Research Article

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Surface modification of nano-sized carbon black for reinforcement of rubber

<https://doi.org/10.1515/ntrev-2019-0036>

Received Feb 24, 2019; accepted Sep 23, 2019

Abstract: The standard sample IRB7# of nano-sized carbon black was reated by different methods, including washing by alcohol, toluene, water, the emulsion of toluene and water, and heating. Surface activity of the obtained nanoparticles was measured using inverse gas chromatography. The results showed that the dispersion free energy could be significantly increased after heating. The surface activity of three kinds of industrial carbon black was studied after heat treatment at different temperature. The results indicated that surface activity, iodine adsorption number and nitrogen surface area values of carbon black nanoparticles increased with the increase of temperature. However, the dibutyl phthalate adsorption value maintained nearly constant. The performance test of rubber showed that with the increasing heat treatment temperature of carbon black, 300% modulus of rubber increased before 450°C and decreased after 450°C.

Keywords: nanoparticles; carbon black (CB); surface treatment; dispersion free energy

1 Introduction

Rubber is widely used in transportation, electronics, military and other fields. However, the rubber without additives cannot meet the requirements in most cases, even after vulcanization [1–3]. The reinforcement of rubbers could

be measured by means of the tensile and tear strength, the abrasion resistance, and the modulus of the vulcanized rubber. The main aim for filler addition is to improve certain properties and reduce the price of the gross rubber. Among several fillers, nano-sized materials (carbon black, silica, clay, etc.) is especially preferable. Carbon black (CB) is the most important reinforcing agent used in the rubber industry [4]. Due to the defect of structure, impurity, hydrogen and chemical groups on the surface of CB nanoparticles, these defect points have the potential to become active sites, and some of the high energy sites plays an important role. At the same time, these active centers can interact well with rubber and improve the performance of rubber. Therefore, the addition of nano-sized CB into rubber is a process of commercial importance [5].

The reinforcement mechanism of rubber by filling CB is interesting in material science and engineering, and still a subject of much speculation [6]. According to existing reports, the better reinforcement effect on rubber is due to the nano size, narrower particle size distribution and higher surface activity of CB nanoparticles [7–9]. Among these factors, the surface activity of nanoparticles plays a significant role in reinforcing rubber in view of recent studies by Roychoudhury and De [10], Sapkota *et al.* [11] and Schröder *et al.* [12]. This can be proved by the performance test of rubber filled with graphitized CB [13]. When CB is heated in an inert atmosphere at a temperature higher than 2700°C, all the functional groups are decomposed, leading to a decreased surface activity of the graphitized CB. The reinforcement effect of graphitized CB on rubber materials decreases drastically. For example, the abrasion resistance and the modulus decrease obviously at high strain [12].

As to the surface activity of CB nanoparticles, the reinforcement effect comes from the filler-filler and filler-rubber interactions, including both chemical and physical aspects [14, 15]. In the chemical sense, it is related to the different chemical groups on the surface, such as carboxyl, quinine, phenol and lactone. While in the physical sense, the surface activity of CB is reflected by the surface free energy of CB, especially its dispersion free energy. Related researches have been reported that graphene or car-

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bon fiber were used as rubber reinforcer [15–17]. Since the cost is high and the improving effect is not obvious, they are rarely used in practical production. At present, carbon black is still an important reinforcing agent for rubber and works mainly through the modifications to enhance the reinforcing ability of carbon black.

Previously, the research on CB surface mainly focused on the improvement of the dispersion of CB nanoparticles in solvent or polymer matrix through the surface modification, making CB better applicable in practice [18, 19]. For example, the graft modification of CB can reduce the intermolecular force among CB, improve the compatibility of CB with medium, and increase the tensile strength, tear resistance and abrasion resistance of rubber and plastics [20, 21]. The oxidation of CB by oxidizing gases (air, oxygen, ozone) or solutions (hydrogen peroxide, hydrogen nitrate, perchloric acid, potassium permanganate) can form hydrophilic groups (such as hydroxyl, carboxyl, carbonyl group, etc.) on CB surface, improve the dispersion of the CB in aqueous solution, and find new application of CB in wide fields [22–25].

At present, the major methods to improve the surface activity of CB nanoparticles belong to the chemical treatment, which soaks CB with acid (e.g., H_3PO_4), alkali (e.g., KOH), hydrocarbon (e.g., C_6H_6) or even gas (e.g., ozone) for a certain period of time. The surface activity of CB could be increased by using the above four kinds of reagents. However, the long treatment time and the residual ions from the reaction will affect the subsequent applications [26–28]. Ozone treatment means to oxide CB with ozone at room temperature, and subsequently the surface free energy, the combination of polar parameters and dispersion free energy increase. However, the low efficiency of reaction requires a large amount of ozone, a long time of treatment and a high demand for investment for equipment. All these greatly impairs the economic benefit of elastomer production [29].

The surface activity of CB has strong impacts on the performance of the vulcanized rubber, e.g., the 300% modulus, wear resistance, tear performance and dynamic hysteresis, which are closely related to the current formulation design of green tire [30, 31]. Therefore, the R&D of new varieties of CB in many multinational corporations is focused on the CB surface activity. However, in the practical application of CB, the research on the influence of surface activity on rubber reinforcement is rare, especially for the actual performance of vulcanizate. Hence, to further explore the effect of the CB surface activity, we designed a series of different surface treatment methods to investigate the change of surface free energy of CB. At the same time, in the industrial applications of CB, the effect of sur-

face activity on rubber reinforcement was analyzed and discussed. The surface activity of CB was improved by heat treatment at different temperatures, and the effect on reinforcement of vulcanizate was studied.

2 Experimental

2.1 Materials and apparatus

IRB7# (standard CB), N330, N375 and N339 were purchased from Suzhou Baohua Carbon Black Co., Ltd. Insoluble sulfur (200 mesh, production number: Crystex HD OT 20) was obtained from Eastman. All other raw materials were purchased from China Carbon Black Institute (CCBI). Alcohol, toluene etc. are analytical grade from Sinopharm Chemical Reagent Co. Ltd.

The apparatus used in this study include Gas chromatograph (GC-17A, SHIMADZU Co., Ltd., Japan); Data acquisition device (CSC-100D, Peking Huibo Jingrui Co., Ltd. China); Rubber process analyzer (RPA2000, Alpha Inc., USA); Box type atmosphere furnace (JQF1400-40 Shanghai Jiugong Electrical Inc., China); Twin-roll mill for rubber (XK-152.5, Guangdong Zhanjiang Experimental Equipment Inc., China); Internal mixer (Haake Torque Rheometer with a volume of 500mL, Thermo Fisher Scientific Inc., USA); Flat vulcanizer (630 kN, Huzhou Rubber Mechanical Co., Ltd., China); Pneumatic slicer (GT-7016-AR, Gaotech Testing Instrument Co., Ltd., China) and Electronic universal material testing machine (double column desktop 2365, Instron Corporation, Illinois, USA).

2.2 Method for treating surface activity of different carbon blacks

Standard CB: The CB IRB7# was soaked by different reagents, such as water, alcohol, toluene and the emulsion of toluene and water. Afterwards, each sample was dried and heated at 280°C for 12 hours.

Industrial CB: The CB samples were heated under the protection of nitrogen at different temperatures, *i.e.* 150, 300, 450, 600, 900°C .

2.3 Properties measurement of treated-CB and CB-filled rubber

The surface free energy of CB was tested by gas chromatograph. Iodine adsorption value, dibutyl phthalate (DBP)

absorption value, nitrogen surface area (NSA) and statistical thickness surface area (STSA) were determined according to GB/T 3778-2011, which is the rubber appraisal system and setup based on the ASTM D 1765-2005.

Mooney viscosity, time of scorch and rheological property were measured by using a rubber process analyzer (RPA2000). Vulcanization of gross rubber was performed by using a flat vulcanizer. Tensile properties were tested by a universal material testing machine.

3 Data treatment methods

3.1 Calculation of surface activity [5]

The surface activity of CB can be quantitatively described by the surface free energy of CB. It can be divided into the non-polar part and the polar part, and can be expressed by a formula: $r = r_s^d + r^{sp}$, where r is the total surface free energy of CB, r^{sp} is the polar parameter of surface free energy, namely the polar parameter. r_s^d is a non-polar component of surface energy, commonly referred to the dispersion free energy.

3.2 Calculation of dispersion free energy [5, 32, 33]

1. Calculation of $-\Delta G_{CH_2}$

$$-\Delta G_{CH_2} = RT \frac{d \ln t(x)}{dx} \quad (1)$$

where, $-\Delta G_{CH_2}$ is the adsorption free energy per mole of methylene group, mJ/m^2 ; R is the gas constant, $8.314 \text{ J/(mol}\cdot\text{K)}$; T is the column temperature in the experiment, K; $t(x)$ is the modulated retain time of the alkane, min; x is the carbon number of the alkane, normally composed of 5 to 8 carbon atoms.

2. Calculation of dispersion free energy, r_s^d

$$r_s^d = \left(\frac{-\Delta G_{CH_2}}{2N_A a_{CH_2}} \right)^2 \frac{1}{r_{CH_2}} \quad (2)$$

where, r_s^d is dispersion free energy, mJ/m^2 ; $-\Delta G_{CH_2}$ is the adsorption free energy per mole of methylene group, J/mol ; N_A is the Avogadro's constant, 6.022×10^{23} ; a_{CH_2} is the area covered by a $-\text{CH}_2-$, 0.06 nm^2 ; r_{CH_2} is the surface free energy of a surface composed entirely of $-\text{CH}_2-$, 35 mJ/m^2 .

3.3 Calculation of polar parameter of surface free energy [5, 32, 33]

1. Calculation of retention volume, V_N

$$V_N = Dj(t_r - t_m)(1 - p_w/p_o) \frac{T_c}{T_f} \quad (3)$$

where, V_N is net retention volume, mL; D is volume of carrier gas, mL/min; j is the gas compressibility factor; t_r is the retention time, min; t_m is the dead-time, min; P_w is the equilibrium pressure, kPa; P_o is the pressure at the outlet of the column, kPa; T_c is the column temperature, K; T_f is the flow meter temperature, K.

where, j is given by:

$$j = \frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \times \frac{3}{2} \quad (4)$$

and P_i is the pressure at the inlet of the column, kPa; P_o is the pressure at the outlet of the column, kPa.

2. Calculation of adsorption energy, $-\Delta G$

$$-\Delta G = RT \ln \frac{CV_N}{Sg} \quad (5)$$

where, $-\Delta G$ is the minus value of adsorption energy, mJ/m^2 ; R is the gas constant, $8.314 \text{ J/(mol}\cdot\text{K)}$; T is the column temperature, K; C is 299; V_N is net retention volume, mL; S is the specific surface area of the filler, m^2/g ; g is the mass of the filler in the column, kg.

3. Calculation of the polar part of the adsorption free energy, $-\Delta\Delta G$

According to the molecular theory of the polar probe, using a series of n-alkanes to plot their molecular cross-sectional area, a linear relationship is obtained. Then, the molecular cross-sectional area of the polar probe molecule is substituted into the relational formula to obtain the theoretical non-polar adsorption free energy of the polar probe molecule. Afterward, the total free energy of the polar molecule minus the non-polar part, that is, the polar part of its adsorption free energy, expressed as $-\Delta\Delta G$.

4. Calculation of the polar parameter of surface free energy, r^{sp}

$$r^{sp} = \frac{-\Delta\Delta G}{N_A a_p} \quad (6)$$

where, r^{sp} is the polar parameter of surface free energy, mJ/m^2 ; $-\Delta\Delta G$ is the polar part of the adsorption free energy of the polar probe molecules, J/mol ; a_p is the area occupied by a probe molecule on the CB surface, nm^2 .

4 Results and discussion

4.1 Effect of treatment methods on surface properties of IRB7#

To investigate the effect of treatment methods on surface properties of IRB7#, the CB standard sample of IRB7# was treated by different methods, including washing by alcohol, toluene, water, the emulsion of toluene and water, and heating. IRB7# was assembled into a packed column to measure the surface free energy by inverse gas chromatography at different carrier gas flow rates. n-pentane was chosen as the probe molecules, and each sample was tested three times, the setting parameters and experimental results are listed in Tables 1-6.

It can be seen from Tables 1-6 that, the test results of the IRB7# treated by each method were consistent under different carrier gas flow and column front pressure, not only dispersion free energy but also the polar parameter of surface free energy, with a range of no more than 5%. The experimental results indicated that the carrier gas flow and the precolumnar pressure hardly affect the surface ac-

Table 1: Surface free energy of untreated IRB7#

Samples	1	2	3	Average	Standard error
$WD(\text{mL} \cdot \text{min}^{-1})$	25.3	17.2	23.2		
$p_i(\text{kPa})$	65	50	61		
$r_s^d(\text{mJ} \cdot \text{m}^{-2})$	87.5	86.3	87.2	87.0	1.4
$r_s^{SP}(\text{mJ} \cdot \text{m}^{-2})$	68.6	70.4	69.2	69.4	1.88

Notes: D is volume of carrier gas, mL/min; P_i is the pressure at the inlet of the column; r_s^{SP} is the polar parameter of surface free energy, mJ/m^2 ; r_s^d is dispersion free energy, mJ/m^2 .

Table 2: Surface free energy of alcohol-treated IRB7#

Samples	1	2	3	Average	Standard error
$D(\text{mL} \cdot \text{min}^{-1})$	25.5	10.9	18.2		
$p_i(\text{kPa})$	215	160	187		
$r_s^d(\text{mJ} \cdot \text{m}^{-2})$	79.5	88.9	90.2	86.2	1.95
$r_s^{SP}(\text{mJ} \cdot \text{m}^{-2})$	63.3	71	77.8	70.7	2.42

Table 3: Surface free energy of toluene-treated IRB7#

Samples	1	2	3	Average	Standard error
$D(\text{mL} \cdot \text{min}^{-1})$	25.5	11.8	30.98		
$p_i(\text{kPa})$	220	180	236		
$r_s^d(\text{mJ} \cdot \text{m}^{-2})$	89.8	96.3	104	96.7	2.37
$r_s^{SP}(\text{mJ} \cdot \text{m}^{-2})$	74.8	65.5	69.4	69.9	1.56

tivity of CB. And that the results of three parallel experiments are consistent which can verify the reliability of the experimental data.

Figure 1 shows that the dispersion free energy of the toluene-treated IRB7# is increased by 11.1% and water-treated IRB7# increased by 65.9%. However, IRB7# treated by the emulsion of water and toluene has less increase (58.0%) compared to only treated by water. It can probably

Table 4: Surface free energy of water-treated IRB7#

Samples	1	2	3	Average	Standard error
$D(\text{mL} \cdot \text{min}^{-1})$	19.6	22.1	27.1		
$p_i(\text{kPa})$	200	230	290		
$r_s^d(\text{mJ} \cdot \text{m}^{-2})$	134.5	142.1	156.3	144.3	3.69
$r_s^{SP}(\text{mJ} \cdot \text{m}^{-2})$	115.8	124.4	137.2	125.8	3.59

Table 5: Surface free energy of IRB7# treated by emulsion of toluene and water

Samples	1	2	3	Average	Standard error
$D(\text{mL} \cdot \text{min}^{-1})$	19.3	25.6	40		
$p_i(\text{kPa})$	130	170	260		
$r_s^d(\text{mJ} \cdot \text{m}^{-2})$	126.5	139.2	146.8	137.5	3.42
$r_s^{SP}(\text{mJ} \cdot \text{m}^{-2})$	83.4	102.7	92.6	92.9	3.22

Table 6: Surface free energy of heat-treated IRB7# at 280°C

Samples	1	2	3	Average	Standard error
$D(\text{mL} \cdot \text{min}^{-1})$	17.9	26.2	21.1		
$p_i(\text{kPa})$	75	110	96		
$r_s^d(\text{mJ} \cdot \text{m}^{-2})$	190.9	175.5	166.1	178.5	4.17
$r_s^{SP}(\text{mJ} \cdot \text{m}^{-2})$	95.4	101.8	96.5	97.9	1.14

Figure 1: Effect of treatment methods on dispersion free energy

Figure 2: Effect of treatment methods on polar parameter

be explained that there were still some toluene molecules left on CB surface. After heating at 280°C, the dispersion free energy is increased by 105.2%. It is attributable to a substantial reduction of surface adsorbates and the exposure of many functional groups on the surface of carbon black, and these functional groups are mainly carboxyl, phenolic hydroxyl, lactones groups and other oxygen-containing groups. In addition, there is no other impurities adsorbed on the CB surface, therefore the surface activity will not be reduced.

Figure 2 shows that polar parameter of the water-treated IRB7# increases by 81.3%. It indicates that the water-soluble adsorbates have a drastic effect on the polar part of surface activity. Polar parameter of IRB7# treated by alcohol and toluene has a minor change. It is due to the adsorbates washed away by ethanol or toluene rarely affected the active points of the surface polar parts. The dispersion free energy increased by 41.1% after IRB7# was heated at 280°C, the phenomenon is caused by the conversion of functional groups such as carboxyl group and phenolic hydroxyl group on the surface of carbon black into lactone groups with the increase of temperature, which reduced the number of functional groups and decreased of surface adsorbates.

It must be pointed out that, the sample treated by water must be dried at 125°C for 5 hours, therefore, the effect of heat treatment has to be taken into account during the drying process. To investigate the actual reason for the change of surface activity of water-treated IRB7#, the verification experiment was performed. The results are shown in Tables 7-8.

Tables 7-8 show that there is little difference in the dispersion free energy of IRB7# treated by the two methods. It can be concluded that the heat treatment is a major fac-

Table 7: Dispersion free energy of IRB7# with different surface treatments

Samples number	1	2	3	Average	Standard error
Untreated	91.5	86.3	83.2	87.0	1.4
Treated by water and after heated at 125°C for 5 hours	168.8	173.6	177.6	173.3	1.47
Only heated at 125°C for 5 hours	153.5	159.2	165.8	159.5	2.052

Table 8: Polar parameter of surface free energy of IRB7# with different surface treatments

Samples number	1	2	3	Average	Standard error
Untreated	68.6	75.4	64.2	69.4	1.88
Treated by water and after heated at 125°C for 5 hours	123.1	130.8	141.1	131.6	3.01
Only heated at 125°C for 5 hours	82.6	90	94.4	89	1.99

tor affecting the dispersion free energy during the treatment using water. As for the polar parameter, the water-treated IRB7# increases by 50% compared with untreated, indicating that the water treatment had a great influence on the polar parameter. It is probably because some water-soluble adsorbates on the surface of IRB7# were dissolved by water. As a result, more polar parts on the surface of IRB7# were exposed, leading to the great improvement of polarity parameters. However, the water-soluble adsorbates cannot be removed by heat treatment, which weakened the interaction between the polar probe molecules and the surface of the sample, thus the polarity parameters decreased [34–37].

4.2 Effect of heat treatment temperature on properties of CB

4.2.1 Effect of temperature on the surface activity of CB

The industrial CB N330, N375 and N339 have been selected to study the surface activity after heat treatment. The surface activity of the samples was measured by inverse gas chromatography. The samples were treated in vacuum and

Figure 3: Dispersion free energy of N330, N375 and N339

the temperatures were set at 150, 300, 450, 600°C. The results are shown in Figure 3.

It can be seen from Figure 3 that within a certain temperature range, the surface activity of samples increases obviously with the increase of heat treatment temperature. This may be due to the reduction of surface adsorbates and the formation of some new sites with high activity after the heat treatment. The experimental results demonstrate that the heat treatment of CB plays a positive role in the reinforcement of rubber.

4.2.2 Effects of temperature on conventional chemical properties of CB

In this experiment, the standard GB/T 3778-2011 was adopted to analyze the chemical properties of three kinds of CB (N330, N375, N339) after the heat treatment at different temperatures, 150, 300, 450, 600, 900°C. The important properties of CB were measured, such as iodine adsorption number, DBP absorption value, NSA and STSA. The experimental results are shown in Figures 4-6.

From Figures 4-6, it can be found that the variation trends of the chemical properties of three kinds of CB (N330, N375, N339) are fairly similar, and the following conclusions can be drawn:

1. Before the heating temperature of 600°C, the NSA, STSA and iodine adsorption values of samples are increased slowly with the increasing temperature, and the difference between NSA and STSA is not significant. The results shows that the surface activity of CB is increased after heat treatment, and the porosity of CB surface does not change much. But after

Figure 4: Effect of different heat treatment temperature on properties of N330

Figure 5: Effect of different heat treatment temperature on properties of N375

Figure 6: Effect of different heat treatment temperature on properties of N339

the heating temperature of 600°C, the NSA and iodine adsorption values of samples increase significantly as the temperature is further increased. However, the growth of STSA value is relatively low, thus,

the difference between NSA and STSA has been dramatically improved. It can be inferred that the adsorbates and chemical groups on the surface of CB have been desorbed or decomposed obviously, resulting in a rapid increase in the porosity of the CB surface, and this desorption also causes the surface activity of the CB increase rapidly.

2. The DBP value does not change too much at various temperatures, due to the fact that the structure of CB is quite stable and is basically not affected by the heat treatment.

4.3 Effect of CB treatment temperature on the performance of rubber

The above experimental results shows that the dispersion free energy could be significantly increased after heating. In order to investigate the reinforcing properties of CB heated at different temperatures on rubber, the heat-treated CB was filled into rubber by mixing method, and explored the different properties of CB-filled rubber, including rheological property, tensile strength and abrasion resistance, strain sweep and so on.

4.3.1 Rheological property

In the rheological experiment, we developed a new mixing technology. The positive vulcanization time (T90) and rheological property were measured using a rubber process analyzer, RPA2000. The experimental results are shown in Figure 7.

Figure 7: The rheological property of gross rubber filled in different CB

Figure 7 shows that T90 increases slightly at first, then decreases obviously with the increasing of CB heat-treatment temperature, while T90 of N375-filled and N339-filled rubber decrease slowly at 600°C. It can be recognized that the surface activity of CB is relatively low below 450°C, and the CB cannot interact well with rubber, and reduces the vulcanization rate. However, with the increase of temperature, the surface activity of CB increases, which makes a better interaction between CB and rubber, leading to an increase of vulcanization rate [34]. Meanwhile, the increase of the surface activity causes easier agglomeration and worse dispersion of CB, hindering the interaction between CB and rubber. The surface activity of CB has little effect on the minimum torque of gross rubber [38, 39].

4.3.2 Tensile strength and abrasion resistance

In the experiment of tensile strength and abrasion resistance, the static tension and wear quality tests were carried out in accordance with the national standard GB/T 3778-2011. The experimental results are shown in Figure 8.

The general trend from Figure 8 is that the 300% modulus increases first, then decreases with the increasing of heat-treatment temperature. The 300% modulus of N330-filled and N375-filled rubber increases slowly below 600°C, and then decreases rapidly above 600°C, while N339-filled rubber increases smoothly below 450°C and drops rapidly above 450°C. It can be explained that the surface activity of CB increases with the increase of temperature, which facilitates the interaction between CB and rubber. When the surface activity increases to a certain extent, CB cannot be dispersed well in rubber because of the strong interaction among CB nanoparticles, and the high surface activity of

Figure 8: 300% modulus and wear mass of vulcanized rubber filled with different CB

CB exhibits adverse effects on the performance of CB-filled rubber [38–42]. The wear mass of all the vulcanized rubber filled with CB does not change obviously in different heat-treatment temperature, that is, the surface activity of CB demonstrates little effect on the abrasion resistance of the CB-filled vulcanized rubber.

4.3.3 Comparison of strain sweep

The influence of temperature on the strain sweep behavior of CB-filled vulcanized rubber was investigated by the measurement of complex modulus at different strain, with independently developed mixing technology. The experimental results are shown in Figures 9–11.

Figures 9–11 shows the strain sweep behavior of the CB-filled vulcanized rubber proves the same trend. With the increase of heat treatment temperature, the modulus of small strain amplitude increases, while the modulus of large strain amplitude does not change obviously. This can be explained that the surface activity of CB increases along with the heat treatment temperature, leading to the high interaction between CB and rubber phase, reducing the low strain amplitudes modulus [38, 43, 44]. However, the modulus of high strain amplitudes does not change obviously. Because the performance of vulcanized rubber cannot be improved only by increasing the surface activity of carbon black in the high strain amplitude condition.

Figure 9: Strain sweep of vulcanized rubbers filled with N330 (heated at different temperatures)

Figure 10: Strain sweep of vulcanized rubbers filled with N375 (heated at different temperatures)

Figure 11: Strain sweep of vulcanized rubbers filled with N339 (heated at different temperatures)

4.3.4 Comprehensive analysis

According to the experimental results, heat treatment can be significantly improved the surface activity of CB. The increase of surface activity improves the reinforcement effect for rubber, but too much surface activity also accrues the agglomeration and hence reduces the dispersion of CB in rubber. The influence of the two aspects should be taken into consideration at the same time. Therefore, it is necessary to illustrate the 300% modulus data and complex modulus ratio together, as shown in Figure 12. The complex modulus ratio is the ratio of low strain amplitude modulus to high strain amplitude modulus.

Figure 12: The complex modulus ratio and 300% modulus of CB-filled vulcanized rubber

From Figure 12, the general trend is that the complex modulus increases with temperature. However, as for the complex modulus, the trend of three samples increase slowly below 450°C, and then decreases. It can be concluded that the increase of surface activity of CB leads to a gradual reinforcement of rubber, and does not affect the dispersion of CB in rubber below 450°C. Over 450°C, the surface activity will be higher, and begins to reduce the dispersion of CB in rubber [45].

5 Conclusions

The CB standard sample of IRB7# was treated by different methods to study the effect of treatment methods on the surface activity of CB. It is found that washing with water can greatly increase the polar parameters, but the effect on the dispersion free energy is relatively small. The surface activity of CB after washing by alcohol or toluene has little change. The heat treatment can greatly improve the dispersion free energy of CB surface, but has little effect on the polar parameters of surface free energy. The surface activity of CB, iodine adsorption number and NSA value increase with temperature, and the changes are noticeable over 600°C with DBP adsorption value unchanged. With increasing heat treatment temperature, the 300% modulus and T90 of the CB-filled rubber are increased below 450°C while decreased over 450°C. With the increasing heat treatment temperature of CB, the complex modulus is gradually decreased, and the minimum torque and the abrasion resistance of the CB-filled vulcanized rubber remain unchanged.

Acknowledgement: This research was financially supported by Minjiang Scholarship of Fujian Province (No. Min-Gaojiao [2010]-117), Central-government Guided Fund for Local Economic Development (No. 830170778), R&D Fund for Strategic Emerging Industry of Fujian Province (No. 82918001), International Cooperation Project of Fujian Science and Technology Department (No. 830170771) and Teaching and Researching Fund for Young Staff of Fujian Educational Department (No. JT180040).

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