술폰화된 뱀부차콜-키토산 혼성체의 제조와 천연고무 강화에의 응용

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(2016년 6월 1일 접수, 2016년 7월 6일 수정, 2016년 7월 9일 채택)

Preparation of Sulfonated Bamboo Charcoal-Chitosan (sBC-CS) Hybrid and Its Application in the Reinforcement of Natural Rubber

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(Received June 1, 2016; Revised July 6, 2016; Accepted July 9, 2016)

초록: 술폰화된 뱀부차콜-키토산(sulfonated bamboo charcol-chitosan, sBC-CS) 혼성체가 천연고무 보강을 위한 바이오고분자를 개발하기 위하여 적용되었다. 공중합은 키토산과 술폰화 반응 방법에 의해 술폰화된 뱀부차콜과 함께 수행되었다. 얻어진 sBC-CS는 FTIR, X-ray 회절, 분산속도 분석, field-emission electron microscopy 및 열무게 분석법에 의하여 분석되었다. 순수한 키토산과 비교하여, sBC-CS의 더 좋은 열안정성이 관찰되었다. 또한 sBC-CS 혼성체로 보강된 천연고무 복합체가 제조되었고, 황이 가교제로 사용되었다. 가황된 복합체의 기계적 물성이 측정되었는데, 순수한 키토산으로 충전된 천연고무 복합체와 비교할 때 sC-CS로 보강된 천연고무 복합체가 개선된 기계적 물성을 보여서, 이 물질이 중요한 고무 보강재임을 나타내었다.

Abstract: A sulfonated bamboo charcoal-chitosan (sBC-CS) hybrid was applied to develop a biopolymer for natural rubber reinforcements. The copolymerization was conducted with chitosan (CS) and sulfonated bamboo charcoal by a sulfonation reaction method. The obtained sBC-CS was characterized by FTIR, X-ray diffraction, dispersion rate analysis, field-emission electron microscopy, and thermal gravimetric analysis. In comparison to pure chitosan, a greater thermal stability of sBC-CS was observed. In addition, sulfonated bamboo charcoal-chitosan (sBC-CS) hybrid reinforced natural rubber composites were produced, and sulfur was used as a vulcanizing agent. Their vulcanizing and mechanical properties were characterized. Comparing to the pure chitosan filled natural rubber composites, the sBC-CS reinforced natural rubber composites showed improved mechanical properties, indicating the this material's potential application for rubber reinforcements.

Keywords: chitosan, sulfonation, natural rubber, bamboo charcoal, reinforcement.

Introduction

Chitosan is a macromolecule amylose abundant in the nature. It has excellent biological compatibility with organisms and various biological activities. Thus chitosan has broad application prospects in food, medicine, chemical industry, and agriculture and becomes attractive in research area in recent years.[1] And chitosan modified with sulfuric acid by sulfonation reaction, the product sulfonated chitosan can provide better anti-bacterial abilities and disinfection properties.[2]

As a replacement for liquid acids, carbon-based solid acids (CBSA) were considered as promising catalysts since the discovery of sugar catalyst.[3] These materials were usually prepared through a carbonization – sulfonation method with biomass such as sucrose, glucose, starch, cellulose, bamboo or corn straw as carbon precursor and concentrated or fuming sulfuric acid as a sulfonation reagent. Such catalysts incorporated high amounts of single bond -SO$_3$H and showed good catalytic performance in esterification, carbon-based solid acid catalyst has many advantages.[4] It is insoluble in common organic sol-

vents, causes low corrosion, and shows environmental acceptability. Also the products could be easily separated from the reaction mixture and the catalyst is recoverable without decreasing its activity.[5] Therefore, it can be successfully used in replacement of sulfuric acid as catalyst. And the sulfonated carbon-based solid acid synthesis by bamboo charcoal which also has varieties of application because of the porous structure and various functional groups on its surface.[6] Because of the carbon-based, sulfonated bamboo charcoal (sBC) also has lager specific surface area which can improve its adsorption capacity of molecules.[7]

And natural rubber is a natural polymer with prominent mechanical properties which is widely applied in auto parts electronic products, aerospace, medical products and other fields.[8] In this research, sulfonated bamboo charcoal-chitosan hybrid (sBC-CS) was synthesized with chitosan (CS) and carbon-based solid acid by sulfonation. It was filled into natural rubber latex as a filler material. The properties of the blends were determined by various methods in order to finding a new material which both have the mechanical strength of natural rubber and the anti-bacterial properties of sulfonated chitosan for applying in the future.

Experimental

Materials. Natural rubber latex (effective mass 61±1%) was obtained from Jungwoo company, Korea; Chitosan (degree of substitution 0.76) was obtained from Sigma-Aldrich company, the U.S.; bamboo charcoal (BC) was provided by Quzhou Minxin charcoal company, Zhejiang, China; sulfuric acid (H_2SO_4), extra pure, 99.5%; acetic acid, extra pure, 99.5%; *N,N*-dimethylformamide (DMF), extra pure, 99.5%, was 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 (H_2O_2), extra pure, 99.5%, was purchased from Samchun pure chemical company, Korea.

Synthesis of Sulfonated Bamboo Charcoal (sBC). A typical process as shown in Figure 1, 5 g of bamboo charcoal was mixed with 25 mL H_2SO_4 in a flask. The mixture was heated and stirred at 140 °C for 6 h, and then the reaction product was filtered and washed with 4% NaOH solution and distilled water for 4 times to remove the unreacted H_2SO_4 until the
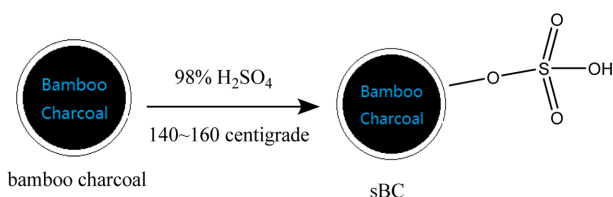
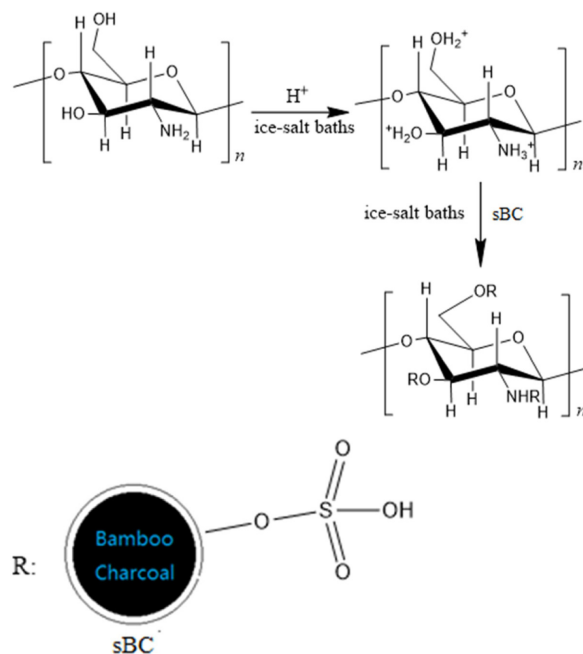**Figure 1.** Mechanism of synthesis of sBC.

value of pH was adjusted to 7. Finally the product was dried at 60 °C for 24 h. Synthesis of sBC is shown in Figure 1.

Synthesis of Low Molecular Weight Chitosan. Chitosan solution of 3 wt% was prepared by dissolving the chitosan powder into distilled water containing 2 wt% acetic acid. Then the solution was added into 5 wt% hydrogen peroxide solution. Stirred at 60 °C for 4 h, then sodium hydroxide solution was added into the reaction product till the value of pH was adjusted to 7. The product was poured into ethanol to precipitate, then washed with ethanol for 4 times, the product was dried in vacuum at room temperature for 1 week.[9]

Synthesis of Sulfonated Bamboo Charcoal-chitosan (sBC-CS) Hybrids. As shown in Figure 2, low molecular weight chitosan had to be activated to conduct the non-homogeneous sulfation.[10] Chitosan (2 g) was dissolved in 1% aqueous acetic acid and 100 mL of methanol was added afterwards. Subsequently, 100 mL of 4% sodium hydrogen carbonated dissolved in water was given to the solution

Figure 2. Mechanism of synthesis of sBC-CS.

Table 1. Formulations of Test Sample Compounds

				Compositions				
	NR (phr[b])	Strearic acid (phr)	DD[a] (phr)	Zinc oxide (phr)	Chitosan (phr)	sBC (phr)	sBC-CS (phr)	Sulfur (phr)
Neat	100	2	0.5	5	0	0	0	2
NR/CS$_5$	100	2	0.5	5	5	0	0	2
NR/SBC$_5$	100	2	0.5	5	0	5	0	2
NR/SBC-CS$_5$	100	2	0.5	5	0	0	5	2

[a]2,2-Dibenzothiazolyl disulfide. [b]phr; part per hundreds of rubber.

followed by another 2 h of stirring. After washing with methanol and DMF, the activated chitosan was dispersed in 50 mL DMF for subsequent sulfonation. Then 5 g sBC and 1 mL sulfuric acid was added into DMF and poured slowly into the chitosan sulfonation reaction system, stirred at 0~5 °C for 4 h. Washed and filtered with 4% NaOH solution and distilled water for 3~4 times. Finally the product was dried at room temperature for 1 week.

Compounding and Curing. sBC-CS and NR latex were mixed drying, compounded with other additives as shown in Table 1 on a two-roll mill at 25 °C. The compounded products were cured at the temperature of 160 °C under a pressure of 10 MPa in a heating press (auto hydraulic press type, Ocean Science) for the optimum curing, determined by a moving die rheometer (MDR 2020, Myung Ji Tech). The vulcanizates had a thickness of 1 mm, and then were cut for the properties test according to ASTM standards.[11]

Characterization

Curing Properties. The curing characteristics for different vulcanizates, expressed in terms of scorch time (t_{s2}), optimum cure time (t_{90}), minimum torque (M_L), and maximum torque (M_H) were obtained from the rheographs determined with the rheometer. Curing rate index (CRI) was calculated for the evaluation of the cure rate of rubber compounds according to the following eq.[12]

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

Fourier Transform Infrared Analysis. Fourier transform infrared (FTIR) analysis of the filling materials was performed on a thin film of about 200-300 μm with Perkin Elmer Spectrum 100®. Samples were scanned in the wave range between 650 and 4000 cm^{-1} with a resolution of 4 cm^{-1}.

Dispersion Rate Analysis. Dispersion rate analysis was performed by U-CAN UD-3500 C.B. dispersion tester.

X-Ray Diffraction. X-ray diffraction (XRD) was performed at 25 °C with Empyrean (manufactured by PANalytical) X-ray diffractometer with a Cu target, operated at 40 kV and 30 mA. X-ray diffraction data were obtained from 4° to 11° (2θ) at a rate of 2 °min^{-1}.

Thermal Gravimetric Analysis (TGA). TGA of vulcanizates was performed with Perkin Elmer TGA 4000 from 30 to 900 °C at a heating rate of 30 °C min^{-1} under air atmosphere.

Mechanical Properties. Tensile test was performed on a Tinius Olsen H5KT-0401 testing machine at a speed of 500 mm min^{-1} according to ASTM D412 with the average of three measurements. Specimens on standard dumb-bell shape were cut from the vulcanizate sheets with dimensions 25×6×1 mm. Shore A hardness of the specimens was obtained with Shore Durometer Type A according to ASTM D2240. Friction test was performed at room temperature by friction test machine and abrasion resistance test was performed using Abrasion resistance tester at 300, 500 and 1000 cycles of abrasion to measure the different mass losses of the samples. Hardness test was performed by shore durometer type a at room temperature.

Morphology. Field emission - scanning electron microscopy (FE-SEM). The tensile fractured surface of vulcanizates was coated with a thin layer of gold and then examined using a JSM-7500 FE-SEM (JEOL) with a magnification of 1000 times.

Results and Discussion

FTIR and XRD Determination. FTIR analysis was carried out for the characterization of filling materials. The spectra of (a) sBC; (b) sBC-CS; (c) low molecular weight chitosan were shown in Figure 3. It can be found that there are specific peaks in spectrum with absorptions at 808, 1265, 1528 and 1631 cm^{-1}.
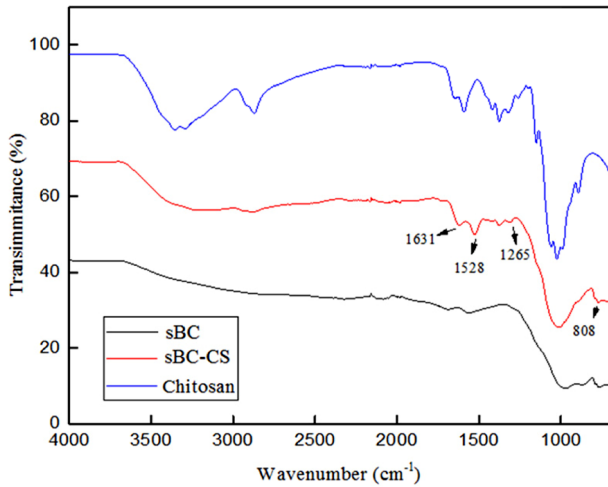
Figure 3. FTIR spectra of sBC; sBC-CS; low molecular weight chitosan.
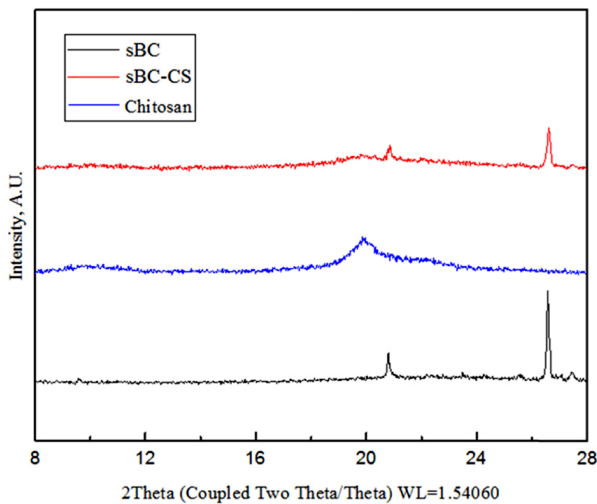
Figure 4. XRD patterns of sBC, sBC-CS and low molecular weight chitosan.

The peak of 1528 cm^{-1} belongs to the N-C=O bond of amide, which means the chitosan sample still have acetyl groups. The peak near to 1631 cm^{-1} belongs to the amide bond. The peak of 1265 cm^{-1} corresponds to the S=O bond, which proves the occurrence of reaction of sulfonated chitosan. It was attributed to chitosan sulfate function groups. The peak of 808 cm^{-1} corresponds to the C-O-S bond.[13] The XRD profiles of sBC, sBC-CS and chitosan were presented in Figure 4. The SBC exhibited two diffraction peaks at 20.82, 26.58. The sBC-CS presented the peaks of 19.83, 20.86 and 26.61. The chitosan presented the peak of 19.86, the pattern of sBC-CS have the typical reflections of solid acid. It also showed the charac-teristics of chitosan, as a large molecular weight polymer, the

typical reflections also mean the same crystal structure. With the results of FTIR and XRD, they proved that the sBC-CS had been synthesized by the methods above.

Thermal Gravimetric Analysis. The TGA plot of the filling materials in air is shown in Figure 5. In the temperature range of 40-270 °C, the TGA plot of the sBC and sBC-CS showed a weight loss about 10%, but concerning bamboo charcoal, the weight loss is over 30%. Then there was a rapid weight loss until 560 °C, indicating the oxidation of bamboo charcoal structure, the weight loss rate of sBC-CS is the lowest. With further increase in temperature at about 700 °C, the mass was almost constant.

The good thermal stability of the sBC-CS filling material can be explained as follows: The bamboo charcoal has large specific surface area and strong adsorption property, when it has modified into solid acid, the electrophilic groups (-SO$_3$-) have been increased on its surface. The structure of chitosan also has some nucleophilic groups (amino groups).

So sBC is more easily adsorbed chitosan structure by van der Waals force and electrostatic force. It can fill the porous structure of bamboo charcoal effectively. It makes sBC-CS more stable thermodynamic property.

The sulfonated vegetable carbon, such as sBC, is a material containing sulfonated polycyclic aromatic-hydrocarbons, and the polycyclic aromatic hydrocarbons which could exert an electron-withdrawing force on bonded sulfonic groups. So the weight loss of sBC is always less than the bamboo charcoal at lower than 700 °C. When the temperature increased into 700 °C, it still has rapid weight loss until 790 °C because the surface of carbon material is seriously corroded by the sulfuric
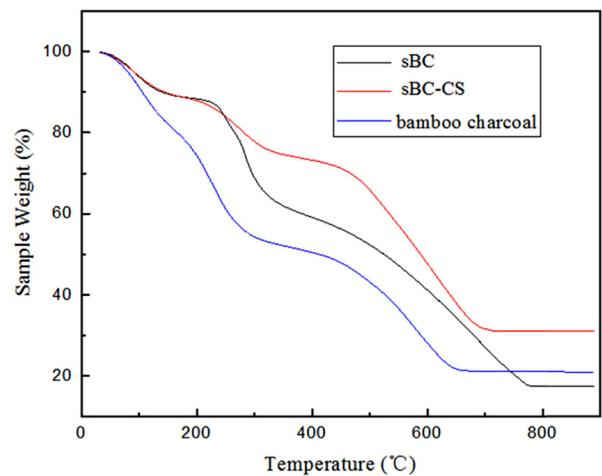
Figure 5. TGA results of bamboo charcoal, sBC-CS, and sBC.

acid after sulfonation, and caused a lot of holes on the surface which increases the specific surface area. So it leads to further thermal decomposition.[14]

Curing Properties. The cure characteristics of the filling materials were presented in Table 2.

The vulcanization characteristics of NR compounds with added fillers were shown in Table 2. With the incorporation of fillers, the torque values were all increased, due to the stiffness of fillers, which strongly restricted the deformation and consequently increased the stiffness of NR composites.

This is also evidenced by the change in the hardness of sBC-CS-NR composites from 53 to 58 as shown in the figure of sBC-CS-NR. sBC-CS possilby increased the activation energy

for vulcanization process. The curing rate index (CRI) was applied to investigate the vulcanization rate. The CRI values of sBC-CS-NR decreased due to the incorporation of sBC-CS, which decreased the vulcanization rate.

The incorporation of sBC-CS in NR matrix decreased the torque values, due to chitosan, which acted like a mat between sBC and NR. The scorch time and optimum curing time of fillers-NR all increased, because with the reaction of sulfonated on chitosan, the size of the filler would be larger, thus it need more time to complete the vulcanization process.[15]

In addition, the different influence of sBC and sBC-CS on NR matrix was presented in Table 2. The ΔM values of sBC-CS were higher than that of sBC at the same filling mass, and

Table 2. Curing Characteristic Results of Neat NR Compound, sBC-NR Compound, sBC-CS-NR Compound and low Molecular Weight Chitosan NR Compound

	Maximum torque, M_H (dNm)	Minimum torque, M_L (dNm)	ΔM (dNm)	Scorch time, t_{s2} (min)	Cure time, t_{90} (min)	Cure rate index (CRI min^{-1})
Neat	15.8	0.3	15.5	3.86	7.92	24.63
sBC	18.2	0.5	17.7	5.24	10.51	18.98
Chitosan	16.6	0.4	16.2	4.47	9.21	21.10
sBC-CS	19.4	0.5	18.9	5.56	10.97	18.48
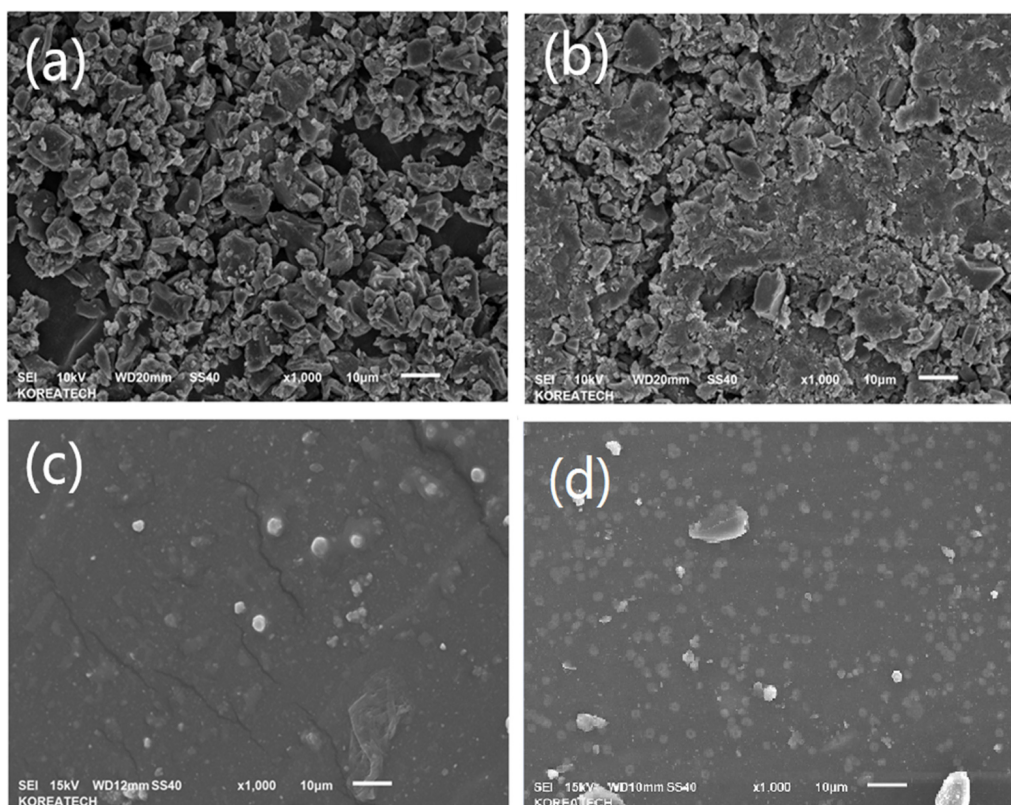
Figure 6. FE-SEM micrographs of (a) sBC powder; (b) sBC-CS powder; (c) chitosan-NR compound; (d) sBC-CS-NR compound.

the CRI values of sBC-CS were lower than sBC.

The possible reason was that the microstructure of sBC-CS is more compact than sBC (as SEM figures showed), resulting to higher ΔM values and lower CRI values of sBC-CS. The possible reason was that the microstructure of sBC-CS is more compact than sBC (see SEM figures), resulting to higher ΔM values and lower CRI values of sBC-CS.

Morphology. FE-SEM micrographs of (a) sBC powder; (b) sBC-CS powder; (c) chitosan-NR compound and (d) sBC-CS-NR compound were shown in Figure 6.

Figure 6(a) and 6(b) shows the difference between sBC acid and sBC-CS. Figure 6(c) and 6(d) showed the picture of rubber samples. It can be found there was few large block in Figure 6(d). Because of agglomeration, the size of fillers looks so large in the SEM pictures, the size of fillers also has been shown in Table 3 and Table 4.

Table 3 and Table 4 show the size data of sBC and sBC-CS. The particle diameter of sBC was smaller than sBC-CS. It also can be found that the agglomeration effect in sBC-NR is more obvious than in sBC-CS-NR. This is because sBC molecular has more protons on its surface than sBC-CS, they will strengthen the electrostatic attraction between the molecules.

**Table 3. Dispersion Rate Analysis Report of sBC-NR**

Analysis item	Reading
1. Particle	797
2. Particle area	2547.962
3. Max particle diameter	8.238
4. Agglomerations	22
5. Ave. Particle area	3.24
6. Ave. Particle diameter (μm)	2.208
7. Particle rate %	4.224
8. Dispersion %	86.31

**Table 4. Dispersion Rate Analysis Report of sBC-CS-NR**

Analysis item	Reading
1. Particle	976
2. Particle area	968.072
3. Max particle diameter	5.882
4. Agglomerations	3
5. Ave. Particle area	4.6
6. Ave. Particle diameter (μm)	2.055
7. Particle rate %	8.586
8. Dispersion %	88.82

But as sBC-CS, protons was replaced by chitosan which has large molecular structure. It can cause steric effect and reduce agglomeration when compounded with NR latex.

Mechanical Properties. The results of abrasion test and hardness test were shown in Figure 7 and Figure 8. The results of tensile test were shown in Figure 9. Abrasion resistance is a critical factor to the service lifetime and safety for tires. From Figure 7, it can be found the mass loss decreased with fillers, which means properties of abrasion were improved especially filled with sBC-CS. This is because the sBC-CS can improve rubber sample's hardness. The carbon structure of sBC-CS will make dislocation in NR compound.[16] It can improve the strength of compound. Chitosan structure in sBC-CS molecular also has many functional groups on its surface, they will produce more covalent bonds with natural rubber molecules. It
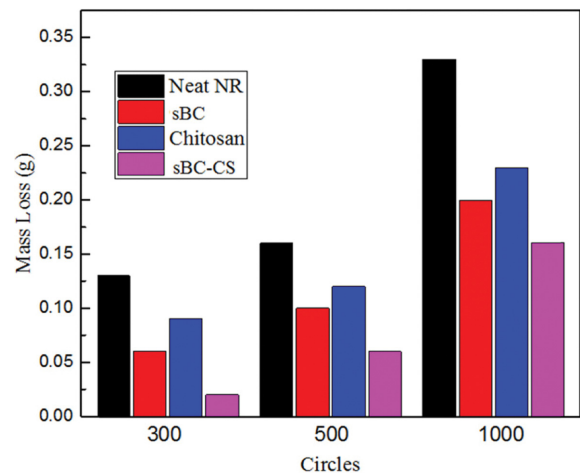
Figure 7. Abrasion test results of test sample compounds.
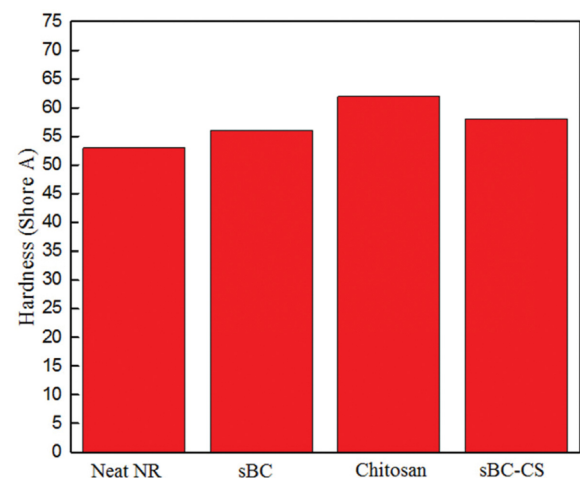
Figure 8. Hardness test results of test sample compounds.
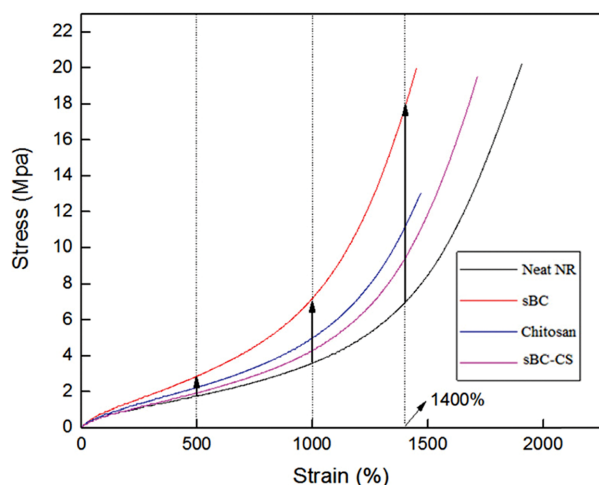
Figure 9. Tensile strengths of neat NR compound; sBC-NR compound; chitosan-NR compound and sBC-CS-NR compound.

can make better combination with NR latex and chitosan is also a solid lubricant, which enhances abrasion resistance of NR. But the pure chitosan can not reinforce natural rubber by directly blending, so it also can not improve abrasion resistance property of compounds so much.[17]

From Figure 8, it can be found that the hardness was increased after filling. The blend filled with chitoan has largest hardness value, however it is not obvious because the filling amount is as low as 5 phr.

Figure 9 shows the stress-strain curves of compounds. From these curves, natural rubber inherently possesses high strength due to strain-induced crystallization. When fillers are incorporated into NR, the regular arrangement of rubber molecules is disrupted and hence the ability for crystallization is lost.[18] It is the reason why fillers reinforced natural rubber blends possess lower tensile modulus than neat NR blend. It also should note that morphological factors are not entirely responsible for the difference in properties because that the milling process breaks down the rubber particles and lowers the average molecular weight of the chains due to mechanochemical degradation.[19] It can be found that the blend filled with sBC and sBC-CS had increased modulus and tensile strength compared to neat NR at the strain value of 500, 1000, and 1400%. This is because the sBC and sBC-CS have carbon-based structure, it can reinforce rubber like carbon. Chitosan structure in sBC-CS molecular has many functional groups on its surface, such as -OH, -NH$_2$, they will produce more covalent bonds with natural rubber molecules than sBC. It can make better combination with NR latex. This is why the compound filled with sBC-CS has better tensile strength than compound filled with sBC.[20,21]

Conclusions

Sulfonated bamboo charcoal-chitosan (sBC-CS) hybrid was synthesized by sulfonation reaction method, then compounded with natural rubber latex. The results of FTIR and XRD test proved that the sBC-CS has been successfully synthesized by sulfonation reaction method. From the result of TGA, It has been shown the sBC-CS has superior thermal stability than sBC and pure chitosan. The highest thermal decomposition temperature of sBC-CS is about 790 °C. The result of curing characteristics shows the values of sBC-CS-NR compound's maximum torque, minimum torque, ΔM, scorch time, cure time of are the largest in this test, and the value of cure rate for sBC-CS-NR compound is least. The data means the sBC-CS filler has superior reinforcement effect of increasing composite stiffness and reducing the vulcanization rate. FE-SEM pictures show the structure of sBC, sBC-CS fillers, chitosan-NR and sBC-CS-NR compounds and C.B. dispersion rating analysis reports show the average diameter size, dispersion, agglomeration of sBC and sBC-CS fillers. From these results, it can be found the average diameter of sBC-CS is slightly larger than sBC, but the agglomeration effect and dispersion of sBC-CS is superior than sBC when filled into the NR composites. The results of abrasion test, hardness test and tensile test have shown sBC-CS can increase tensile strength and hardness of NR composites and also improve the properties of abrasion resistance of NR composites as well. Generally, the sulfonated bamboo charcoal-chitosan hybrid showed contribution to the reinforcement of natural rubber latex. This study also provide a new idea for the combination of chitosan derivatives and natural rubber latex. It will become a potential hot research topic in the future.

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