

## 숯πον화된 뱀부차콜-키토산 혼성체가 SBR 고무의 보강에 미치는 영향

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## Reinforcement Effects of Sulfonated Bamboo Charcoal-Chitosan (sBC-CS) Hybrid for Styrene-Butadiene Rubber Latex

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**초록:** 스티렌-부타디엔 고무에 4가지 충전제(키토산, 뱀부차콜 분말, 숯πον화된 뱀부차콜, 숯πον화된 뱀부차콜-키토산 혼성체)를 사용하여 라텍스 컴파운드법으로 고무복합체를 제조하였다. 주사전자현미경과 카본블랙 분산 테스트를 통해서 균일하게 충전제가 고무 매트릭스 내에 분산되었음을 확인하였으며, 가황된 고무복합체의 인장강도, 저장 탄성률, 내마모성, 마찰 계수, 팽윤 특성, 산소 투과도를 조사하였다. 숯πον화된 뱀부차콜-키토산 혼성체가 다른 충전제보다 고무 매트릭스에 분산된 입자가 더 작고 잘 분산된 상태를 보였다. 또한 좋은 소수성 성질과 균일한 분산도로 충전제 중 가장 우수한 보강 성능을 보였다.

**Abstract:** Styrene-butadiene rubber (SBR) composites, incorporated with four kinds of fillers (chitosan, bamboo charcoal powder, sulfonated bamboo charcoal and sulfonated bamboo charcoal-chitosan hybrid) with similar filling ratio, were fabricated by a latex compounding method. Field emission scanning electron microscopy and carbon black dispersion tests were employed to confirm the uniform dispersion of filler in the matrix. The tensile strength, storage modulus, abrasion resistance, friction coefficient, swelling property, and oxygen transmission rates of the vulcanized rubber composites were investigated. The sulfonated bamboo charcoal-chitosan hybrid (sBC-CS) showed a smaller particle size and a better dispersion state compared with those of other fillers. In addition, this compound exhibited the best mechanical reinforcing performance among the four fillers with its great hydrophobic property and good dispersion rate.

**Keywords:** chitosan, sulfonation, styrene-butadiene rubber, bamboo charcoal, abrasion resistance.

### Introduction

In the 1940s, due to the discovery of sugar-carbon as a catalyst, carbon-based solid acid had attracted much interest among researches.<sup>1,2</sup> Solid acid was regarded as a promising replacement of liquid acid because it is easy to be isolated and reusable, which meets the requirements of green chemistry. Carbon based solid acids are usually produced by sulfonation method with bio-char (such as rice bran carbon), bamboo charcoal and other activated carbon, and using fuming sulfuric acid

as a sulfonation reagent.<sup>3</sup> These materials have a high concentration of  $-SO_3H$  groups and show significant catalytic performance in its sulfonation reaction.

In recent years, Li *et al.* used solid acid synthesized from bamboo charcoal to observe and its effect as a reinforcing filler for natural rubber latex.<sup>4</sup> They observed that the solid acid can be used as a sulfonating agent to get sulfonated chitosan, which has a similar structure to chitosan and bamboo charcoal. They also observed that sulfonated bamboo charcoal-chitosan hybrid (sBC-CS) could act a reinforcing agent in natural rubber. All the mechanical properties were improved after the filling process. Styrene-butadiene rubber (SBR) is the rubber material which is synthesized by styrene and butadiene monomer.<sup>5</sup> It has great abrasion resistance property and superior

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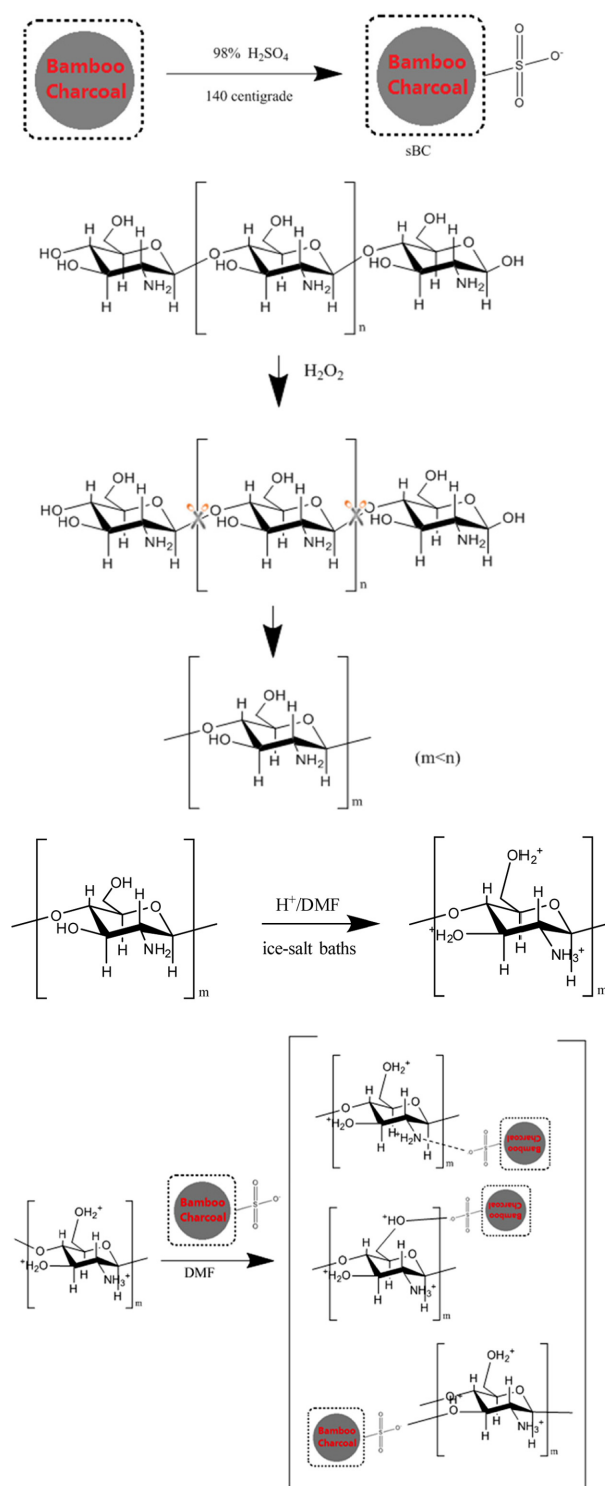
aging stability.<sup>6</sup> Due to these properties, more than half of all car tires are produced by SBR rubber.

In this research, styrene-butadiene rubber has been used as the base of matrix, chitosan (CS), bamboo charcoal (BC), sulfonated bamboo charcoal (sBC) and sulfonated bamboo charcoal-chitosan hybrid (sBC-CS) have all been used as reinforcing fillers, after the compounding and curing processes, abrasion resistance, friction, coefficient, tensile strength, storage modulus in different temperatures, oxygen transmission, and swelling test of compounds filled with different fillers were characterized.

## Experimental

**Materials.** Styrene-butadiene rubber latex 1502 (effective mass  $61 \pm 1\%$ ) was obtained from Jungwoo Company, Korea; chitosan powder (degree of substitution 0.76) was obtained from Sigma-Aldrich Company, U.S.; bamboo charcoal powder (BC) was provided by Quzhou Minxin Charcoal Company, Zhejiang, China; sulfuric acid ( $\text{H}_2\text{SO}_4$ ), extra pure (99.5%); acetic acid, extra pure (99.5%); *N,N*-dimethyl-formamide (DMF), extra pure (99.5%), were purchased from Samchun Pure Chemical Company, Korea; sodium hydroxide (NaOH), extra pure (above 95%), was purchased from Dae Jung Company, Korea; methanol, extra pure (99.5%), was purchased from Samchun Pure Chemical Company, Korea; sodium hydrogen carbonate, extra pure (above 95%), was purchased from Dae Jung Company, Korea; hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), extra pure (99.5%), was purchased from Samchun Pure Chemical Company, Korea.

**Synthesis of Sulfonated Bamboo Charcoal-Chitosan Hybrid (sBC-CS).** The mechanisms<sup>4</sup> are shown in Figure 1. First, 5 g bamboo charcoal powder was mixed with 25 mL 98 wt% sulfuric acid in a three-necked flask and then heated and stirred at 140–160 °C for 6 h, after this, the product was filtered with 4 wt% NaOH solution and distilled water several times until the value of pH was adjusted to 7. Finally the product (sBC) was dried at 60 °C in an oven for 24 h. Chitosan must be activated to conduct non-homogeneous sulfonation at first.<sup>1</sup> Chitosan (2 g) was dissolved in 1% aqueous acetic acid and 10 mL  $\text{H}_2\text{O}_2$  solution was then dropped into reaction system before being stirred for 2 h at 60 °C. Methanol of 100 mL was then added afterwards. After that, 100 mL of 4% sodium hydrogen carbonated solution was added to the reaction system to adjust the pH value to 7, followed by another 2 h of stirring. After precipitation, the product was



**Figure 1.** Mechanisms of sBC-CS.

washed with methanol and DMF and dried at room temperature, the activated chitosan powder was dispersed in DMF for subsequent sulfonation. sBC powder (5 g) and

sulfuric acid (99.5%, 1 mL), which can provide  $H^+$  as catalyst, were then added into DMF, poured slowly into the chitosan sulfonation reaction system, and stirred in an ice-salt bath (0~5 °C) for 4 h. It was then washed and filtered with a 4% NaOH solution and distilled water 3~4 times. Finally, the product was dried at room temperature for 1 week.

**Synthesis of the Composites.** With the optimization on the reaction factors in advance, a typical procedure for synthesis is provided: The fillers were dispersed in water with a ratio of 0.1 g/mL, then poured the aqueous suspension into the SBR latex which has been stabilized by DBS-Na, stirred at 25 °C for 4 h. After that step, the mixture was co-coagulated with 500 mL of calcium chloride aqueous solution ( $0.18 \times 10^{-3}$  mol/mL), then the product was dried in vacuum at 65 °C for 32 h. The composites filled with different kinds of fillers had been synthesized. The neat SBR was fabricated by directly precipitating SBR latex into calcium chloride aqueous solution and then dried in vacuum at 65 °C.

**Compound and Curing.** The composites and neat SBR were blended with other ingredients on a two-roll mill at 40 °C. The formulations for synthesis and compounding process are summarized in Table 1.

At the last step, the vulcanized composites with a thickness of 1 mm were achieved at 160 °C under a pressure of 15 MPa with a heating press machine (Auto hydraulic press type, Ocean Science). Finally, the vulcanizates were cut into specimens for mechanical characterizations.

**Characterizations.** The curing/vulcanization characteristic of compounds, including minimum torque ( $M_L$ ), maximum torque ( $M_H$ ), scorch time ( $t_{s2}$ ), and optimum cure time ( $t_{90}$ ) were determined by an RPA. Curing rate index (CRI) was employed to evaluate the cure rate of rubber compounds, which was calculated by the following eq. (1):<sup>7</sup>

$$CRI = \frac{100}{t_{90} - t_{s2}} \quad (1)$$

The morphology of the samples after abrasion are coated with gold to avoid electrostatic changing and poor image resolution, and then observed with a field emission scanning electron microscopy by an energy dispersion X-ray analyzer.

The dispersion rate analysis was performed by U-CAN UD-3500 C.B. dispersion tester (U-CAN Dynatex Inc.).

The static precipitation test was test with pure water according to ASTM D91-02.

Tensile strength was performed on a Tinius Olsen H5KT-0401 testing machine at a speed of 500 mm min<sup>-1</sup> according to ASTM D412 with the average of three measurements. Specimens on standard dumb-bell shape were cut from the vulcanizate sheet with dimensions 25 mm×6 mm×1 mm (length×width×thickness).

Strain sweep was perform with an RPA. It was carried at 60 and 100 °C with an 1.67 Hz frequency. Shear storage modulus was recorded at each strain according the ASTM D 6204-97. Shore A hardness of the specimens was obtained with Shore Durometer Type A according to ASTM D22-40.

Density of samples had been measured by density test machine according to ASTM D792-13.

Friction factor test was performed at room temperature by friction test machine like Figure 2.

Abrasion resistance test was performed by Taber Abrasion tester 5135 with a rotate speed of 80 r/min according to ASTM D1044. The working mechanism of the abrasion tester is shown in Figure 3.

The OTR (oxygen transmission rate) of the vulcanizates is measured with an oxygen permeation analyzer (Illinois Instruments Inc., Model 8001, IL) following ASTM D39-85. The

**Table 1. Formulations of Test Sample Compounds**

	Compositions									
	SBR	Stearic acid	CBS <sup>a</sup>	DD <sup>b</sup>	Zinc oxide	Chitosan	BC	sBC	sBC-CS	Sulfur
	(phr <sup>c</sup> )									
Neat	100	2	2	0.5	3	0	0	0	0	1.75
SBR/CS	100	2	2	0.5	3	5	0	0	0	1.75
SBR/BC	100	2	2	0.5	3	0	5	0	0	1.75
SBR/sBC	100	2	2	0.5	3	0	0	5	0	1.75
SBR/sBC-CS	100	2	2	0.5	3	0	0	0	5	1.75

<sup>a</sup>N-Cyclohexyl-2-benzothiazole-sulfonamide. <sup>b</sup>2,2-Dibenzothiazolyl disulfide. <sup>c</sup>phr, part per hundreds of rubber.

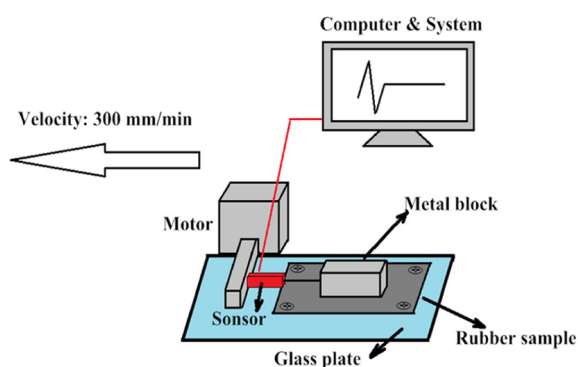


Figure 2. Working mechanism of friction coefficient tester.

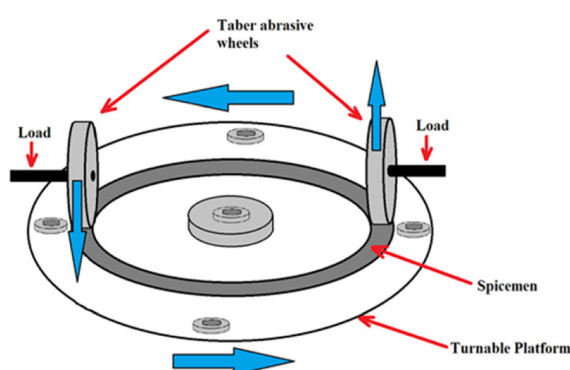


Figure 3. Working mechanism of abrasion resistance tester.

mechanism is shown in Figure 4.<sup>8</sup>

Swelling tests were carried out in toluene for 1, 3, 6, 12 and 24 h according to ASTM D71-79.

## Results and Discussion

Curing test results of SBR compounds with additives were displayed in Table 2. The torque values of all the samples had been increased, due to the strength of fillers, which strongly restricted the deformation and consequently increased the mechanical properties of SBR composites. The curing rate

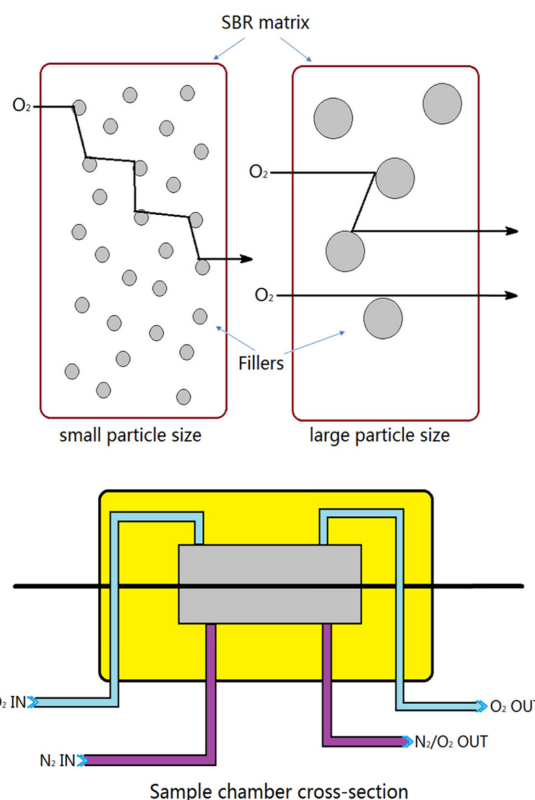


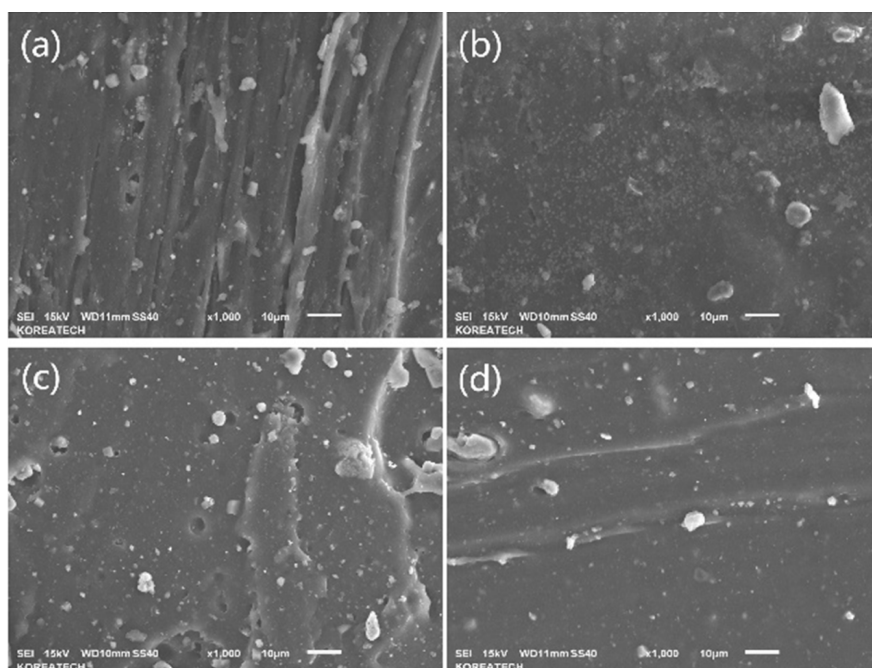
Figure 4. Working mechanism of OTR tester.

index (CRI) was applied to indicate the vulcanization rate. The CRI values of sBC-CS-SBR were decreased because when SBR compounded with sBC-CS, the filler aggregation affected chain mobility,<sup>9</sup> which will reduce the vulcanization rate.

The incorporation of sBC-CS in SBR matrix reduced the torque value, due to chitosan, which worked like a mat in the middle of sBC and SBR. The  $t_{s2}$  and  $t_{90}$  of fillers-SBR all increased, because after the reaction of sulfonated with chitosan, the filler's size would be larger than before, which also affects polymer chain mobility, and reduce the curing rate, so it need longer period to finish the vulcanization process. The curing difference of sBC and sBC-CS was also shown in this

Table 2. Curing Characteristic Results of Neat SBR Compound, BC-SBR Compound, CS-SBR Compound, sBC-SBR Compound and sBC-CS-SBR Compound

	Maximum torque, $M_H$ (dNm)	Minimum torque, $M_L$ (dNm)	$\Delta M$ (dNm)	Scorch time, $t_{s2}$ (min)	Cure time, $t_{90}$ (min)	Cure rate index (CRI min <sup>-1</sup> )
Neat	6.4	0.5	5.9	6.71	13.05	15.77
BC	10.2	0.8	9.4	8.51	15.20	14.95
CS	8.3	0.9	7.4	8.12	13.27	14.04
sBC	10.4	0.9	9.5	9.10	16.43	13.64
sBC-CS	10.6	0.8	9.8	9.4	16.9	13.33



**Figure 5.** FE-SEM micrographs of (a) compound filled with CS; (b) compound filled with BC; (c) compound filled with sBC; (d) compound filled with sBC-CS.

table. It can be seen the  $\Delta M$  values of sBC-CS are larger than sBC at the similar filling ratio, and the CRI value of sBC-CS is less than sBC.<sup>10</sup> The possible reason is the microstructure of sBC-CS is more compact than sBC which may get better effect than other fillers. (As dispersion results showed), and it will cause higher  $\Delta M$  value and lower CRI value of sBC-CS.

H. Ismail *et al.*<sup>11</sup> indicated that the interaction between organic filler groups (-OH or -NH<sub>2</sub>) and rubber additives would be the reason for the cure enhancement and tensile strength reinforcement. However, until now, there is no appropriate explanation for this result.

From the results of vulcanization studies, it can be concluded that sBC-CS not only acted as reinforcing filler, also behaved as effective vulcanizing agent for SBR compound.

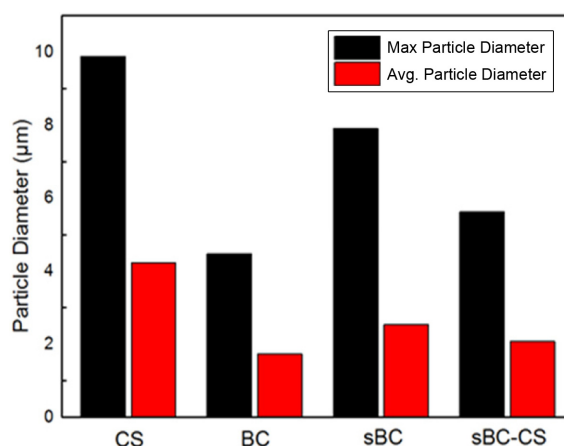
FE-SEM micrographs of (a) CS filled compound; (b) BC filled compound; (c) sBC filled compound; (d) sBC-CS filled compound are displayed in Figure 5.

From Figure 5(a) to 5(d), It can be observed the dispersion states of fillers are compared by the sample surface after abrasion test on a FE-SEM. It is apparent that the CS had destroyed the matrix of SBR, after abrasion test, the surface of sample looks so rougher than others. And in Figure 5(b), (c) and (d), it can be observed the surface of samples is smoother than the sample in Figure 5(a), which means these three fillers may

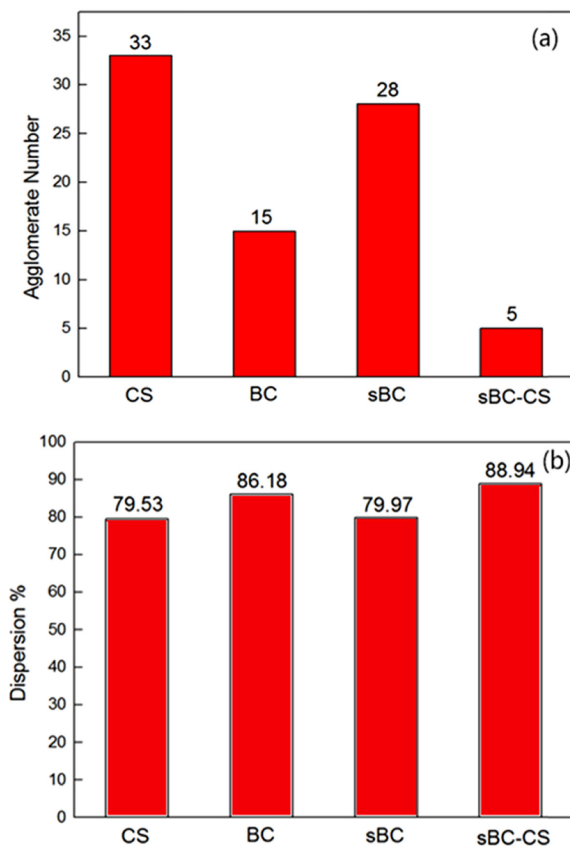
have better reinforcement effect than pure CS,<sup>12</sup> BC and sBC-CS have better dispersion states than CS and sBC when filled with SBR latex.

Figure 6 and Figure 7 show the size data of all fillers in this research. The BC powder has the smallest size and second lowest agglomeration. The particle diameter of sBC-CS is the second smallest.

It also can be found that the agglomeration effect in sBC-SBR is more obvious than in sBC-CS-SBR. The possible rea-



**Figure 6.** Max and avg. particle diameter of fillers in composites.

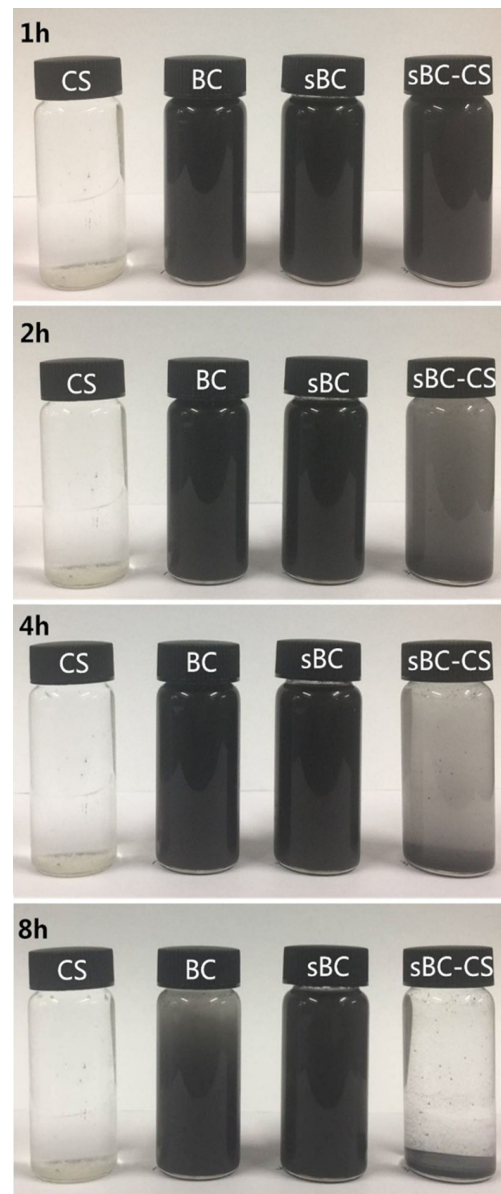


**Figure 7.** Agglomerate number (a); dispersion % (b) of fillers in composites.

son is sBC molecule has more protons on its surface than sBC-CS, they will strengthen the electrostatic attraction between the molecules. But as sBC-CS, protons were replaced by chitosan which has a large molecule structure. It can cause steric effect and reduce agglomeration when compounded with SBR rubber latex.<sup>13</sup>

The hydrophilic properties of fillers are demonstrated by the static precipitation experiment. As can be observed in Figure 8, BC and sBC suspension exhibited very stable in water dispersion and no precipitation can be observed until 4 h, but CS was the first to start precipitating within 1 h, the reason of this phenomenon is due to the hydrophobicity of chitosan powder, which cannot make this filler stable in the aqueous phase.<sup>14</sup> Because of the reason above, the sBC-CS filler also started precipitating during 2 h.

The possible reason is sBC-CS also has the structure of chitosan after sulfonation reaction, so there are some hydrophobic groups on its surface. But as BC and sBC, there are many hydrophilic functional groups on their surface,<sup>15</sup> which will exhibit stronger water-affinity. And after 8 h, BC



**Figure 8.** Static precipitation of CS, BC, sBC, and sBC-CS.

had started precipitating, but sBC still keep very stable state in water medium. This is because after sulfonation by sulfuric acid which also can be considered as acid treatment, there will be more hydrophilic functional groups on sBC's surface after sulfonation reaction. From the static precipitation experiments, it can be observed that sBC has significant hydrophilic property but sBC-CS has hydrophobic property. The greater hydrophobic property, the filler will get better dispersion effect when mixed with rubber material, and the compound will have better tensile strength.<sup>16</sup>



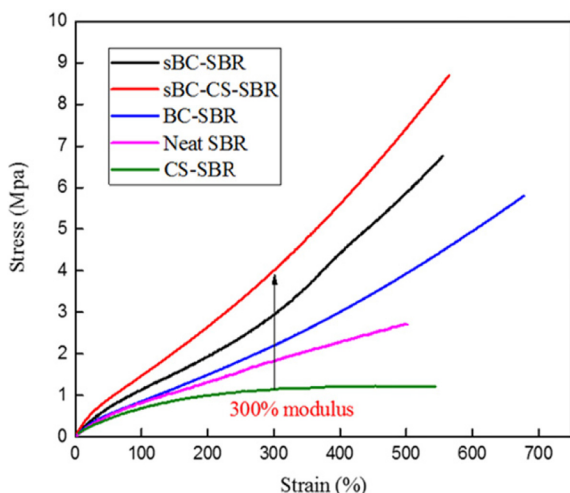
The dispersion test samples and the samples of static precipitation test are different. The dispersion test was measured by the U-CAN UD-3500 C.B. dispersion tester.

This machine was used to take pictures of samples which are dried on test papers and analyzed by the computer software. But in static precipitation test, we just took pictures of the fillers which were dispersed into pure contradictory. And when the fillers filled into rubber composites, they are not only dispersed in water phase, DBS-Na is also added as a stabilizer. After the step of desiccation, the stabilizer will not work at all, and then fillers will show the difference due to the different hydrophilicity at the step of compounding.

When the filler shows obviously hydrophobicity, it cannot get good dispersion effect in organic phase (rubber), and it will reduce the reinforcement effect. But if the filler showed hydrophobicity, it will disperse well in rubber matrix, which could improve the tensile strength and other mechanical properties of rubber material.

So sBC-CS can make better reinforcing effect in this research.

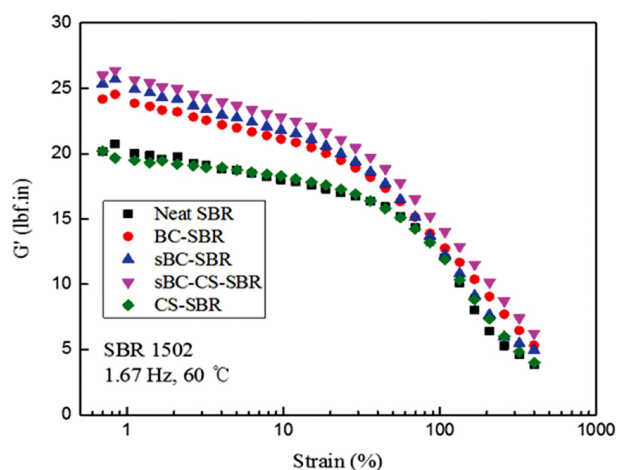
Figure 9 shows the comparison of stress-strain curves of compounds. From these curves, It can be observed BC, sBC and sBC-CS had increased modulus and tensile strength compared to neat SBR, especially at the strain value of 300%, the values on the curves prove that these fillers had improved the tensile strength of SBR rubber after filling process, and the effect of sBC-CS is the best, but the compound filled with CS got the worst tensile strength result. The reason for this result is that BC, sBC and sBC-CS have carbon-structure, it can reinforce rubber like carbon. And chitosan structure in sBC-CS



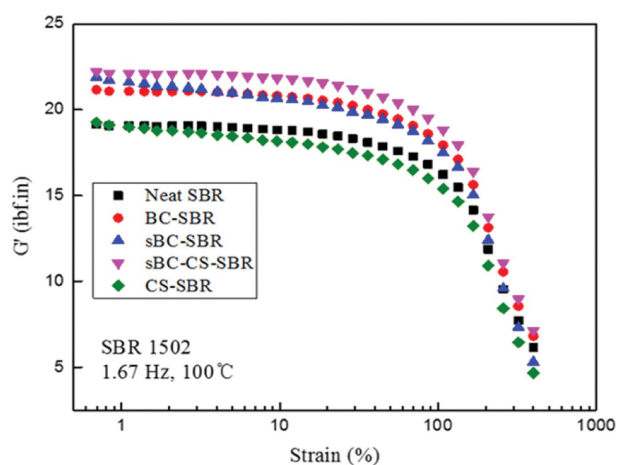
**Figure 9.** Tensile strength test results of test sample compounds.

molecule has many functional groups on its surface like -OH, -NH<sub>2</sub>, they will produce more hydrogen bonds between sBC and vulcanizing agent sulfur which provide single sulfur bonds for crosslinking.<sup>17</sup> It could make better combination with SBR latex. That's the possible reason that the compound filled with sBC-CS has the best tensile strength reinforcement effect.

Figure 10 and Figure 11 displayed the effect of temperature on the variation of storage modulus with strain (or Payne effect<sup>18</sup>) at the constant pressure of 15 MPa for SBR/ fillers composites with 5 phr of fillers. It can be observed that the slope of the storage modulus decreased with the increase of temperature from 60 to 100 °C. The possible reason for this phenomenon is the curing time decreased with the increase of temperature. The higher curing temperature, the shorter curing time. Most of the rubber chains are in melting state when in curing process. It will facilitate the contact with fillers. So at



**Figure 10.** Strain sweep results of test sample compounds at 60 °C.



**Figure 11.** Strain sweep results of test sample compounds at 100 °C.

that state, the curing process will become faster when filled with fillers, and it will reduce the time for filler aggregation, and cause more uniform dispersion effect.

But the initial storage modulus of compounds also decreased with the increase of test temperature. It is due to the high temperature will increase the molecule thermal motion at the beginning of curing process. It can increase the probability of fillers contact, which may lead to the aggregation effect of fillers, and cause worse dispersion state. The worse dispersion state, the lower storage modulus. Thus, the initial storage modulus of compounds decreased.

Figure 12 shows the results of hardness test, from the figure, it can be observed that the hardness value of compounds was increased after filling process. The reason of this result may be the fillers themselves have high hardness value,<sup>19</sup> when they dispersed into rubber matrix, the matrix had become a whole uniform state, so the hardness value had been increased.

The compound which filled with chitosan got the large hardness value, this is because when chitosan powder filled into rubber matrix, it got the most agglomeration which make filler size larger than before, it just looks like blocks, and it also make the matrix ununiformed, so the hardness value of blend filled with chitosan is the largest. But hardness data is just a part of mechanical properties of rubber material, it also need other test measurements to prove the fillers can make reinforcement or not.

The density results of samples have been shown in Figure 13. It can be observed compare to the neat SBR, the densities of other compounds which filled with fillers are larger, because the filling process can make SBR rubber matrix more compact

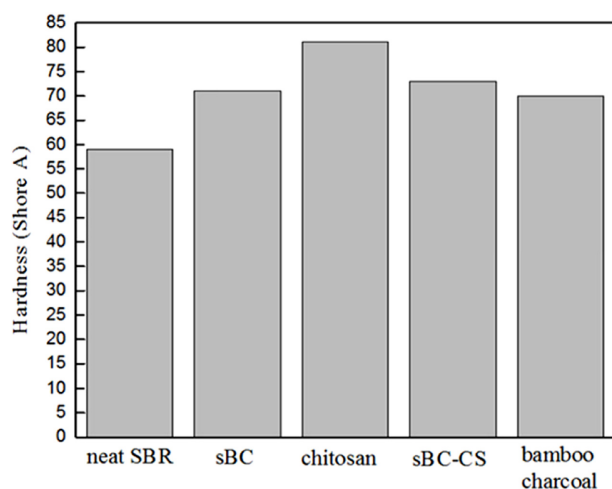


Figure 12. Hardness test results of test sample compounds.

due to the contact between the fillers and rubber molecules, so the densities are also larger than neat SBR.

The results of friction test are shown in Figure 14. It can be observed all the samples friction coefficient (static friction coefficient and dynamic friction coefficient) had been reduced comparing to the neat SBR sample. And the friction coefficient of sBC-CS-SBR is the lowest among all samples. Because filling process caused higher hardness property and compacter structure which made compound's surface relatively smoother than other compounds. The less friction, the more abrasion resistance life.

As for abrasion resistance, it is a critical factor to the service lifetime and safety for tires or conveyor belts. It doesn't only rely on the roughness and friction factor, but also depends on hardness and density of rubber samples. From the Figure 15, it can be observed the mass loss decreased after filling process,

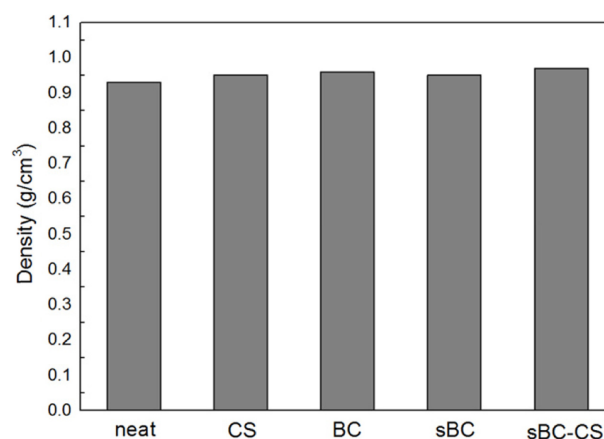


Figure 13. Density results of test sample compounds.

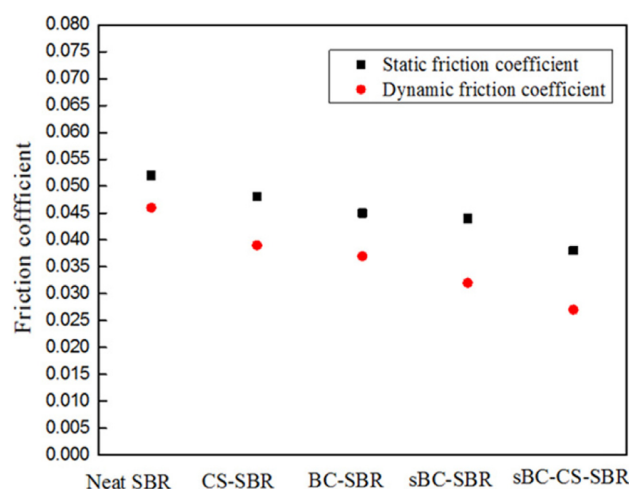


Figure 14. Friction test results of test sample compounds.

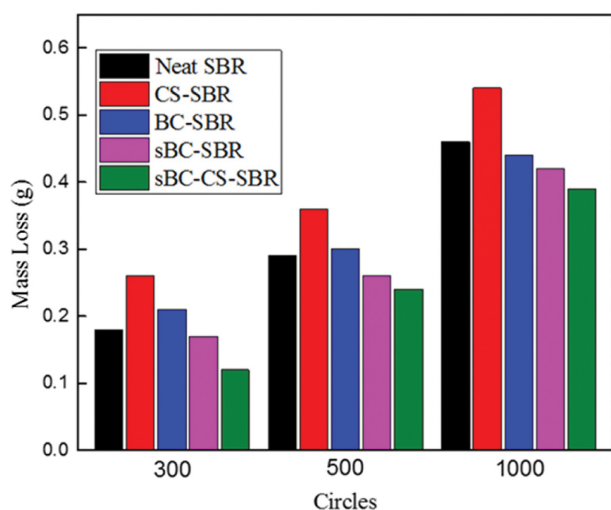


which means these compounds' properties of abrasion were improved.

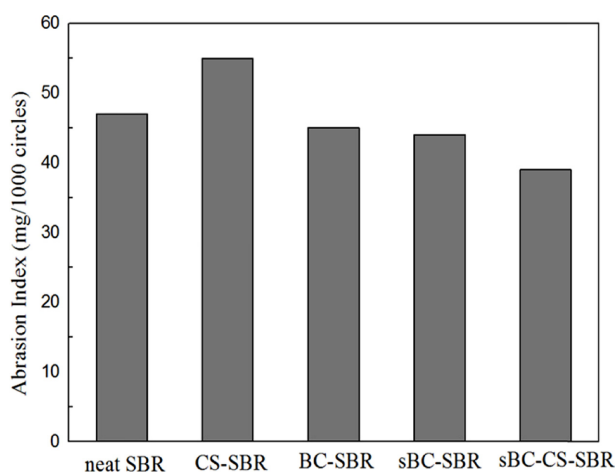
The abrasion index of samples is shown in Figure 16. Taber abrasion index ( $I$ ) indicates the rate of abrasion, and it is calculated by measuring the loss of mass (in milligrams) per thousand cycles of abrasion. The lower the abrasion index, the better the abrasion resistance, and the longer using life. The abrasion index is calculated using the following eq. (2):<sup>20</sup>

$$I = \frac{(A-B) \times 1000}{C} \quad (2)$$

Where " $I$ " means abrasion index, " $A$ " means mass of samples before abrasion test, " $B$ " means mass of samples after abrasion test, " $C$ " means number of test cycles. The obtained



**Figure 15.** Abrasion resistance test results of test sample compounds.



**Figure 16.** Abrasion index of test sample compounds.

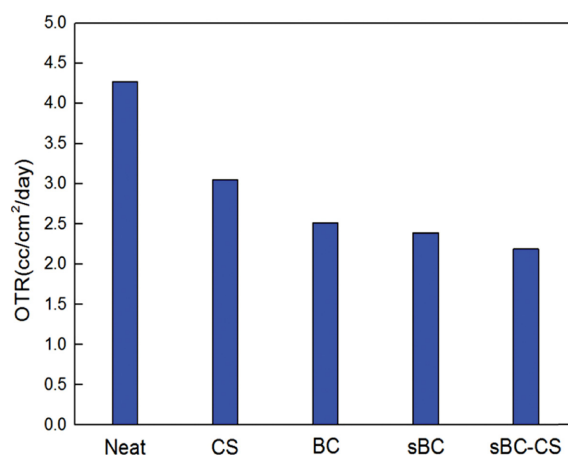
data of abrasion index further shows the sBC-CS exhibited the best abrasion resistance. This is because the sBC-CS can improve rubber sample's hardness. The carbon structure of sBC-CS will make dislocation effect in SBR compound. It can improve the strength of compound but also reduce the bounce/rebound property. And chitosan structure in sBC-CS molecule also has many functional groups on its surface, they will produce more covalent bonds with SBR rubber molecules. It can make better combination with SBR latex. And chitosan is also a solid lubricant, which can enhance abrasion resistance of SBR. But as pure chitosan, it cannot reinforce rubber by directly blending, so it also cannot improve abrasion resistance property of compounds so much.

Oxygen gas-barrier properties of the samples are shown in Figure 17. It could be seen that fillers significantly decreased the oxygen permeability due to the formation of tortuous path, which caused by well dispersed fillers in the SBR matrix. Generally, barrier performance of a polymer is strongly dependent on the morphological structure of the films. The addition of filler can typically increase the barrier property if the filler had a good compatibility with the polymer matrix. The OTR value of sBC-CS decreased to 2.19, which is the lowest among the samples.

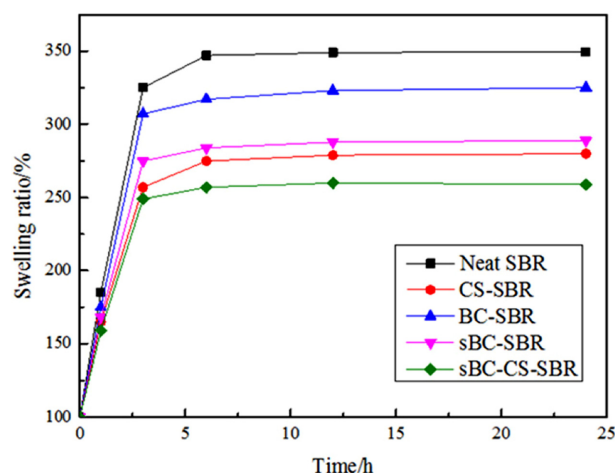
Figure 18 shows the swelling ratio of fillers/SBR vulcanizates in toluene solvent, the swelling ratio is calculated using the following eq. (3):<sup>21</sup>

$$\text{Swelling ratio}\% = \frac{w_2 - w_1 / \rho_s}{w_1 / \rho_r} \times 100\% \quad (3)$$

Where  $w_1$  is the original weight of specimens and  $w_2$  is the weight of specimens after swelling,  $\rho_r$  is the density of rubber



**Figure 17.** OTR test results of test sample compounds.



**Figure 18.** Swelling ratio test results of test sample compounds.

( $\rho_{\text{SBR}}=0.933 \text{ g/cm}^3$ ), and  $\rho_s$  is the density of solvent ( $\rho_{\text{toluene}}=0.867 \text{ g/cm}^3$ ).

It can be seen that the swelling ratio increased very fast at the early 6 h and then changed little from 6 to 24 h, indicating the adsorption saturated. The swelling ratio of neat SBR was 351.5%. When BC incorporated, the swelling ratio decreased to 327.5%, not obviously. This may be attributed to the porous structure of BC surface, which can provide more adsorption sites. sBC-SBR and sBC-CS-SBR vulcanizates exhibited much lower swelling ratio compared with BC-SBR vulcanizates, indicating the higher crosslinking density values, and it also means sBC-CS has great hydrophobic property, it can improve dispersion effect of filler when mixed with rubber material, and it also can improve tensile strength of compounds.

## Conclusions

Sulfonated bamboo charcoal-chitosan (sBC-CS) hybrid was synthesized by sulfonation reaction method, then compounded with SBR rubber latex. The results of curing characteristic shows the value of sBC-CS-SBR compound's  $\Delta M$  is the largest in this test, and the value of cure rate for sBC-CS-SBR compound is least. The data means the sBC-CS filler has superior reinforcement effect of increasing stiffness and reducing the vulcanization rate.

FE-SEM pictures show the state of compounds, it can be found CS cannot make reinforcement in SBR matrix, and dispersion rate test showed the average diameter size, dispersion and agglomeration of fillers in compounds. From the results, it can be found the ave. diameter size of sBC-CS

is smaller than sBC, and the agglomeration effect is less than sBC, the dispersion rate is superior to sBC when filled with SBR matrix. From the results of static precipitation test, it can be seen sBC-CS has hydrophobic property which can improve strength of rubber materials.<sup>22</sup>

The results of tensile strength, strain sweep, and hardness test show sBC-CS can improve the mechanical properties of SBR rubber, and the results of density, OTR and swelling test show sBC-CS can make the SBR matrix more compact than neat compound.

The possible reasons are: first, sBC-CS has the structure of BC, which has a large special surface with some functional groups like -OH, it can cause more adsorption effect of chitosan molecule and make the hybrid state more stable. Second, it is also a kind of carbon, and almost carbon with small particle size can make reinforcement in rubber materials as fillers. Third, sBC grafts with chitosan, which has obviously hydrophobic property by sulfonation reaction. In this way, it also exists hydrophobic groups in sBC-CS. Hydrophobic groups will cause better dispersion effect in non-polar organic phase (SBR rubber). And after grafting with chitosan, the structure of chitosan molecule will replace the original proton, and achieve steric effect, which could reduce filler aggregation.

In addition, it could be found from the results of friction factor and abrasion resistance test that sBC-CS will reinforce the abrasion resistance property and reduce the friction factor of SBR rubber, which is very useful for SBR rubber industry. Above all, the sBC-CS will become a potential filler of rubber material in the future.

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