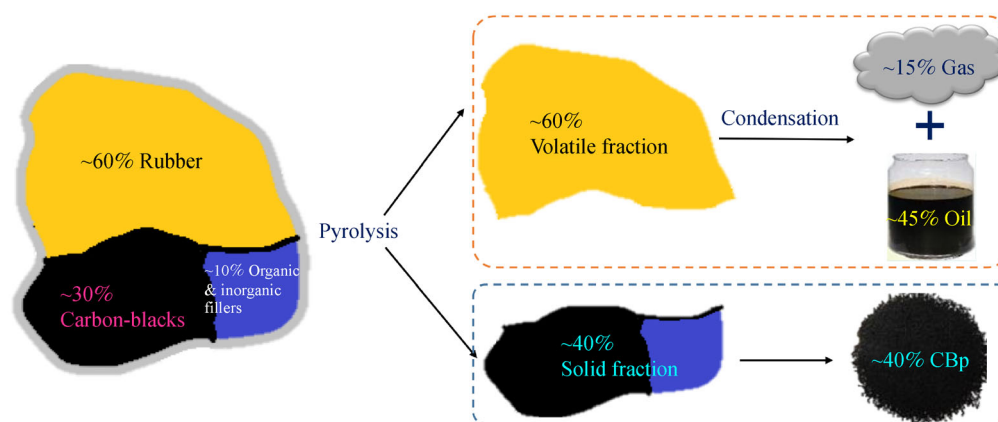


Fig. 2 Scheme of tire pyrolysis.

2.1 Pyrolysis mechanisms of ELTs

The mainly researches about pyrolysis of ELTs can be generally divided into two scales: 1) study on overall behavior of ELTs in pyrolysis reactors, focusing mainly on the reactor design and analysis of physicochemical properties of pyrolysis products so as to optimize the pyrolysis conditions; 2) study on thermal analysis kinetics and pyrolysis mechanism, which is necessary for pyrolysis products as well as the economic evaluation of pyrolysis processes.

In general, tires are complex composites, in which rubber accounts for more than 90% of pyrolysis products, making the essential component of pyrolysis reaction. Three types of rubber are mainly used in tires production: natural rubber (NR), butadiene rubber (BR) and styrene-butadiene rubber (SBR). Although with the identical molecular structures, rubbers show different behaviors even, under the same pyrolysis conditions. For example, NR has a low pyrolysis temperature compared with SBR while BR decomposes under both low and high temperatures.

Further analyzing the DTG curve and pyrolysis products, indicates that rubbers in tires are cross-linked with the addition of sulfur, resulting in the inevitable interaction of each component during pyrolysis. Besides, the presence of a variety of organic and inorganic additives also exacerbates the complexity of the pyrolysis process by producing new substances that didn't exist in the rubber pyrolysis products.

The pyrolysis process of ELTs composed of complex series-parallel reaction networks is divided into various reaction stages by different researches. Such as, Atal and Levendis (1995) and Brazier and Schwartz (1978) believed that the process could be categorized into primary and secondary pyrolysis due to different reaction rate. Primary pyrolysis (low-temperature stage) is corresponding to the

liquefaction and depolymerization process of cross-linked rubber chains. This stage shows a high weight loss rate with the formation of carbonaceous deposits as well as large quantities of olefins. Secondary pyrolysis (high-temperature stage) produces a large number of aromatic hydrocarbons via the Diels-Alder cycloaddition reaction of olefins. Besides, coke gasification reaction also occurs at this stage, which is characterized by a linear burn-down chart. According to Murena's work (Murena et al., 1996), hydrogen donor in the secondary pyrolysis helps to saturate the free radicals and avoid the coking reactions. Conesa et al. (1997) divided the tire pyrolysis into three stages including decomposition of mineral oil, NR and SR, but Senneca et al., (1999) indicated four steps corresponding to main chain scission, depolymerization, cyclization and secondary pyrolysis of cyclized products, respectively.

The big difference between pyrolysis products is generated from the difference in raw tire materials and working conditions. Aguado et al. (2005; 2008)) found that products like monomers and dimers were derived from NR/SBR while the aromatic hydrocarbons and other products came from the non-selective fracture of chemical bonds. Benallal et al. (1995) pointed out that aromatics compounds occurred at high temperature, but aliphatic compounds occurred at low temperature. The studies reported further indicated that aromatics were derived from the Diels-Alder cycloaddition reaction of olefins (Fairburn et al., 1990; Williams et al., 1990; Williams and Taylor, 1993; Williams and Besler, 1995; Williams et al., 1995; Williams and Bottrill, 1995; Cunliffe and Williams, 1998; Williams et al., 1998; And and Williams, 1999; Kyari et al., 2005). Moreover, recent researches concerning pyrolysis ELTs with internals in fixed-bed reactor can considerably suppressed secondary reactions (including cracking) occurring to volatile products in the reactor (Xu et al., 2018).

2.2 Physiochemical properties of CBp

CBp is a complex mixture consisting of carbonaceous deposits and oils absorbed during pyrolysis process, together with various organic and inorganic additives. Therefore, the systematic analysis of the physiochemical properties of CBp is necessary for further modification.

2.2.1 Yield

As the most common experimental result, the yield analysis is involved in almost all studies concerning ELTs pyrolysis. The yield of CBp is about 35–45 wt% at a pyrolysis temperature of 500°C, as shown in Table 1. This value is slightly higher than the amount of CB and inorganic additives in raw materials, due to the ash content and carbonaceous deposits. A fraction of rearrangement product deposits directly on the surface of CBp, while the other part is converted to coke by dealkylation and dehydrogenation reactions. The ratio between the two fractions is depending on the intensity and complexity of the pyrolysis process. The CB obtained by pyrolysis under vacuum prevents the deposition effectively due to the lower pressure, making a lower yield than that under the atmospheric pressure. According to Roy's work (Roy et al., 1995), the quality of CBp obtained by vacuum pyrolysis at a temperature of 500°C and an operating pressure of 0.3 kPa is close to semi-reinforcing grades commercial CB.

During the pyrolysis process, it is expected that a slight increase in yield will occur for carbonaceous deposits on surface and pyrolysis oil absorbed in the pores. The yield of pyrolysis directly relies on the working conditions and the tire raw materials since the quantity and quality of CB and inorganic fillers play an essential role in the end product.

2.2.2 Proximate and ultimate analysis

The proximate and ultimate analysis is a commonly used analytical method for solid materials by providing an overview of the basic chemical properties of an unknown substance. As shown in Table 1, CBp is pyrolyzed at different working conditions with a high calorific value ranging from 15 to 35 MJ/kg as well as a relatively high C content (generally 75%–85%). Besides, CBp has a high ash content which is attributed to the presence of inorganic fillers during tire manufacturing, generally 7%–15% and even up to 40% due to different tire materials (Ucar et al., 2005). Most of the S content in the raw materials remain in the end product, with the rate of ~50%. Hence, CBp always has a relatively high S content (generally 1.5%–2.0%) comparing with commercial CB.

2.2.3 Surface chemical properties

The surface chemical properties and surface activity of

CBp are two significant indicators to determine the interaction between CB and rubber. Analysis of CBp surface by ESCA reveals that only zinc oxide and sulfur could be detected and more than 80% of inorganic substances are not detected, differing with the result of ultimate analysis (Roy et al., 1995). A higher C_{1s} peak appears on the CBp surface than that of N539, indicating the formation of carbonaceous deposits on the CBp surface through condensation and dealkylation of hydrocarbons process. As mentioned above, pyrolysis temperature and pressure are the dominant factors to affect carbonaceous deposition, which can be visualized by the area of C_{1s} peak. Both the works of Williams (Williams and Besler, 1995; Williams et al., 1995) and Sahouli (Sahouli et al., 1996a; Sahouli et al., 1996b) found high Zn content in CBp and mainly in the form of ZnS, which was formed by the reaction of sulfur and zinc oxide during tire pyrolysis. Zabaniotou (Zabaniotou and Stavropoulos, 2003) also pointed out that ZnS was the primary inorganic crystal phase in CBp by using elemental analysis and XRD analysis. Lee (Lee et al., 1999) applied XPS to analyze the C element distribution and chemical structure on the CBp surface obtained under inert atmosphere and H_2 atmosphere. All above mentioned results showed that C-H/C-C was the major CB component on its surface, followed by C=O and C-O.

2.2.4 Surface activity

Surface activity of CB not only indicates various chemical reactions between its functional groups and matrices from a chemistry perspective, but also reveals the surface free energy judging adsorption capacity from a physics perspective. Inverse gas chromatography (IGC) is widely used to determine surface activity by injecting probe molecules into a gas chromatograph equipped with a CB filled column. The non-specific portion of the CB surface energy (γ_s^d) can be obtained by the IGC method by determining specific interaction between CB and the polar probe (F^p). Roy et al. (1999) used the IGC method to analyze CB before and after pyrolysis and suggested that the active sites on the CB surface are mainly covered by carbonaceous deposits. Thus, it was expected that γ_s^d , F^p and surface activity for the CBp obtained under atmospheric pyrolysis are lower than the corresponding values for the CBp obtained under vacuum pyrolysis. Besides, the relationship between the surface free energy of CBp and the amount of surface carbonaceous deposits was also obtained. The ratio of active sites covered by carbonaceous deposits on CBp obtained by vacuum pyrolysis at 500°C and 6 kPa was found to be about one third.

2.2.5 Surface physical properties

The surface area and pore characteristics of CBp are

essential parameters for defining its surface physical properties. As shown in Table 1, the specific surface area of CBp is mostly concentrated at 50–80 m²/g, which is significantly lower than that of commercial CB commonly used in tire production such as N234 (112.7 m²/g) and N330 (80.5 m²/g). The temperature has a more significant effect on specific surface area compared with reactor forms and other pyrolysis conditions. In fact, CBp obtained at a pyrolysis temperature of 500°C–550°C has a specific surface area with the range from 60 to 70 m²/g, regardless of atmospheric (Kyari et al., 2005; Ucar et al., 2005; Munillo et al., 2006; Zhou et al., 2010; López et al., 2011; Mikulova et al., 2013) or vacuum (Zhang et al., 2008) and using spray bed reactor (Lopez et al., 2009) or fixed bed reactor. Coincidentally, CBp through plasma pyrolysis also got a close value (Tang and Huang, 2004,2005). Besides, the surface area of CBp increased rapidly with increase of pyrolysis temperature. A higher specific surface area could be obtained by increasing the temperature to 600°C – 700°C, and Ucar (Ucar et al., 2005) pointed out that BET surface area of CBp increased nearly 20% when the pyrolysis temperature risen from 550°C to 800°C.

The increase of CBp surface area was attributed to the escaping of volatiles and the forming of new pores. Yan (Yan et al., 2006) which was divided the pyrolysis into three stages to describe the process. In the first stage (450°C – 500°C), a slight increase was attributed to less volatile content and incomplete developed pores on the surface. In the second stage (550°C–600°C), more volatile compounds were created to generate more pores while some were blocked since carbonaceous deposits. In the third stage (650°C), fewer deposits and volatile content resulted in smoother pores, leading to an increase in the surface area again.

Higher pyrolysis temperatures and decompression condition have now been considered as an effective means to increase the surface area. The reasons can be summed up as

follows: 1) high temperature can effectively avoid rubber molecules from coking and covering active sites on the surface or blocking its pores; 2) negative pressure can accelerate the volatilization and diffusion of unstable compounds, thereby reducing the amount of hydrocarbons residues on the surface and pores. However, some studies have shown that high temperature together with long residence time could have negative impacts on the mechanical strength of CBp (Roy et al., 1995) so that other methods should be studied to circumvent this shortcoming.

It is well-known that CB is formed by incomplete combustion or pyrolysis of many hydrocarbons. Thus, a specific pore structure is built on the surface through intense oxidation and granulation process under high temperatures. By analyzing CBp obtained at a temperature about 500°C, many studies (Merchant and Petrich, 1993; López et al., 2011; Song et al., 2012; López et al., 2013; Zhang et al., 2018) found that almost all CBp should be classified into mesoporous materials, as micropores with a diameter < 2 nm were not detected. López et al. (2013) conducted a detailed analysis concerning the pore characteristics of CBp, and in CBp the pores were mainly composed of mesopores of 20–200 nm and macropores of 2–200 μm.

2.2.6 Morphology analysis

As described in pyrolysis mechanism, CBp surface are covered by the converted coke of the organic vapors released during pyrolysis. For this reason, CBp shows much rougher particle sizes than the original CB (Senneca et al., 1999). According to Senneca' work, the CB particles were likely to act as nuclei seed (core) where the carbonaceous deposits grow above to become the shell by cyclisation and/or crosslinking, as shown in the upper of Fig. 3. Further activation under steam or CO₂ conditions

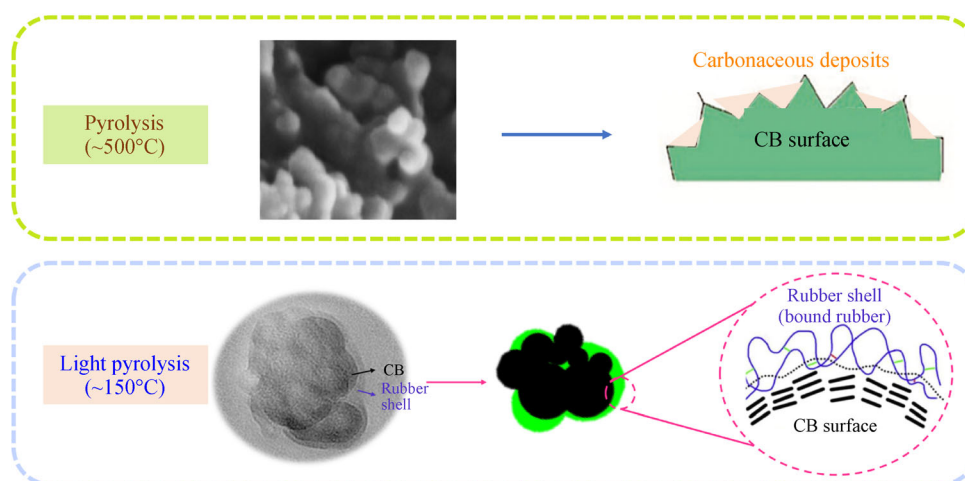


Fig. 3 Scheme of “core-shell structure” of CBp

Table 1 Elemental, proximate and calorific value of the CBp reported in literature.

Pyrolysis temperature (°C)	Reactor type	CBp yield (wt%)	Elemental analysis on dry basis (wt%)				Proximate analysis on as received basis (wt%)				CV (MJ/kg)	Sulfur in tire (wt%)	Sulfur retention (%)	BET surface (m ² /g)	Ref.
			C	H	N	S	Ash	Volatile matter	Moisture	Fixed carbon					
600	Fixed bed	38.00	81.57	0.84	0.33	2.95	13.82	2.51	0.26	83.41	n.r	1.87	59.95	n.r	Aylón et al. (2008)
600	Moving bed	38.00	82.10	0.97	0.35	3.41	13.17	3.50	1.24	82.09	n.r	1.87	69.29	n.r	Aylón et al. (2008)
500	Fixed bed	36.10	85.18	1.15	0.64	2.03	13.25	n.r	n.r	n.r	n.r	0.92	79.66	67.96	Zhang et al. (2008)
450	Fixed bed	40.00	88.00	1.70	0.30	1.10	8.40	7.10	n.r	n.r	31.40 ^a	1.70	25.88	n.r	Napoli et al. (1997)
550	Fixed bed	35.00	89.40	0.30	0.10	0.80	7.70	3.50	n.r	n.r	30.90	1.70	16.47	n.r	Napoli et al. (1997)
600	Fixed bed	37.00	n.r	n.r	n.r	n.r	16.30	5.20	0.00	78.50	27.20 ^b	1.40	n.r	n.r	González et al. (2001)
550	Rotary kiln reactor	49.09	85.31	1.77	0.34	2.13	15.33	12.78	3.57	71.89	30.71	2.30	45.46	n.r	Galvagno et al. (2002)
600	Rotary kiln reactor	47.40	85.56	1.33	0.28	2.32	13.19	10.75	3.01	76.06	30.18	2.30	47.81	n.r	Galvagno et al. (2002)
680	Rotary kiln reactor	48.86	85.16	0.93	0.22	2.57	11.78	5.24	1.44	82.98	29.50	2.30	54.60	n.r	Galvagno et al. (2002)
450	Fixed bed	40.00	95.9	0.70	0.10	3.30	16.00	3.10	1.50	79.50	28.60	1.90	69.47	n.r	Diez et al. (2004)
550	Fixed bed	33.00	95.9	0.50	0.20	3.40	16.50	1.20	1.00	81.30	28.57	1.90	59.05	n.r	Diez et al. (2004)
450	Rotary kiln reactor	43.90	82.13	2.10	0.54	2.28	12.51	16.61	3.40	67.47	31.20	1.51	66.29	89.10	Li et al. (2004)
500	Rotary kiln reactor	41.30	82.17	2.28	0.61	2.32	12.32	16.14	2.35	69.19	31.50	1.51	63.54	89.10	Li et al. (2004)
550	Rotary kiln reactor	39.90	80.82	1.46	0.53	2.41	14.58	6.92	1.28	77.22	30.00	1.51	63.68	89.10	Li et al. (2004)
600	Rotary kiln reactor	39.30	81.00	1.38	0.51	2.53	14.30	5.86	1.98	77.93	30.40	1.51	65.85	89.10	Li et al. (2004)
650	Rotary kiln reactor	38.80	81.03	1.98	0.45	2.40	13.94	6.27	1.48	78.32	30.10	1.51	61.67	89.10	Li et al. (2004)
–	Plasma pyrolysis	57.83	82.69	0.42	0.42	2.51	15.14	n.r	n.r	n.r	n.r	1.57	92.35	64.80	Tang and Huang (2004)
–	Plasma pyrolysis	23.00	85.06	0.24	0.38	1.97	16.25	n.r	n.r	n.r	n.r	1.57	28.86	70.00	Tang and Huang (2005)
500	Fixed bed	37.90	82.70	0.40	<0.10	2.20	n.r	n.r	n.r	n.r	n.r	n.r	n.r	69.50	Kyari et al. (2005)
550 ^c	Fixed bed	42.00	n.r	n.r	n.r	0.80	40.30	n.r	n.r	56.30	14.80	1.71	19.65	55.50	Ucar et al. (2005)
650 ^c	Fixed bed	41.70	n.r	n.r	n.r	1.00	40.80	n.r	n.r	56.20	15.70	1.71	24.39	60.50	Ucar et al. (2005)
800 ^c	Fixed bed	41.50	n.r	n.r	n.r	0.90	40.80	n.r	n.r	55.90	15.20	1.71	21.84	63.50	Ucar et al. (2005)
550 ^d	Fixed bed	33.80	n.r	n.r	n.r	2.10	14.30	n.r	n.r	82.40	33.90	1.44	49.29	56.50	Ucar et al. (2005)
650 ^d	Fixed bed	33.80	n.r	n.r	n.r	2.30	14.80	n.r	n.r	82.60	33.40	1.44	53.99	63.50	Ucar et al. (2005)
800 ^d	Fixed bed	33.20	n.r	n.r	n.r	2.00	13.50	n.r	n.r	84.30	34.20	1.44	46.11	66.00	Ucar et al. (2005)
550	Fixed bed	38.00	90.27	0.26	0.16	1.22	8.41	0.67	0.09	90.80	28.00	1.43	32.42	63.00	Munillo et al. (2006)
425	Spouted bed	35.36	86.19	1.25	0.45	3.06	n.r	n.r	n.r	n.r	n.r	2.00	54.10	61.10	Lopez et al. (2009)
500	Spouted bed	36.92	87.36	0.91	0.44	3.29	n.r	n.r	n.r	n.r	n.r	2.00	60.73	77.90	Lopez et al. (2009)
600	Spouted bed	38.30	87.24	0.73	0.39	3.37	n.r	n.r	n.r	n.r	n.r	2.00	64.54	84.10	Lopez et al. (2009)
425	Spouted bed	33.91	86.46	0.70	0.34	3.59	n.r	n.r	n.r	n.r	n.r	2.14	56.89	36.90	Lopez et al. (2009)

(Continued)

Pyrolysis temperature (°C)	Reactor type	CBp yield (wt%)	Elemental analysis on dry basis (wt%)				Proximate analysis on as received basis (wt%)				CV (MJ/kg)	Sulfur in tire (wt%)	Sulfur retention (%)	BET surface (m ² /g)	Ref.
			C	H	N	S	Ash	Volatile matter	Moisture	Fixed carbon					
500	Spouted bed	34.05	86.62	1.39	0.75	2.24	n.r	n.r	n.r	n.r	n.r	2.14	35.64	65.20	Lopez et al. (2009)
600	Spouted bed	35.81	86.57	7.66	0.44	2.13	n.r	n.r	n.r	n.r	n.r	2.14	35.64	116.30	Lopez et al. (2009)
550	Fixed bed	34.00	86.30	0.30	0.30	2.80	12.50	1.80	0.40	91.30	29.70	1.90	50.11	64.00	López et al. (2011)
500	Fixed bed	39.00	87.35	1.05	0.24	2.70	8.24	n.r	n.r	n.r	~15 ^b	1.38	76.30	n.r	Kordoghli et al. (2017)
500	Spouted bed	~34.00	80.30	1.30	0.30	2.70	n.r	n.r	n.r	n.r	29.3 ^b	0.89	103.14	83.00	Olazar et al. (2008)
550	Fixed bed	36.50	n.r	n.r	n.r	n.r	16.18	n.r	n.r	n.r	n.r	1.40	n.r	69.23	Zhou et al. (2010)
400	Fixed bed	55.90	83.80	2.40	0.30	2.30	9.00	n.r	n.r	n.r	27.30	1.50	85.71	n.r	Rodriguez et al. (2001)
500	Fixed bed	44.80	83.50	0.60	0.30	2.40	12.10	n.r	n.r	n.r	28.80	1.50	71.68	n.r	Rodriguez et al. (2001)
600	Fixed bed	44.20	83.70	0.50	0.30	2.60	12.00	n.r	n.r	n.r	29.00	1.50	76.61	n.r	Rodriguez et al. (2001)
700	Fixed bed	43.70	82.50	0.50	0.30	2.30	13.20	n.r	n.r	n.r	29.10	1.50	67.01	n.r	Rodriguez et al. (2001)
500	Fixed bed	23.20	93.30	0.80	0.80	3.00	11.40	2.80	0.00	85.80	n.r	1.40	49.71	151.50	Roy et al. (1995)
0.3 kPa															
n.r	n.r	n.r	87.80	0.33	n.r	1.97	9.61	0.88	0.25	89.26	n.r	n.r	n.r	62.00	Murillo et al. (2005)
550	Fixed bed	n.r	81.50	1.00	0.50	3.30	13.80	3.50	0.70	82.10	29.40	1.90	n.r	37.00	López et al. (2013)
500	Fixed bed	25.00	80.40	0.40	0.70	3.60	14.60	3.22	0.41	82.18	n.r	1.40	64.29	n.r	Mchoul et al. (1996)
20kPa															
N-234			94.80	0.80	0.80	0.60	0.60	4.20	0.00	95.20	n.r	n.r	n.r	112.70	Roy et al. (1995)
N-330			96.00	0.70	0.60	0.70	0.30	3.30	0.00	96.40	n.r	n.r	n.r	80.50	Roy et al. (1995)

Notes: n.r: not reported; A) Low; b) High; c) passenger car tire, PCT; d) truck tire, TT.

also confirmed the presence of carbonaceous deposits on the CBp surface from another perspective. Recently, a new kind of core-shell structured CBp was separated by light pyrolysis under relatively low temperatures (generally about 150°C). A series of researches concerning light pyrolysis CB (CBlp) were conducted by Professor Wang Shifeng's team at Shanghai Jiao Tong University (Li et al., 2016a; 2016b; Cheng et al., 2018; Song et al., 2018a; 2018b; 2018c; Wu et al., 2018). According to the above works, the degradation of the covalently cross-linked rubber networks can be achieved by the synergistic effects of vegetable-derived oil and mild oxidation. A layer of bound rubber including loosely bound rubber and tightly bound rubber could be observed by TEM forming the shell of CBlp, as shown in the lower of Fig. 3. And the bound rubber encapsulated CBp particles can be easily recovered by a “layer-by-layer” solvent extraction. These two kinds of “core-shell structure” have different shell composites, both greatly hindering the future application of the CBp. Therefore, pyrolysis integrated with the modification process has great potential in solving the problem of ELTs as well as obtaining higher value-added products, which is very sensitive to the economics of the pyrolysis plant.

3 Modification methods for CBp upgrading

To some extent, modification methods determine the surface chemistry of CBp, which is vital in various industrial applications. Two kinds of modification approaches are in situ modification occurred in the process of CB manufacture, and post-modification happened on the surface of CB, respectively, to improve its properties. In this review, all of the CBp modification methods discussed below are post-modification.

One common modification method for CBp was activation at high temperatures with steam or CO₂ to produce active carbon and therefore using as absorbent (Ariyadejwanich et al., 2003; Murillo et al., 2005; Song et al., 2012; López et al., 2013; Danmaliki and Saleh, 2016), which were widely used for heavy metals (Saleh et al., 2013; Karmacharya et al., 2016; Smith et al., 2016) and organics (Tanthapanichakoon et al., 2005; Shah et al., 2006; Mui et al., 2010; Gupta et al., 2011b,a; Nunes et al., 2011). Besides, CBp can be used in other fields such as pigment for printing ink (Roy et al., 2005; Zhou et al., 2006; Ding et al., 2013), shielding materials (Jia et al., 2017) and energy storage materials of batteries (Chen et al., 2018) and supercapacitors (Zhi et al., 2014; Boota et al., 2015; Zhao et al., 2015; Varaprasad et al., 2017).

However, the primary use of CB is a reinforcing material in tires as well as other rubber products. The growing demand of tire industry is also a challenge for CB filled rubber to achieve optimum mechanical properties. Therefore, using modified CBp as the reinforcing agent of

elastomers is of immediate significance. The modification methods discussed below of CBp can be divided into 2 steps — purification and surface modification.

3.1 Purification

CBp is a carbonaceous material with higher carbon concentration (>80 wt%), with a very heterogeneous material regarding the ash content, particle size, morphology and both surface chemistry and activity. All these variables will affect its recovery and consequently, the economic feasibility of the ELTs pyrolysis process (Daniel Martinez et al., 2013). The purification process can be regarded as the pre-treatment for surface modification, eliminating the carbonaceous deposits, ash, sulfur content and odor from CBp. The CBp after purification treatment can be considered as a mature commercial product to directly utilize in tires manufacture.

It is noteworthy that there is a mass loss of approximately 25 wt% during purification process because of the removing of inorganic component and carbonaceous deposits. The percentage of weight-loss is defined as the mass difference between the origin CBp and the purified CBp divided by the mass of origin CBp, with both mass on a dry basis. This weight loss inevitably leads to a lesser amount of purified CBp, which will bring in a disadvantage in yield but a significant upgrading in the quality CBp products.

3.1.1 Post-pyrolysis

Post-pyrolysis is an optional treating step for CBp modification. In addition, to the pyrolysis process of gaining CBp, an extra-heating at higher temperature using the same reactor to reduce carbonaceous deposits on CBp surface has been aroused some researchers' interests. The carbonaceous deposits formed during ELTs pyrolysis are likely located in the void space between the primary particles of the CB aggregate as well as blocking a portion of CBp surface (Pantea et al., 2003) so that significantly affect the surface activity and morphology of CBp. The results showed that post-pyrolysis CBp gained a higher specific surface area while retaining mechanical strength to some extent. Based on Pantea' work (Pantea et al., 2003), CB was first pyrolyzed in vacuum at a low temperature of 500°C and then post pyrolyzed it at a higher temperature of 670°C–860°C, and the results showed that specific surface area of CBp can reach 53–80 m²/g. The specific surface area of CBp increased from 51 m²/g to 67–91 m²/g by post-carbonization at 600°C and 900°C (Helleur et al., 2001). According to Martínez (Martínez et al., 2019), the decrease of the volatile matter (from 4.7 to 2.4 wt%) resulting in an increase in surface area (from 65.7 to 72.4 m²/g). However, volatile matter in CBp produces agglomerated particles, leading to the difficult of break. Another attempt was to pyrolyze CB at a lower temperature of 500°C in N₂

atmosphere first and then under steam activation at a higher temperature of 850°C, to obtain mesoporous activated carbon with a specific surface area of 737 m²/g while the specific surface area before activation was 30–90 m²/g (Ariyadejwanich et al., 2003). CBp with such a large specific surface area is not suitable for rubber composites, but shows unique potential in pollution adsorption. What's more, post-pyrolysis also plays an irreplaceable role in removing trace oil and odor from CBp (Helleur et al., 2001) while it is difficult to break agglomerated particles in CBp produced by volatile matter through post-pyrolysis.

3.1.2 Demineralization

The most significant difference between CBp and commercial CB lays in ash and sulfur content, because the inorganic components cannot be removed through pyrolysis. Untreated CBp has a narrow range of industrial applications such as a low-grade rubber filler. Therefore, ash and sulfur removal is the first step to purify CBp.

Table 2 summarizes the documented demineralization process of the acid-base method. Chaala (Mchoul et al., 1996) first reported the ash removing of CBp by acid-base washing method in 1996. A synoptic scheme of common acid-base treatment is shown in Fig. 4. By comparing different treating conditions of reagent concentration, reagent/CBp ratio, treating temperature, treating time, the results showed that high removal ratios of both ash and sulfur were achieved by using 4M HCl and 5M NaOH solution with stirring at 60°C for both 1 h. The removal ratio of ash and sulfur under the optimum conditions were 79.33 wt% and 70.37 wt%, respectively. The changes in bulk and surface components of CBp before and after acid-base washing were compared as well. Unfortunately, the efficiency of sulfur removal was not mentioned in previous researches, and the studies about all metal elements to metallic oxides also remained to be discussed. Many studies of a few changes in washing conditions such as acid type, temperature, reaction time, have been reported (Ucar et al., 2005; Shah et al., 2006; Zhou et al., 2006; Alexandre et al., 2010; Bernardo et al., 2012; Iraola-Arregui et al., 2018; Sugatri et al., 2018). It is noteworthy that recent researches have achieved good results by using other fields of microwave (Banar et al., 2015) and ultrasonic (Zhang et al., 2018). Compared with the average removal rate of 50%–60% in ash and sulfur content, the use of HCl and HF dual-reagent in microwave reached a removal rate of sulfur by 70.16% and ash by 98.33%, respectively. The specific surface area after treatment reached 92.10 m²/g, to replace commercial CB N326. In this research, HF of high concentration can dissolve silicate that HCl cannot deal with, which plays a vital role in removal efficiency. However, HF is weak in sulfur removal.

It must be pointed out that the studies of demineralization mechanism are urgent to optimize the washing procedure for the different ash and sulfur components under a variety of tire production and pyrolysis conditions, but the coal deashing and desulfurization technology are relatively mature. As there are many similarities between CBp and coal, purification methods of coal can be used as attempts. Besides, the acid-base method can be used to re-expose the active sites on CBp surface due to the dissolve of impurities, which can be considered as an essential way to upgrading CBp to produce high-valued active carbon (Namane et al., 2005).

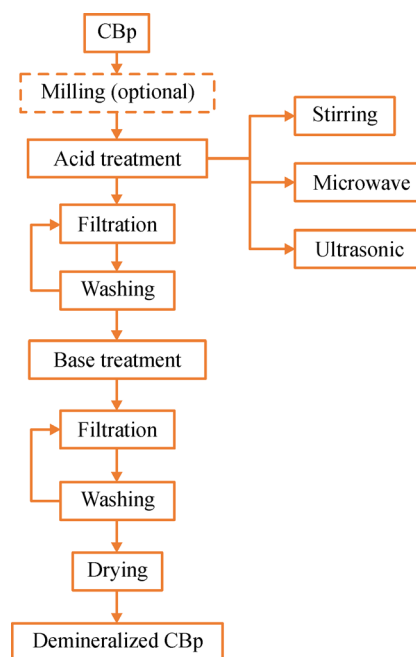


Fig. 4 Flow chart of acid-base demineralization.

3.2 Surface modification

The agglomeration tendency of CB particles after demineralization leads to the difficulty of their dispersing uniformly in the rubber matrix, to decreases the mechanical strength of hybrid rubber materials. Surface modification provides a feasible way to prepare high-performance tires and other rubber-based materials, which has been extensively studied recently. Here, we have discussed the surface modification methods in the following, which include surface oxidation, polymer grafting, plasma modification, and reaction with diazonium salts.

3.2.1 Surface oxidation

Surface oxidation is the most common modification method to increase the hydrophilicity of CBp, which is

Table 2 Literature survey in related to improvement of CBp by demineralization process

Material	Demineralization medium	Medium usage (mL/g)	Demineralization Temperature (°C)	Demineralization Time (h)	Demineralization Method	Ash removal (%w/w)	Sulfur removal (%w/w)	BET (m ² /g)	BET Increased %	Ref.
CBp	0.5M H ₂ SO ₄ + 5M NaOH	10 in H ₂ SO ₄ /10 in NaOH	60	0.5 in H ₂ SO ₄ + 0.5 in NaOH	Vigorous stirring	79.04	36.11	64.8	n.r	Mehoul et al. (1996)
CBp at 550°C ^a	4M HCl + 5M NaOH	10 in HCl/10 in NaOH	60	1 in HCl + 1 in NaOH	Stirring	79.33	70.37	n.r	n.r	Martínez et al. (2019)
CBp at 500°C ^a	20wt% HNO ₃	15	80	1	Vigorous stirring	53.52	n.r	88.62	28.00	(Zhou et al. (2006)
CBp at 400°C ^a	0.5M HNO ₃	10	Boiling point of HNO ₃	24	Stirring	30.99	n.r	n.r	n.r	Alexandre Franco et al. (2010)
CBp at 800°C ^a	10wt% HCl	n.r	100	2	n.r	68.97	n.r	72.2	8.59	Ucar et al. (2005)
CBp at 450°C ^a	1M HCl	n.r	r.t	24	n.r	n.r	65.38	870	923.53	(Shah et al. (2006)
50% tires + 50% plastics	1M HCl	100	60	1	Stirring	64	n.r	n.r	n.r	Bernardo et al. (2012)
CBp at 410°C ^a	1M HCl	n.r	r.t	2	Gently stirring	n.r	60.86	n.r	n.r	Sugatri et al. (2018)
CBp at 550°C ^a	4M HCl	10	60	1	Stirring	67.33	59.26	76.3	5.39	Martínez et al. (2019)
Tire-derived fuel(TDF)	37wt% HCl + 65wt% HNO ₃	20	175	0.17	Microwaves 400W	54.20	87.13	185	76.19	Banar et al. (2015)
CBp at 650°C ^a	4M HCl + 40 wt % HF	10 in HCl + 2 in HF	60 in HCl + 25 in HF	6 in HCl + 5 in HF	Ultrasonic 200W 40khz	98.33	70.16	92.10	n.r	Zhang et al. (2018)

Notes: n.r: not reported; r.t: room temperature; a) the temperature mentioned refers to pyrolysis temperature.

widely used for creating active sites for other surface modification strategies. By adding oxygen-containing polar groups on CBp surfaces such as hydroxyl, carboxyl, carbonyl, quinone and lactone groups, the agglomeration of CBp particles decreases with the increase of the dispersion of CBp, to achieve better compatibility between CBp fillers and the rubber matrix.

Surface oxidation of CBp can be achieved by gas, liquid, and plasma. Gas oxidation is the most traditional way by using O_2 , NO_2 , CO_2 , and O_3 as oxidants at 200°C – 700°C . Generally speaking, with the increase of temperature and time, the number of oxygen groups and specific surface area increase while the pH value decreases, resulting in a better dispersion in rubber matrices. Many studies confirmed the enhancement of reinforcing effect (Payne, 1966, 1967; Medalia and Kraus, 1994). Besides, Sutherland (Sutherland et al., 1996) found that the tensile strength of oxidized CBp filled polar nitrile-butadiene rubber (NBR) increased but that of non-polar natural rubber (NR) decreased. The increased tensile strength of rubber composite was due to the enhanced interaction of between polar CBp and polar NBR, and the reducing tensile strength was due to the reduced interaction between polar CBp and non-polar NR. Bandyopadhyay (Bandyopadhyay et al., 1996) also found out that by using surface oxidized intermediate super abrasion furnace black (ISAF black) can achieve better mechanical and dynamic properties because of the chemical bonding between hydroxyl groups on CBp and carboxylic groups on carboxylated nitrile-butadiene rubber (XNBR). Manna (Manna et al., 1997; Manna et al., 1998) revealed the interaction between surface oxidized ISAF and natural epoxy rubber (ENR), and oxidized CB can form ether bond and ester bond with ENR compared with untreated ISAF. While the primary network was formed by chemical bonding, the secondary network was established by Van der Waals force between CB and the rubber matrix, therefore improving the mechanical hysteresis and strain-related dynamic properties. It should be pointed out that these secondary networks are easily destroyed under relatively high strains. The aggregation structure of CB could be observed under a microscope, and the average size of oxidized CB particles decreased from $30\text{ }\mu\text{m} \times 40\text{ }\mu\text{m}$ to $1.0\text{ }\mu\text{m} \times 1.5\text{ }\mu\text{m}$, while the non-oxidized CB remained the average size decreasing from $20\text{ }\mu\text{m} \times 30\text{ }\mu\text{m}$ to $3\text{ }\mu\text{m} \times 4\text{ }\mu\text{m}$.

Moreover, some works reported on the enhancement methods of the interaction between oxidized CB and other elastomer matrices, such as the epoxy resin (Nakahara et al., 1995), liquid crystal epoxy resin (Bae et al., 2002).

In addition, Yuan et al. (2014) found out that hydroxymethyl groups ($-\text{CH}_2\text{OH}$) can be introduced on the surface of CB by formaldehyde solution under alkaline conditions, to increase the hydrophilicity of CB and subsequently accelerate the efficiency of HNO_3 oxidation (Li et al., 2001; Zhang et al., 2010; Kumar et al., 2013).

3.2.2 Polymer grafting

Grafting polymers on CB surfaces will result in better compatibility with rubber matrices by the enhancement of the filler-polymer interaction as well as the reduction of the filler-filler interaction. Advances in polymer grafting can induce the polymers with well-controlled composition, structure and molecular weight, to achieve the performance adjustment of the composites. Tsubokawa (1992) generalized the preparation methodologies of polymer-grafted CB under three categories, including grafting onto carbon black, grafting from carbon black and the reaction of carbon black with functional polymers. Grafting polymers onto CB refers to the deactivation of growing polymer radical by chain termination and chain transfer with functional groups on CB surfaces. Grafting polymers from carbon black refers to graft polymerizations initiated by reactive groups introduced onto CB surfaces. The reaction of carbon black with functional polymers means the reaction of functional polymers with the reactive functional groups on CB surfaces. The author reviewed the work on polymer grafting on CB up to 1991.

Inspired by the double bond reaction between nitroso compounds and rubber molecules, Cataldo (1999) introduced nitro ($-\text{NO}_2$), nitroso ($-\text{N}=\text{O}$) and nitrate groups ($-\text{O}-\text{NO}_2$) on the surface of CB by chemical adsorption of N_2O_3 , NO , and N_2O_4 . The IR and Raman spectra of NR/SBR composites showed that chemical bonding with rubber molecules which occurred on the surface of CB without affecting the internal structure. Compared with the untreated CB, the at 70°C had a reduction of 14%, and the $\tan\delta$ at 0°C showed an increasing, suggesting that $\tan\delta$ the modified CB reduced the hysteresis of NR/SBR compound and effectively decreased the rolling resistance without affecting the braking performance.

Atif et al. (2013) used mercaptopropyltrimethoxysilane (MPTS) monomers to graft silane moieties onto the CB surface, aiming to weaken the aggregation by enhancing the interaction between them and the rubber matrix. The results showed that the modified CB achieved extremely favorable dispersion in different solvents without macroscopic separation occurred in pristine and oxidized CB.

Polymer-grafting plays an irreplaceable role in improving the dispersion and stability of grafted CB in various matrices and solutions. The multi-functionalized polymer-grafted CB has dramatically benefited from the progress in grafting methods and molecular design of polymers chains in recent years. Moreover, the characterization of grafted polymer and accurate control of polymer structure need a further detailed investigation, which will be the focal points for future research.

3.2.3 Plasma modification

It is well known that the distribution and dispersive

processes control the dispersion of CB in the rubber matrix. After decomposition of the bulk initially, a good dispersion is depended on the fillers' wettability and its compatibility with rubber. To get better compatibility, the difference in surface energy between filler and matrix should be as little as possible. A big surface energy difference will result in an enhanced filler-filler interaction, which will adversely affect the stability of the dispersion system during the mixing process.

Plasma modification is one of the most widely methods to tailor the surface properties of many solid materials, including fillers. There are three main advantages of plasma modification of CB: (1) the plasma modification only occurs on the surface of the material; (2) a variety of plasma can be used to produce different change; (3) plasma treatment can reduce the surface energy of CB particles and increase their compatibility with a variety of matrices. The surface energy of CB is significantly higher than rubber materials such as styrene-butadiene rubber (SBR), butadiene rubber (BR) and ethylene-propylene-diene rubber (EPDM). Akovali and Ulkem (1999) polymerized styrene and butadiene monomers onto the surface of CB by plasma, and proposed that plasma could change the interfacial tension of CB surface to match the rubber matrix to improve the filler-matrix compatibility, for the first time. After that, based on surface energy judgment, Mathew et al. (2011) used acetylene monomers to construct a hydrophobic shell on the surface of CB by plasma polymerization. The modified CB was characterized by thermogravimetric analysis, wetting behavior with various liquids of known surface tension and time of flight secondary ion mass spectrometry. The results showed that unless longer time of modification than silica, the amount of plasma polymer on the surface of CB was lower, which can be explained by the thermodynamic feasibility of different bond energies. Strong adhesion occurred only at the edge of CB microcrystalline for the short life of active sites on the surface of CB microcrystalline, which usually go back to their initial state before the adhesion of active monomers. The formation of a plasma polymer layer on the surface of fullerene black was more clearly demonstrated due to the TEM images. The higher resistance value of modified CB indicated a reduced filler-filler interaction. Furthermore, the modified CB had better compatibility with the rubber matrix due to its lower surface energy than unmodified CB. It was worth noting that the tensile properties were better than those in the saturated EPDM matrix, due to the possible interaction between the unsaturated bonds of the plasma polymer layer and the unsaturated bonds in SBR and NBR.

Plasma modification of CB not only take place in plasma torch but also in methane, ethylene, pyrolysis fuel oil and even renewable vegetable oil (Probst et al., 2002). The modification of CB with different raw materials was analyzed, and the properties of the composites of various modified CB fillers were compared in SBR matrix.

Nowadays, plasma modification is not widely applied for its high cost and remained technical issues. This modification method is more suitable to be called in-process modification instead of post-process modification.

3.2.4 Reaction with diazonium salts

Twenty years ago, Cabot's researchers (Belmont et al., 1998; 1999; 2000; 2002; 2004) proposed a spontaneous reaction between CB and diazo salts without electrochemical assistance, and obtained a series of patents, providing a feasible route to graft various organic functional groups on CB surface. Sulfur-containing groups modified on CB can couple with SBR macromolecular chains during vulcanization, thus establishing a relationship between modified fillers and polymer matrix. Compared with unmodified N234 and Si-69 silica, APDS-N234 exhibited lower Payne effect. $\tan\delta$ at 70°C is close to that of Si-69 silica and much lower than that of unmodified N234, indicating that APDS modified N234 can be compared with modified silica in rolling resistance and hysteresis effect and its performance is much better than commercial CB.

4 Conclusions and future perspective

The management of ELTs is a complicated issue containing technological, ecological and economic challenge. If pyrolysis integrates with the modification process could obtain higher value-added products, the economics of the pyrolysis plant will have a capital improvement. The establishment of modification methods can be based on the study of pyrolysis mechanism and the analyze of the physiochemical characteristics of CBp. After modification treatment, CBp also has a foundation for achieving well dispersion in rubber matrix, which in turn supports for the ELTs pyrolysis process.

From our perspective, it is noteworthy that:

- CBp is a very heterogeneous material, regarding not only the ash content, particle size, morphology and both surface chemistry and activity but also the fact that CBp is a mixture of more than one grade of commercial CB, which significantly hinders its utilization in rubber manufacture. And it can't be solved even after the upgrading processes of demineralization and surface modification. However, CBp as a new material instead of a 1 to 1 substitute to commercial CB is the latest opinion emerged from the Recovered Carbon Black Congress held in Berlin on May 21–22, 2019. In addition, CBp as a new material for rubber manufacture always changes the opinion, because CBp can only be an imperfect alternative for one specific grade of commercial CB.

- The "carbonaceous nanofillers" or "graphene-based fillers" such as carbon nanotube and graphene can induce the rubber nanocomposites with unique properties, and

will become one of the hot research topics in the future. The synergistic effect between traditional filler and carbon nanomaterials of high modulus and conductivity will provide the rubber nanocomposites with superior performances in mechanical property, thermal and electrical conductivity.

• It is worth noting that the European Commission adopted a long-awaited Circular Economy Package in December 2015 due to facing with the scarcity of resources. A concrete and ambitious “closed loop tyre-to-tyre recycling (present in Fig.5)” was established with the measurements covering the whole cycle: from production and consumption to waste management and the market for secondary raw materials. Honestly, the cycle is not yet within reached due to tire safety and environmental performance and technological constraints to achieve materials recovered from tires going back into tires. But

the development of ELTs pyrolysis and modification methodologies makes us put faith in this.

• Further research concerning the economic viability and LCA process of the CBp upgrading process is of significantly recommended. The costs affecting the development of a viable upgrading process include: pretreatment costs, equipment and infrastructure cost, process development cost, operating costs, energy costs, product post-treatment cost, product certification costs, product storage, marketing, security of location, product price, production capacity, total production cost, capital investment and the applied tipping fee (Antoniou and Zabanitou, 2018). An LCA could also highlight the crucial aspects of a complete operation either targeted to solid materials or electricity production.

“Pyrolysis-purification-surface modification” has achieved the application of CBp, not only to solve the

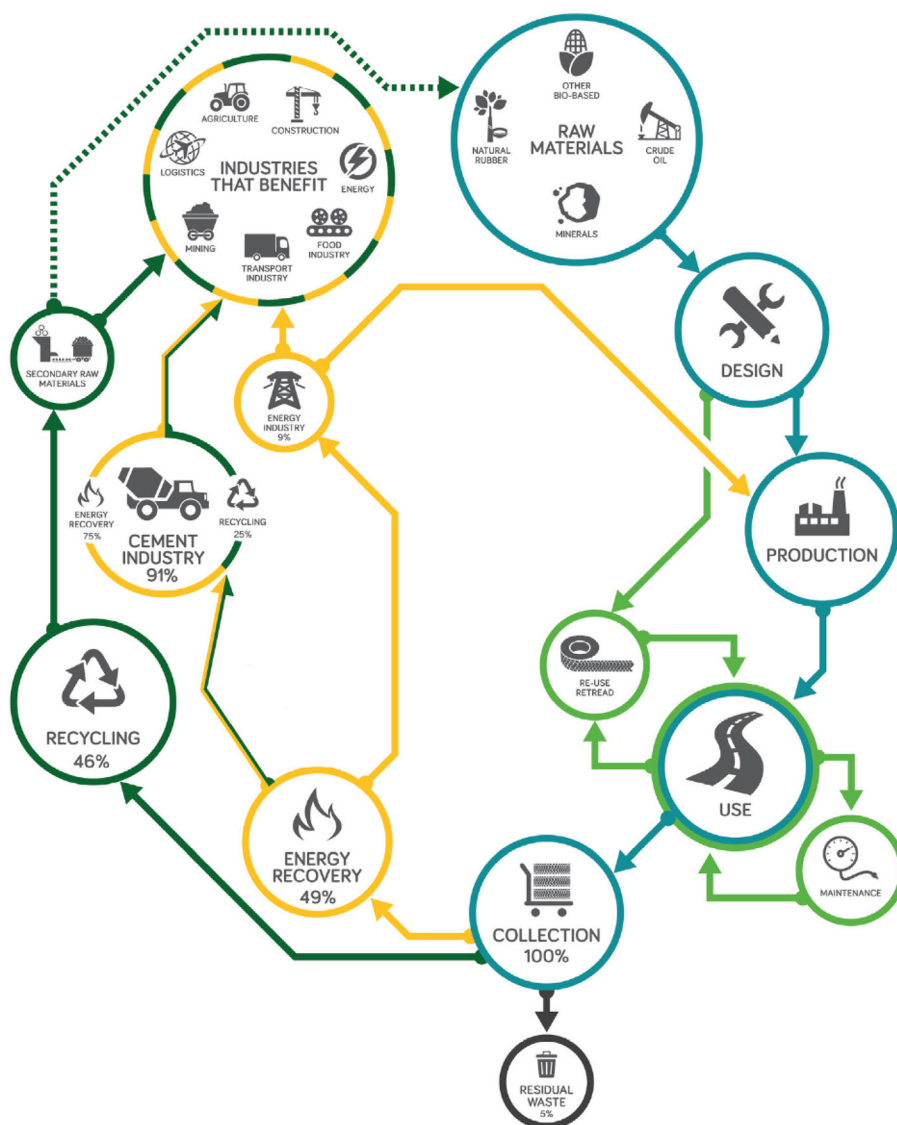


Fig. 5 The “closed loop tyre-to-tyre recycling” of tires.

problem of recycling ELTs worldwide but also upgrade CB from traditional material to vital material, which used in many nanotechnology fields. It means a lot to increase the range of applications for CB, and changes it into a new kind of nanomaterial from traditional material.

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