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Technical research of pyrolytic carbon black prepared on rotating moving bed equipment

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Abstract. Nowadays, waste tires have been one of the worst environmental pollution sources. How to solve the waste tires is a hot potato for the environment. Pyrolysis is one of the most commonly used method. In China, rotary kiln reactor has been widely used for pyrolysis and can be used as a large-scale production equipment form, but there is no mature case of rotating moving bed. In this paper, CBp was produced in rotating moving bed. The continuous pyrolysis device, rotating moving bed, which is a new type of equipment to replace the batch reactor. Temperature is studied as the most important character in the cracking process. The results showed that the productivity of CBp, Pyrolytic oil and gas were obviously affected by temperature. The oil could improve the compatibility of CBp with rubber, increasing the dispersion in rubber, resulted in the good reinforce property. High temperature causes more groups be detected on the surface of CBp by FT-IR spectrometer. The Payne effect of CBp reinforced NR compound increases with the increasing of pyrolysis temperature.

Keywords: pyrolytic carbon black (CBp), waste tires, pyrolysis, rotating moving bed

1. Introduction

Waste tires have been one of the worst environmental pollution sources nowadays. Around 1.5 billion waste tires, which are over 52 million tons, are generated annually. The network structure of waste tires formed in the curing process leading to hardly degradation in nature environment. Pyrolysis treatment is a kind of commonly used treatment for waste tires. After pyrolysis treatment, waste tires can obtain pyrolytic oil, gas, pyrolytic carbon black and steel etc [1]. Commonly, pyrolytic oil is one of the major products and for instance, can be used as diesel oil as its calorific value is high [2]. The pyrolysis gas is usually used as fuel to supply heat energy for pyrolysis reaction, because it is difficult to transport and store. In order to control the ratio of oil and gas, appropriate pyrolysis process needs to be adjusted [3].

Pyrolytic carbon black (CBp), another product from waste tire pyrolysis, has become one of commercial carbon black materials. The CBp is prepared from the solid residue of waste tire pyrolysis after grinding and modification [4]. As a recyclable resource, CBp can replace part of commercial carbon black as filler applied to rubber. It can reduce the use of commercial carbon black and reduce carbon emissions while solving the problem of recycling waste tires. CBp is a complex mixture arising from the compounds used during tire manufacture, such as carbon black (CB) , inorganic fillers and additives. Meanwhile, the tar steam of pyrolysis gas will undergo secondary pyrolysis reaction to generate asphaltene and coke like substance attached to the surface of CBp, which lower the surface activity. In that case, reducing the occurrence of secondary pyrolysis reaction is conducive to improve the property of CBp.

In China, the most used CBp production equipment is rotary kiln reactor, which has been used as a large-scale production equipment form. As a non-continuous reactor, the rotary kiln showed poor automation and bad producing environment. The rotating moving bed, one kind of continuous pyrolysis equipment, is regarded as an ideal candidate for CBp production. However, there is few cases reported about pyrolysis in rotating moving bed [5]. In this paper, the continuous pyrolysis device, rotating moving bed, was used for waste tires pyrolysis. Different pyrolysis process

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temperatures of this device were studied to compare the performances of pyrolysis products. The effects of temperature on the pyrolysis process of waste tires were studied and the influence rules of different reaction temperature on the product distribution and composition were obtained.

2. Experiment

2.1 Experimental device

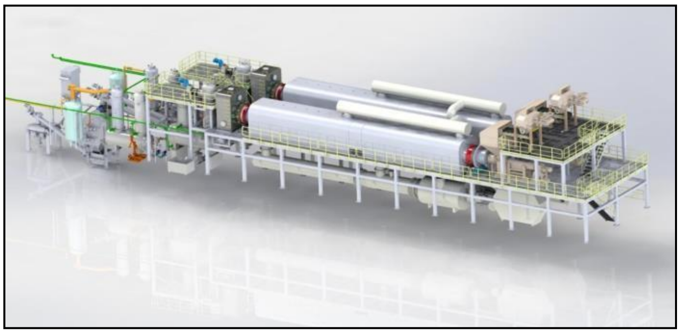

Figure 1. Diagram of rotating moveing bed pyrolysis device

The rotating moving bed is a continuous pyrolysis device in Fig.1, which can realize the function of automatic continuous feeding and continuous pyrolysis. The rotating moving bed reactor is composed of a feeding module, a pyrolysis module, a slag discharging module and a condensing module. The designed processing capacity is 1t/h. Waste tire was crushed at room temperature to produce colloidal material (steel wire content < 1%) prior to pyrolysis, which was transported to the feed module by a conveyor. A certain amount of colloidal material was piled up in the feed silo to avoid air entering the reaction kettle. The material was forced to be extruded and transported into the reaction kettle by the feeding device. The pyrolysis reactor was provided with spiral blades. The reactor works in the external rotation mode, and the material was transported by spiral blades for continuous cracking. Outer wall of the reaction kettle was heated by circulating hot air, and heat was transferred to the pyrolysis material through the cylinder wall. The reaction kettle was kept in a state of slight negative pressure from -1 kPa to 0.5 kPa, and the generated gas substances were extracted in time through an induced draft fan to reduce the occurrence probability of secondary pyrolysis. The remaining solid material was cooled by a slagging system and transported to the carbon black deep processing line. The technological process is shown in Fig.2.

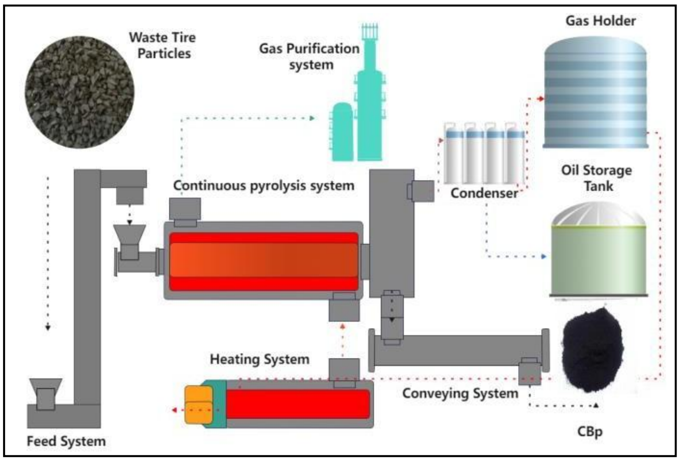

Figure 2. Scheme of rotating moving bed

Continuous pyrolysis process is the main research object of waste tire pyrolysis industry in recent years. Compared with the batch process, it has the following advantages: The reactor does

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not need to heat up and cool repeatedly when switching materials, thereby increasing production efficiency; The heating uniformity of rotating moving bed is better than that of the batch reactor because of the lower filling rate; Automatic feeding and discharging process to improve production environment.

The heat transfer situation and material movement of reactor as shown in Fig.3. The Rubber particles are pushed forward by spiral blades. Heat transfer in reactor includes: heat transfer between gas and cylinder surface where not covered by material (Q1), radiation heat transfer between material bed surface and gas (Q2), heat transfer between material and cylinder wall surface (Q4) and contact heat transfer between materials (Q3). In this exothermic reactor, most of the heat of material comes from Q4. Therefore, the heating temperature of the external wall of the hot blast stove is higher than the temperature required by the material.

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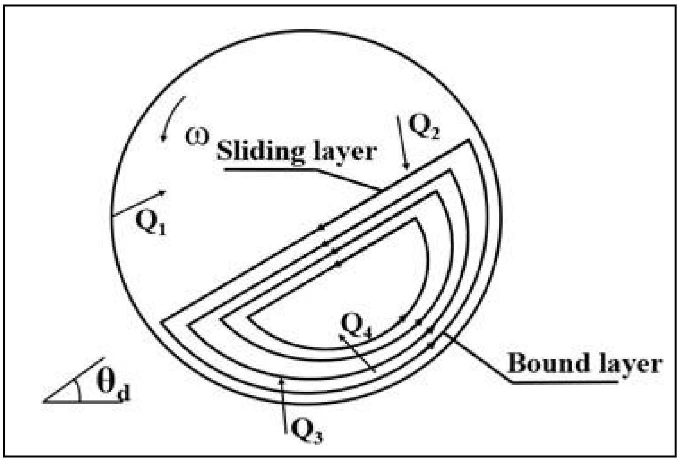

Figure 3. The heat transfer situation and material movement of reactor

The pyrolysis reaction of tires is mostly performed between 350-550 ℃, which the radical reaction dominated in this period [6]. The furnace temperature is 100~150℃ higher than the pyrolysis temperature, and the thermal efficiency of hot air cycle heating is usually about 70%. With using time increased of the reactor, the temperature difference between furnace and reactor temperature will gradually expand, which is caused by coking inside the reactor wall leading to heat transfer efficiency decreased. By observing the change value of furnace temperature and pyrolysis temperature, the coking condition of the inner wall of the reaction kettle can

be judged, so as to guide the maintenance and cleaning of the equipment.

2.2 Characterization

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Table I. National standard for cbp test

Performance test	National standard
Tensile stress-strain	GB/T 528-2009
Iodine absorption value	GB/T3780.1
DBP absorption value	GB/T3780.2
Ash content	GB/T3780.10
Toluene transmittance	GB/T3780.15
NSA/STSA	GB/T10722-2014

The performance test of CBp is determined according to the corresponding national standard of carbon black in Table I.

changed much. That is to say, increasing temperature couldn’t result in a higher productivity of CBp. On the other hand, temperature affects the molecular weight of hydrocarbon products because the increase of temperature leads to the intensification of pyrolysis reaction, and more liquid products are converted into small gas molecules by molecular chain fracture. As the structure of the rotating moving bed is long and thin, the oil and gas outlet are located at the end of the reactor. If the reaction temperature is too high, the oil and gas can’t be extracted in time, leading to the secondary pyrolysis reaction. As a result, excessive temperature would affect the quality of pyrolysis carbon and reduces the oil yield to affect the economic benefits.To characterize the reinforce property, a commonly used rubber formula was introduced as Table II. The mechanical strength test was performed on Model 5965 electronic universal material testing machine (Instron Co. Ltd., USA). The hardness test was performed on WAH17A Shore A hardness tester (Wallace Co. Ltd., UK). The other tests were all performed on test instrument (High-speed Railway Testing Instrument Co. Ltd, China).

Table II. Formula of rubber refining

Compounds	Amount (phr)
NR	100
Stearic acid	3
ZnO	5
Captax M	0.6
S	2.5
CBp	50

3. Result and discussion

3.1 Pyrolysis process and production distribution

Pyrolysis reaction is to heat the material to a certain temperature in anoxic environment, leading to the breaking of polymer chain. The state of materials is from solid to liquid, and/or further generate gaseous substances. The generated alkanes, if are overheated, may undergo secondary pyrolysis to generate PAHs or asphaltenes, which would affect the performance of CBp [7]. Therefore, the study of thermal history of the pyrolysis reaction is of great significance to the product properties.

Fig.4 shows the influence of pyrolysis temperature on the yield of pyrolysis products. In the experiment, the rotation frequency of the same reactor was fixed at 20Hz, and the reaction time was

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67min. In the range of 380℃ to 600℃, the yield of gas increased gradually, and the yield of pyrolytic oil decreased gradually. The yield of CBp, however, didn’t

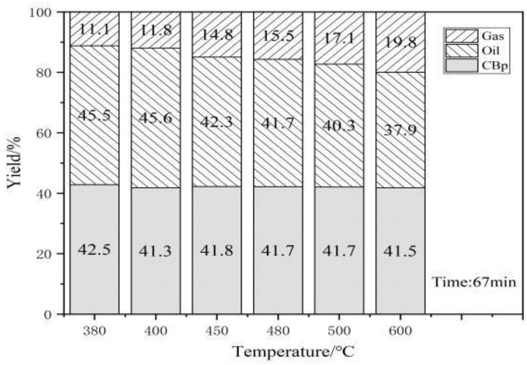

Figure 4. Yield of pyrolysis products

3.2 Granulation rate

Table III. Granulation rate and light transmittance of toluene of cbp

Pyrolysis temperature (℃)	Granulation rate (%)	Light transmittance of toluene extract(%)
380	0.8	11.3
400	1.2	22.6
450	67.2	69.6
480	69.5	68.3
500	69.1	88.4
600	75.8	92.0

The granulation rate of CBp is showed in Tab III. Generally, it is eligible that granulation rate of CBp is higher than 65%. It can be seen that the carbon black is hardly to be granulated while the pyrolysis temperature is lower than 400℃. The granulation rate is increased with the increasing of the pyrolysis temperature from 450℃ to 600℃. This is owing to the oleic materials on the carbon black. The higher the pyrolysis temperature, the less oil content on CBp. The light transmittance of toluene extract of carbon black is increasing from 380℃ to 600℃, indicating that the oleic substance is getting lower. As we discussed above, when the pyrolysis temperature is lower than 400 ℃ , the oleic substance is much higher, preventing the combinationbetween water and carbon black powder. That’s why the granulation rate is much lower under 400 ℃.

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3.3 Surface property and aggregation

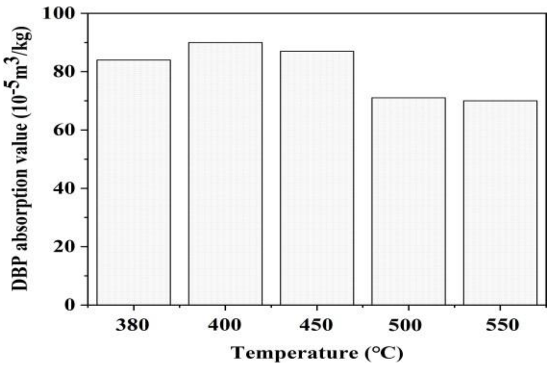

Figure 5. DBP absorption value of CBps at different temperatures

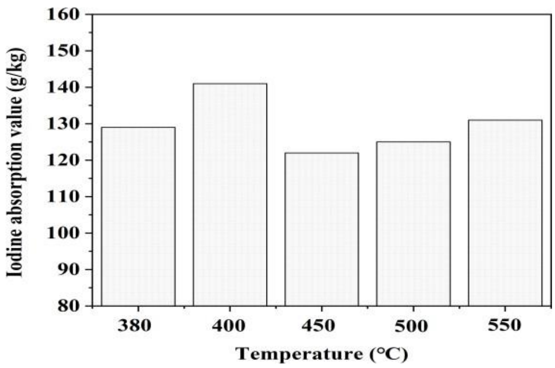

Figure 6. Iodine absorption value of CBps at different temperatures

The surface property and aggregation of CBp was analyzed from DBP absorption value, iodine absorption value, nitrogen surface area (NSA) and statistical surface area (STSA), respectively. From Fig.5, it can be observed that the DBP absorption value is over 80 from 380 ℃ to 450 ℃ and the maximum is obtained at 400 ℃, close to the commercial carbon black N660. DBP absorption value is used to characterize the degree of CBp aggregation, and the larger the value is, the larger the structure degree of carbon black aggregate is. According to the above discussion, the aggregation of CBp is affected by uncracked organic component in the pores. The organic component is much higher under low pyrolysis temperature, leading to good performance for aggregation of CBp. The aggregation structure had been broken with temperature over 500 ℃ and the DBP value is under 80 g/kg. From Fig.6, the iodine absorption value is increased via temperature above 450 ℃. Iodine absorption value reflects the specific surface area and particle size of carbon black particles, and the larger the value, the smaller the particle size of CBp. It is implied that temperature had impact to particle size of CBp over 450 ℃. The higher the temperature, the smaller the CBp.

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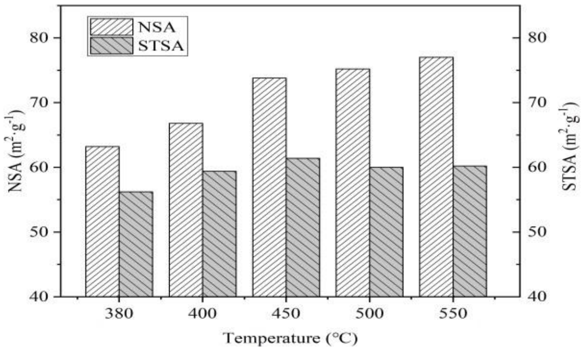

Figure 7. NSA and STSA of CBps at different temperatures

The NSA and STSA values are also showed in Fig.7. Generally speaking, NSA value is used to characterize total specific area of carbon black and STSA is for surface specific area. Considering the reinforce progress of CBp, the rubber molecular chains could hardly enter the inside pore of carbon black. The specific area can better reflect the reinforcing property of carbon black. In that case, the overall consideration of NSA and STST is more rational. It can be seen that, the total specific area is increased accompanied with temperature. It is probably contributed to the complete pyrolysis reaction under high temperature to form large total specific area. However, the surface specific area showed an upward and then downward trend. It is believed that the secondary reaction caused by high temperature produces carbonaceous sediments covering the micropores on the outer surface leading to the STSA decreased, while the inner pores are basically unaffected, so the NSA was not affected.

3.4 Ash content

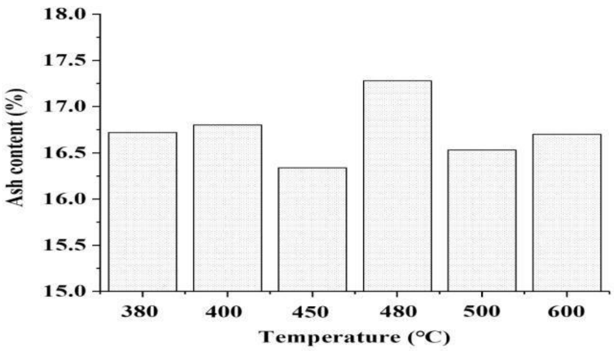

Figure 8. Ash content of CBp

Ash content is one of the most important characters of CBp. The ash content results are shown in Fig.8 The ash content of CBp is from 16.34% to 17.28% and no obviously difference among those groups. The ash in CBp mainly come from the inorganic fillers in waste tires, such as calcium carbonate, silica and so on. A small quantity of ash is from

soil on the used tires. Commonly, the ash content of commercial carbon black is less than 1%. As excessive ash would reduce the reinforcing property of CBp, the ash content should be as little as possible. It has been reported that the acid-base treatment is an efficient way to decrease the ash content of CBp [8].

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3.5 Characterization of CBps by FT-IR

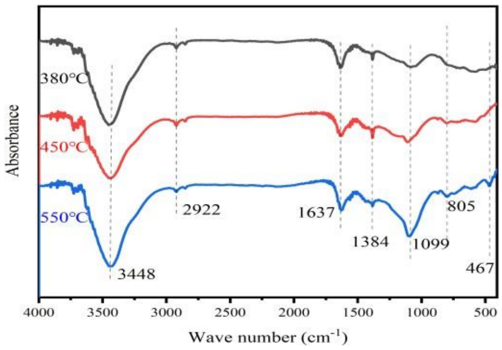

Figure 9. FT-IR spectra of CBps at different temperatures

Fig.9 shows the FT-IR analysis obtained from CBps pyrolysis at 380℃, 450℃ and 550℃. The surface groups of CBp at different pyrolysis temperatures are similar. The absorption band at 3448cm-1 is attributed to the stretching of-OH group. The bands between 2885cm-1 and 2922cm-1 attributed to the stretching of C-H in the -CH2 group. The absorption peak at 1637 cm-1 corresponds to the characteristic vibration of C=C bond in the aromatic compounds, and the peak was particularly enhanced at 550℃. It may be owing to the secondary reaction while more aromatic produced at this temperature. Meanwhile, the absorption peaks at 467 cm-1, 805 cm-1 and 1099cm-1 of CBp at 550℃ were significantly stronger than those at 380℃ and 450℃, which were attributed to the bending vibration of Si-O-Si, stretching vibration of Si-O-Si and asymmetric stretching vibration of Si-O-Si, respectively. The Si-O-Si bond is mainly derived from the silica in pyrolytic carbon black, which is covered by organic matter and not detected in CBps at low temperature pyrolysis. The organic matter on the surface of silica is volatilized when the pyrolysis temperature increased to 550℃.

3.6 Reinforce property

The reinforce property of CBp is characterized and the result was showed in Table Ⅳ. The density and hardness of CBp reinforced rubber showed no difference from 380℃ to 600℃. The tensile strength and the elongation at break are decreased with the increasing of pyrolysis temperature. Commonly, the larger the specific area is, the better reinforce property is. However, according to the NSA value in section 3.3, the specific area is larger under 600 ℃ than 380 ℃, which is inconsistent with the commonly consideration. The crack oil attached on the surface of CBp is a possible reason for this phenomenon. The CBp pyrolyzed under 600 ℃ possess larger specific area, however, it showed poor compatibility with rubber, leading to bad dispersion in rubber and self-aggregated to larger particles. The crack oil could improve the compatibility of CBp with rubber, increasing the dispersion in rubber, resulted in the good reinforce property. Unlike to granulation rate, high temperature had an adverse effect to CBp. Overall consideration, the temperature should be moderated (400 ℃ or 450 ℃) in the production progress.

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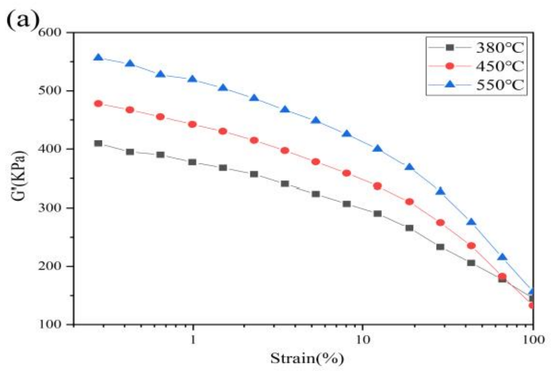
Table IV. Mechanical property of cbp

Pyrolysis temperature (℃)	Density (mg/m^3)	Hardness (degree)	Tensile strength (MPa)	Elongation at break (%)
380	1.134	59	22.64	609
400	1.134	58	21.83	584
450	1.136	59	18.62	452
480	1.133	60	17.83	455
500	1.133	60	16.79	447
600	1.136	61	15.94	380

3.7 Dynamic mechanical properties



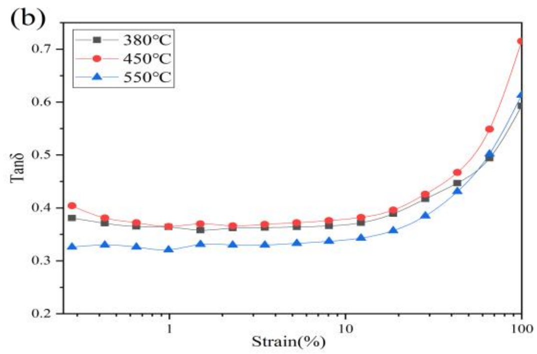


Figure 10. The strain dependence of (a) storage modulus(G′) and (b) tanδ of NR compounds filled with CBps in different temperatures

Fig.10 a shows the strain dependence of storage modulus G' of CBp filled NR rubber at different pyrolysis temperatures. At low strain, the storage modulus(G') of each sample decreases slightly with the increase of strain, but decreases obviously at high strain. The phenomenon that the storage modulus of filled rubber decreases sharply with the increase of strain is called the Payne effect [9]. The Payne effect of CBp reinforced NR compound increases with the increasing of pyrolysis temperature. Meanwhile, the force of filler-rubber network is enhanced which may lead to poor dispersion of filler in rubber, indicated that the oil on CBp surface has a positive effect on the dispersion. Fig.10b shows the strain dependence of loss factor (tanδ) of CBps. At low strain, the tanδ of 550℃ CBp is lower than the other groups. Because the network structure is not destroyed under small strain, the more developed the packing network is, the lower its tanδ value is. When the strain increases, the heat generation of the compound with poor filler dispersion increases during shear, so the tanδ value increases rapidly, and the tanδ value of CBp obtained by high temperature

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pyrolysis is larger, which also indicates that the low temperature pyrolysis carbon black has better dispersion in rubber.

4. Conclusion

The continuous pyrolysis device, rotating moving bed, which is a new type of equipment to replace the batch reactor was used to produce CBp in this paper. The influence of different pyrolysis temperature was detailed studied in this work. The productivity of CBp, pyrolytic oil and gas were obviously affected by temperature, higher temperature leading to more gas production, which would cause adverse effect to CBp. The surface property, aggregation, and reinforce property of CBp was also affected by temperature. The organic component leading to good performance for aggregation of CBp. When the pyrolysis temperature is lower than 400℃, the oleic substance causes the granulation rate decreased. The oil could improve the compatibility of CBp with rubber, increasing the dispersion in rubber, resulted in the good reinforce property. High temperature causes more groups be detected on the surface of CBp by FT-IR spectrometer. The Payne effect of CBp reinforced NR compound increases with the increasing of pyrolysis temperature.

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