실리카와 전분이 보강된 스티렌-부타디엔 고무 복합체

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Silica-Starch Reinforced Styrene-Butadiene Rubber Composites

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Abstract: Silica-starch-reinforced styrene-butadiene rubber (SBR) was prepared by a modified sol-gel method of mixing the silica sol, the starch paste, and then *in situ* blending the SBR latex. The fracture surface of the samples after the tensile test was characterized by FE-SEM. The tensile strength, the storage modulus, the hardness and the swelling test of the vulcanized samples were systematically discussed. The results showed the elongation at break, the hardness and the storage modulus increased with the increasing of silica in the as-prepared samples. The swelling ratio decreased with increase in the content of silica, indicative of the excellent crosslink density in the silica-starch-reinforced SBR.

Keywords: silica, starch, styrene-butadiene rubber, sol-gel, in situ.

Introduction

Silica has been recognized as the most important filling material in the rubber industry with the exception of carbon black.¹ Conventional silica offers a lot of advantages, such as a high tear strength, tensile strength, reduced heat up buildup and abrasion resistance to the rubber composites.^{2,3} The abundant silanols group on the surface of silica could result in the strong silica-silica attraction by hydrogen bonding.^{4,6}

Hence, the conventional silica-reinforced rubber is usually exhibited as highly aggregated and unevenly dispersed in the rubber matrix due to the filler-filler interaction. To improve this problem, silane coupling agents, such as bis-(3-triethoxysilyl propyl) tetrasulfane,⁷ alkyltrialkoxysilanes⁸ and iso-butyltriethoxysilane⁹ are usually applied to modify the surface of the silica. However, it is difficult to make sure every silica molecule could connect with the silane coupling agent.

In recent years, the sol-gel process of tetraethoxysilane

(TEOS) has been developed to obtain silica particles inside the rubber matrix instead of mixing the solid silica with the rubber matrix. The advantage of this method could open another way for improving the dispersibility of silica in rubber matrix.¹⁰ Based on this method, different polymer systems, such as styrene-butadiene rubber (SBR),¹¹ butadiene rubber (BR),¹² acrylonitrile-butadiene rubber (NBR),¹³ natural rubber (NR),¹⁴ and epoxidized NR¹⁵ were reported previously. Although the base rubber latex showed the catalytic property to the hydrolysis of TEOS, the conversion and the reaction duration usually last for a long time.^{2,16,17} Hence, here the acid catalyst was firstly used to hydrolysis of TEOS and then was blended with the rubber latex. Thus, the gel composite could be formed quickly at certain temperatures, and this could save a lot of time for the preparation process.

In addition, starch obtained from renewable resources as a natural, cheap and easily biodegradable polymer, was tentatively applied as a rubber additive.¹⁸⁻²¹ For instance, using starchbased material partially replaced the conventional carbon black and silica could reduce the tire weight and rolling resistance.²² At the same time, this replacement can decrease the energy consumption and save a lot of fuel in the automobile industry.

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Scheme 1. The process for preparation of starch-silica-reinforced SBR.

For this study, the linear silica sol was obtained by hydrolyzing of TEOS over nitric acid catalyst. Then the silica sol was mixed with a certain amount of starch under stirring at 80 °C. Subsequently, the SBR latex was blended with the above silica-starch liquid system. Finally the silica-starch-SBR solid composites was obtained after drying in an oven. The preparation process was summarized in Scheme 1. The solid silica-starchreinforced SBR was vulcanized after the above procedure, and the properties such as the static mechanical properties, the dynamic rheological property and the swelling test were then systematically discussed.

Experimental

Materials. Commercial styrene-butadiene rubber latex 1502 was purchased from GemHoo company, Korea. Tetraethyl orthosilicate (TEOS), absolute ethanol and sulfur were obtained from Daejung chemicals & metals Co., Ltd.. Nitric acid and starch were purchased from Duksan pure chemicals Co., Ltd.. Acetic acid and zinc oxide were purchased from Samchun pure chemicals Co., Ltd.. N-cyclohexyl-2-benzothiazolyl sulfonamide (CBS) and 2,2'-dibenzothiazolyl disulfide (DD) were purchased from Tokyo chemicals industry Co., Ltd..

Synthesis of Silica Sol Precursor and SiO₂-starch/SBR Composites. Silica sol precursor was synthesized following the literatures in the lab.23,24 Briefly, ethanol and deionized water were added to the solution of TEOS. Then proper nitric acid was added and the pH value was kept at about 4.5. The molar ratio of the TEOS, ethanol, deionized water and nitric acid was 1:3.8:6.4:0.085. The above system was stirred at 70 °C for 3 h in the water bath, and obtained the silica sol.

The synthesis of SBR, silica and starch composites was obtained by the following process: A certain amount of the starch was dispersed in the above silica sol, ultrasonic for 10 min, and then stirred at 80 °C for 30 min. The SBR latex was finally poured into the above mixture and further stirred for 30 min. The obtained mixture was then dried in an oven at 60 °C for about 48 h. The different amount of starch and theoretical silica is summarized in Table 1. The neat SBR was directly dried in an oven at 60 °C for about 48 h.

The above samples were blended with zinc oxide, CBS, DD, stearic acid and sulfur on a two-roll mill at about 40 °C. The contents of the composition are shown in Table 1. Finally, the vulcanized samples were fixed in a 1 mm mold under the pressure of 15 MPa at 150 °C (the curing time (t_{90}) for all the samples from the RPA test are shown in Table 2) on a heating press machine (Auto hydraulic press type, Ocean science) and for the tensile test in the following procedure.

Characterizations. The morphology of the samples after the tensile test was carried out on a FE-SEM (JSM-7500F, JEOL Ltd., Japan). The cure/vulcanization characteristic of asprepared samples were measured by a rubber process analysis (RPA) (RPA-V1, U-CAN DYNATEX INC.). The minimum torque (ML), maximum torque (MH), scorch time (t_{s2}) , and

	SBR (phr)	Starch (phr)	Theoretical SiO ₂ (phr)	CBS (phr)	DD (phr)	Zinc oxide (phr)	Stearic acid (phr)	Sulfur (phr)
(A)	100	0	0	2	0.5	3	2	1.75
(B)	100	10.00	0	2	0.5	3	2	1.75
(C)	100	0	10.00	2	0.5	3	2	1.75
(D)	100	3.34	6.66	2	0.5	3	2	1.75
(E)	100	5.00	5.00	2	0.5	3	2	1.75
(F)	100	6.66	3.34	2	0.5	3	2	1.75

Table 1. The Composition of As-prepared Samples

phr: part per hundred of rubber. CBS: N-cyclohexyl-2-benzothiazolyl sulfonamide. DD: 2,2'-dibenzothiazolyl disulfide.

	Maximum torque MH (dNm)	Minimum torque ML (dNm)	ΔM (dNm)	Scorch time T_{s2} (min)	Cure time t_{90} (min)	Cure rate index (CRI min ⁻¹)
(A)	6.54	0.87	5.67	1:19	12:54	8.64
(B)	14.80	1.33	13.47	1:38	4:30	34.84
(C)	25.32	1.51	23.81	2:11	6:20	24.10
(D)	19.55	1.65	17.9	2:33	6:10	27.62
(E)	17.47	1.49	15.98	2:48	5:41	34.72
(F)	13.50	1.17	12.33	2:41	4:52	45.66

Table 2. Curing and Hardness Characteristic of As-prepared Samples



Figure 1. Mechanism of the friction coefficient tester.

optimum cure time (t_{90}) were determined by the above RPA. The cure rate index (CRI) was calculated by the following equation:

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

The strain sweep was also performed on the above RPA. The shear storage modulus was recorded for each strain at 60 °C according to the ASTM D 6204-97. The hardness of asprepared samples were obtained by a shore durometer type A according to the ASTM D 22-40. The tensile strength test was measured three times on a Tinius Olsen H5KT-0401 testing machine at a speed of 500 mm/min according to ASTM D412. The samples was made of dumb-bell shape with the dimensions of 25 mm×6 mm×1 mm after the vulcanization on the heating press machine. The friction test was performed by a friction test, and seen in Figure 1. The swelling test of as-prepared samples were performed in a solution of toluene for 1, 2, 3, 5, 7, 12 and 24 h according to the ASTM D71-79. The swelling ratio of the samples is calculated in the following equation:

Swelling ratio (%)=
$$\frac{(m_{\rm s}-m_0)/\rho_{\rm t}}{m_0/\rho_{\rm t}} \times 100\%$$
 (2)

where m_0 stands for the initial weight of as-prepared samples, and m_s stands for the as-prepared samples after swelling. ρ_t stands for the density of toluene solvent (ρ_t =0.867 g/cm³), and ρ_r stands for the density of SBR (ρ_r =0.933 g/cm³).

Results and Discussion

Table 2 shows the curing characteristic of SBR, starch, silica and their mixture. As can be seen that the cure time (t_{90}) for the SBR blend with starch, silica, or the starch and silica mixture were lower than the cure time of neat SBR, while the scorch time (T_{s2}) was exhibited the opposite trend. The cure time of silica was longer than that of starch in Table 2. After the blending of silica and starch, the cure time also increased with the increasing of silica contents. In other words, the cure rate index for sample (D), (E) and (F) was also increased with the increasing of silica contents, which is shown in Table 2.

The maximum and minimum torques of samples (D), (E) and (F) increased with the increasing of silica contents, while the maximum and minimum torques of the sample (B) were lower than the torques of sample (C). This may be mainly because the increased effective network chain density makes movement of the rubber molecules more difficult.²⁵ In other words, the crosslink density in sample (C) was better than the crosslink in sample (B). From the table it can also be seen the ΔM of sample (C) was higher than that of sample (B), indicating the better crosslink density.

Figure 2 shows the SEM fracture surface for the neat SBR, the starch-reinforced SBR, the silica-reinforced SBR, and the different contents of starch-silica-reinforced SBR after the tensile test, respectively. As can be seen from the graph, the relative smooth surface was observed in sample (C), (D), (E) and (F). This was attributed to the interaction between SBR and the highly dispersion of small silica particle size in SBR. The small particles in graph (A) mainly due to the additive such as ZnO. Besides, the silica particles were not seen clearly



Figure 2. SEM of as-prepared samples.

Table 3. Static Mechanical Properties of the	Samples	the Sa
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Modulus at 100% (MPa)		Modulus at 300%Tensile strength(MPa)(MPa)		Elongation at break (%)	Hardness (°)
(A)	0.83	1.32	2.19	642	44
(B)	1.17	1.99	2.70	536	55
(C)	1.20	1.92	3.77	839	57
(D)	1.27	2.04	5.99	1044	63
(E)	1.33	2.08	6.25	994	61
(F)	1.60	2.57	5.74	955	60

in samples (C), (D), (E) and (F). This may be due to the small particle size of the silica and insufficient magnification.

The static mechanical properties of the neat SBR, the starchreinforced SBR, the silica-reinforced SBR, and the different contents of starch-silica-reinforced SBR are shown in Figure 3 and Table 3. It is well known that tensile properties are affected by the size of agglomerates formed by the filler^{26,27} and rubber matrix and the filler interaction.²⁸ For the samples with weak or without rubber-filler chemical bonding, the fracture firstly occurs at the rubber-filler interface during the stretching.²⁹ Though the modulus at 100% and 300% among sample (D), (E) and (F) increased slightly, the difference among them was not obvious. The elongation at break for sample (D) was higher than sample (E) and (F), indicating the higher hardness level among them, and is shown in the table. Furthermore, the elongations for sample (D), (E) and (F) were bigger than sample (A) and (B), this may be due to the chemical bond formation during the high temperatures of the experiment process.



Figure 3. Tensile strength test results of as-prepared samples.

The shore A hardness of as-prepared samples were stronger than that of the neat SBR, mainly due to the rigid phase in the rubber matrix. The hardness of the silica filled rubber matrix was higher than that of the starch filled ones, which meant that the silica particles contained a higher level of filler-filler networks. Accordingly, the *in situ* silica generated by the method in this paper could act as a "soft- composite materials" with relatively good mechanical properties in terms of modulus, and also the good modulus of silica could be shown in the following part.³⁰ Besides, the hardness of sample (D) was higher than that of (E) and (F), this mainly due to the excellent crosslink density of silica-starch with the rubber matrix.

The dynamic rheological property of the neat SBR, the starch-reinforced SBR, the silica-reinforced SBR, and the different contents of starch-silica-reinforced SBR was carried



Figure 4. Strain sweep results of as-prepared samples.

out on an RPA. The strain amplitude dependence of the storage modulus (G') of as-prepared samples is usually to explain the filler network. As can be seen in Figure 4, the G' decreased with the increasing of the strain amplitude for all the above samples. This result can be explained by the breakdown of the aggregated secondary network among filler particles or the aggregates formed by van de Waals- London attraction forces, and as illustrated by Payne.³¹

Generally, the Payne effect could be illustrated in the filler network for filler-filler and filler-polymer interaction. A lower Payne effect usually implies a stronger filler-polymer interaction and better dispersion of the filler.^{32,33} The *G*' of sample (C) was stronger than that of sample (B), mainly due to the small particles size of silica in SBR matrix. In other words, the filler of silica in the SBR matrix more easily aggregated with each other compared with starch in the SBR matrix. Besides, among sample (D), (E) and (F), the *G*' was increased gradually, which indicated the poor dispersion. This meant the more silica filling ratio in the SBR matrix could lead to the aggregation. On the contrary, the more starch among the silica-starch SBR could improve the dispersion of the filler.

The friction properties of the neat SBR, the starchreinforced SBR, the silica-reinforced SBR, and the different contents of starch-silica-reinforced SBR are shown in Figure 5. During the friction tests, a metal block was moved on the fixed samples, and the data was recorded by a computer. The velocity for the metal block on the surface of as-prepared sample was kept at 300 mm/min, and lasted for 10 s during the friction test process (seen in Figure 4). As can be seen in the Figure 5, the neat SBR showed the highest friction coefficient (not only for



Figure 5. Friction test of as-prepared samples.



Figure 6. Swelling ratio test of as-prepared samples.

the static friction coefficient, but also for the dynamic friction coefficient) among all the samples. This meant the surface of the neat SBR was rather rough than the other samples. Furthermore, the friction coefficient increased with the decreasing of silica among samples (D), (E) and (F). This indicated that the surface of sample (D) was smoother than the surface of sample (E) and (F). This may be due to the higher content of silica in starch-silica-reinforced SBR of sample (D) than samples (E) and (F). Figure 6 exhibits the swelling test of the neat SBR, the starch-reinforced SBR, the silica-reinforced SBR, and the different contents of starch-silica-reinforced SBR. As can be seen in the figure that the swelling ratio for all samples increased sharply during the first 3 h. Subsequently, the slope for all samples decreased rapidly and was nearly parallel to the x axis, and this indicated that the swelling ratio was almost kept the same during this process. In other words,

the adsorption was almost saturated among all the samples after 3 h. Moreover, the swelling ratio of neat SBR (about 402%) was obviously higher than the other samples, indicating that the crosslink density was improved significantly after the SBR matrix blend with starch, silica or starch-silica fillers. In addition, the swelling ratio of silica-reinforced SBR (about 287%) was lower than starch-reinforced SBR (about 287%) was lower than starch-reinforced SBR (about 332%). This was mainly because of the rigidity of the silica particle in the SBR exhibited a higher crosslink density compared with the flexible molecule chain of starch in the SBR matrix. That is also the main reason for why sample (D) exhibited a lower swelling ratio than sample (E) and (F).

Conclusions

The starch-silica-reinforced SBR was prepared by hydrolysis of TEOS over an acid catalyst, then mixed with the starch paste and SBR latex, finally obtained the starch-silicareinforced SBR after the gel process dried in an oven. The SEM graphs showed the smooth surface after the tensile test. For the starch-silica-reinforced SBR, the elongation at break and the hardness increased with the increasing of the silica contents, indicating the excellent crosslink density for the fillers in the matrix of SBR. The storage modulus for the above samples also showed the same trend. This shows that the more silica filling ratio in the matrix of SBR did not benefit from the dispersion of fillers. Besides, the swelling ratio of the starchsilica-reinforced SBR was lower than the neat SBR, also indicating the good crosslink density. This work was only for the low content of fillers, for the other factors will be discussed in the following stage. This improved sol-gel method could not only shorten the preparation process, but also broaden the preparation methods for new rubber materials in the future.

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