

## Preparation and Physical Properties of Polybutadiene Grafted onto Silica

SHINZO YAMASHITA and SHINZO KOHJIYA, *Kyoto Institute of Technology, Department of Chemistry, Matsugasaki, Sakyo-ku, Kyoto, Japan*, and ATSUSHI KITA and AKIHIKO SHIMIZU, *Toyo Soda Manufacturing Co. Ltd., Central Research Laboratory, Shinnanyo-shi, Yamaguchi, Japan*

### Synopsis

Polybutadiene grafted to silica (PG) was prepared by the reaction of living polybutadiene with chlorinated silica. The graft efficiency was below 10%. PG and PG-commercial butadiene rubber blend were cured with sulfur. In either vulcanizate, the following phenomena were found as compared with the controlled samples: tensile modulus increased, degree of swelling and elongation lowered, and tensile strength unchanged. These results showed nearly the same tendency as had been found in the case of the rubber compounded with silica which was treated by coupling agents. In spite of a high tensile modulus of PG vulcanizate, it resulted in a lowering of the dynamic modulus compared with the controlled sample.

### INTRODUCTION

It was already reported that calcium carbonate, the reinforcing ability of which is poor for synthetic diene rubbers, was brought to greater efficiency by introducing functional groups on the surface of the precipitated one.<sup>1-5</sup> Later it was found that the tensile stress was increased by compounding silica together with silane coupling agents, and many studies on this subject were published.<sup>6-9</sup>

Yet the reason of this reinforcing effect has not been understood completely, and there has not been any final proof that the effect is due to the formation of chemical bonds between silica and rubber. Additionally, these studies have focused their attention mainly on the reaction of the functional group toward the internal part of the rubber molecule and not toward the terminal end.

Recently, Donnet and his co-workers<sup>10-12</sup> reported the reaction of activated carbon black with living polyisoprene and the formation of polyisoprene-grafted carbon black, but they did not investigate the physical properties of the product.

Therefore, in the present study more attention was paid to the influence of the chemical bonding between rubber molecule ends and the surface of silica upon the properties of the rubber vulcanizates.

## EXPERIMENTAL

### Materials

**Butadiene.** Commercial butadiene was passed through granular KOH and a molecular sieve 5A, distilled in a flask containing  $\text{LiAlH}_4$  at  $-78^\circ\text{C}$  which was connected to a vacuum line. The required amount of the monomer was obtained in an ampoule after passing through sodium mirrors.

***n*-Hexane.** Guaranteed reagent was shaken with concentrated sulfuric acid and washed with water. After standing over baked calcium chloride for a day, the upper, clear solution was removed and refluxed over calcium hydride for a few days, followed by distillation in the vacuum line on the sodium mirror. The required amount was distilled in an ampoule.

**Initiator.** *n*-BuLi from Merk Co. was used. It was diluted with *n*-hexane and distributed in small ampoules under vacuum.

**Silica.** Wet-process silica supplied by Nippon Silica Co. (Nipsil VN-3) was used. Its properties are shown in Table I.<sup>13</sup>

TABLE I  
Properties of Nipsil VN-3

Composition	$\text{SiO}_2 \cdot n\text{H}_2\text{O}$
Diameter	ca. 16 $\mu$
pH (4%)	5.8-6.8
Specific Gravity	1.9-2.0
Weight loss after ignition	5-6%
$\text{SiO}_2$	93-94%

**Chlorinated Silica.**<sup>14</sup> Nipsil VN-3, 20 g, and 120 ml thionyl chloride were mixed and allowed to react at  $80^\circ\text{C}$ - $90^\circ\text{C}$  for two days. After the reaction was completed, the excess of thionyl chloride was distilled off under reduced pressure, followed by vacuum drying at  $160^\circ\text{C}$ - $200^\circ\text{C}/10^{-4}$  mm Hg for 24 hr. After weighing, the product was hydrolyzed by NaOH standard solution, and the excess alkali was titrated with standard hydrochloric acid solution. The chlorine content of the chlorinated silica was  $2.30 \times 10^{-3}$  mole/g.

### Polymerization

Polymerizations were carried out in the 2-liter necked flask using *n*-BuLi as an initiator and *n*-hexane as a solvent. The polymerization procedure was as follows. The reaction system shown in Figure 1 was warmed by a gas burner under high vacuum for several hours; thus the system was thoroughly degassed and as moisture free as was experimentally possible. The breakseal of ampoule B which contained purging solution (*n*-BuLi in *n*-hexane) was then broken and the system was cleaned. After the purging solution was recovered, solvent I and monomer H were distilled in flask D and the polymerization was started by introducing ini-

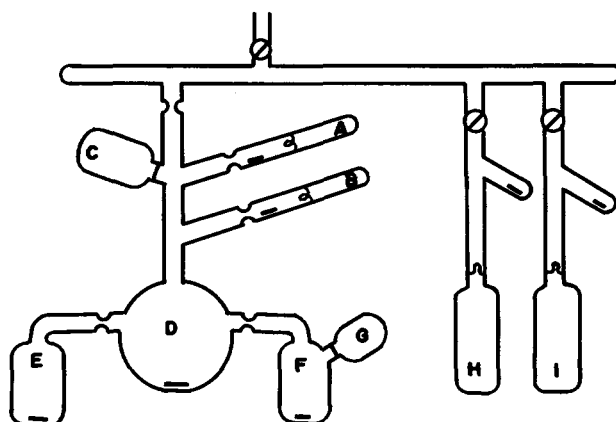


Fig. 1. Polymerization apparatus: (A) initiator; (B) purging solution; (C) chlorinated silica; (D) flask for polymerization with magnetic stirrer; (E), (F) flasks for separation; (G) silica; (H) monomer; (I) solvent.

tiator solution A into the flask. After the fixed period of time, the living polymer solution was divided into three parts, each of which was terminated by methyl alcohol, chlorinated silica, and commercial silica, respectively. The polymerization recipe is shown in Table II. The polymer was purified by reprecipitation using a benzene-methanol system.

TABLE II  
Recipe for Polymerizations

Run no.	P-1	P-2
Butadiene, g	61.8	16.7
<i>n</i> -BuLi, mole	$1.0 \times 10^{-3}$	$1.5 \times 10^{-3}$
<i>n</i> -Hexane, ml	1100	500
Polymerization temperature	room temperature	room temperature
Polymerization time, days	3	3
Terminator		
(1) methanol, ml	ca. 3 (PM <sub>1</sub> ) <sup>a</sup>	ca. 3 (PM <sub>2</sub> )
(2) chlorinated silica, g	9.0 (PG <sub>1</sub> )	2.4 (PG <sub>2</sub> )
(3) silica, g	3.0 (PSi)	—

<sup>a</sup> Symbol for the polymer reacted with each terminator; for example, PM<sub>1</sub> denotes the polymer terminated by methanol at polymerization run P-1.

### Polymer Analysis

**Extraction.** The polymer reacted with chlorinated silica and the mixture of polybutadiene and silica were Soxhlet extracted using benzene as solvent. The residual silica was dried under vacuum and the extractions were conducted till constant weight of the residue was obtained.

**Infrared Spectra.** IR spectra were recorded on a Japan Spectroscopic Co. Model 402 G spectrometer.

**Elemental Analysis.** Elemental analyses were performed at the Elemental Analyses Center of Kyoto University.

### Vulcanization

Various compounds of polybutadiene and silica were cured with sulfur according to the recipes in Tables III and IV.

TABLE III  
Compounding Recipe for Polymer P-1

	PG <sub>1</sub> -GSi <sup>a</sup>	PM <sub>1</sub> -ClSi <sup>b</sup>	PM <sub>1</sub> -Si <sup>c</sup>
Polybutadiene	100	100	100
Silica	30	30	30
ZnO	5	5	5
Stearic acid	2	2	2
DPG <sup>d</sup>	0.5	0.5	0.5
DM <sup>e</sup>	1.4	1.4	1.4
SP <sup>f</sup>	1.0	1.0	1.0
Sulfur	1.6	1.6	1.6
DEG <sup>g</sup>	4.0	4.0	4.0

<sup>a</sup> GSi denotes silica grafted with polybutadiene. Thus, this sample is a mixture of polymer PG<sub>1</sub> and silica GSi.

<sup>b</sup> ClSi means chlorinated silica.

<sup>c</sup> Si indicates untreated silica.

<sup>d</sup> Diphenylguanidine.

<sup>e</sup> Dibenzothiazyl disulfide.

<sup>f</sup> Condensation product of styrene and phenol.

<sup>g</sup> Diethylene glycol.

TABLE IV  
Compounding Recipe for Polymer P-2 and Butadiene Rubber

	BR-GSi	PM <sub>2</sub> -Si	BR-Si
BR <sup>a</sup>	91.1	91.1	100
PM <sub>2</sub>	—	8.9	—
Silica	38.9 <sup>b</sup>	30	30
ZnO	5	5	5
Stearic acid	2	2	2
DPG <sup>c</sup>	0.5	0.5	0.5
DM <sup>e</sup>	1.4	1.4	1.4
D <sup>d</sup>	1.0	1.0	1.0
Sulfur	1.6	1.6	1.6
DEG <sup>c</sup>	5.0	5.0	5.0

<sup>a</sup> Low-*cis*-polybutadiene rubber (Diene NF-35R, Asahi Chemical Industry Co. Ltd.).

<sup>b</sup> GSi from PG<sub>2</sub> extracted with benzene was used. This silica contained polybutadiene 8.9/38.9 by weight.

<sup>c</sup> See footnotes in Table III.

<sup>d</sup> Phenyl- $\beta$ -naphthylamine.

### Mechanical Measurements

Tensile tests were done at room temperature with an autographic tensile tester. The rate of elongation was set at 50 mm/min. Test samples were prepared as shown in Table V.

TABLE V  
Prepared Samples for Mechanical Measurement

Samples	Composition	Vulcanization
PG <sub>1</sub> -GSi	see Table III	150°C, 25 min
PM <sub>1</sub> -Si	see Table III	150°C, 25 min
PM <sub>1</sub> -ClSi	see Table III	150°C, 60 min
BR-GSi	see Table IV	150°C, 80 min
PM <sub>2</sub> -Si	see Table IV	150°C, 80 min

Dynamic measurements were effected by using a Vibron DDV-2 (Toyo Baldwin Co., Ltd.) under measuring conditions of 110 cps and a rising rate of 1°C/min.

### Swelling Test

The degree of swelling was measured by dipping the samples in benzene at 25°C for 30 hr.

## RESULTS AND DISCUSSION

The reaction of chain ends of rubber molecules with the surface of silica can be conducted by the following methods:

1. The functional group is introduced on the surface of silica, from which the polymerization of butadiene starts.

2. On the surface of silica are introduced the functional groups which can react with the chain ends of the polybutadiene, which is done by either of two methods: (a) chlorinated silica is reacted with living polybutadiene; (b) chlorinated silica is reacted with polybutadiene with terminal hydroxyl group. This paper treats method 2a.

Living polybutadiene was reacted at room temperature with chlorinated silica or with silica under high vacuum till the yellow color characteristic of living polybutadiene disappeared. To confirm the formation of chemical bonds between rubber and silica, the polymer was analyzed by IR spectroscopy and elemental analysis. Further, the mechanical properties of the vulcanizates of the polymer were investigated.

### Polymer Characterization

Table VI shows the analytical results of the polybutadienes having reacted with chlorinated silica, silica, and methanol. Grafting efficiency ( $GE$ ) and degree of grafting ( $G$ ) were calculated from the results of elemental analysis. If the quantity of homopolybutadiene in the polymer matrix is  $a$ , that of grafted polybutadiene  $a'$ , and the quantity of silica  $b$ , the following equation could be obtained, since almost all the homopolybutadiene was removed by the present extraction procedure:

$$(a + a')/(a + a' + b) = \text{polybutadiene weight fraction in the system} \quad (1)$$

TABLE VI  
Analytical Results of the Polymers

Sample	P-1			P-2	
	PG <sub>1</sub>	PSi	PM <sub>1</sub>	PG <sub>2</sub>	PM <sub>2</sub>
Terminator	ClSi	silica	methanol	ClSi	methanol
[ $\eta$ ] <sup>a</sup>	—	—	1.38	—	0.35
IR peaks <sup>b</sup>	present	absent	—	present	—
Elemental analysis (Bd%)					
polymer <sup>c</sup>	82.10	—	—	80.52	—
residual silica <sup>d</sup>	25.56	—	—	18.63	—
GE, % <sup>e</sup>	7.49	—	—	5.54	—
G <sup>f</sup>	0.34	—	—	0.23	—

<sup>a</sup> In toluene at 30°C.

<sup>b</sup> The peaks due to polybutadiene were checked for the residual silica after the extraction.

<sup>c</sup> Polybutadiene reacted with each terminator.

<sup>d</sup> Polybutadiene-grafted silica which is a residue after the extraction.

<sup>e</sup> Graft efficiency: (grafted polybutadiene/total polybutadiene)  $\times$  100.

<sup>f</sup> Degree of grafting: grafted polybutadiene (g)/silica (g).

$$a'/(a' + b)$$

$$= \text{polybutadiene weight fraction in the extracted residual silica.} \quad (2)$$

Grafting efficiency is defined as

$$GE = a'/(a + a') \times 100(\%) \quad (3)$$

and degree of grafting, i.e., grams of grafted polybutadiene per 1 g chlorinated silica, is

$$G = a'/b. \quad (4)$$

From these equations,  $GE$  and  $G$  could be calculated as indicated in Table VI.  $GE$  does not exceed 10%. This relatively low efficiency is probably due to the difficulty of the chemical reaction between high polymers in solution and inorganic substances present in the heterogeneous phase.

The IR spectra of the polymers are shown in Figure 2. The peaks due to *trans*-1,4- and 1,2-polybutadienes appear at 960 and 910  $\text{cm}^{-1}$ , respectively. The spectrum (a) exhibits the extracted residual silica of polymer PG<sub>1</sub>, that is, silica grafted with polybutadiene. Peaks due to polybutadiene are clearly seen at around 3000, 960, and 910  $\text{cm}^{-1}$ , while these peaks are absent in the spectrum (b), which is of the extracted residual silica of the polymer PSi. The IR of the chlorinated silica gave the same spectrum as (b), except for the absorption of Si-OH at 3400  $\text{cm}^{-1}$  which was interpreted as the hydrolysis of Si-Cl bond during the experimental procedure or as the incompleteness of the chlorination reaction.

Elemental analysis of the extracted residual silica of the polymer PG<sub>1</sub> or PG<sub>2</sub> indicated the presence of polybutadiene as shown in Table VI.

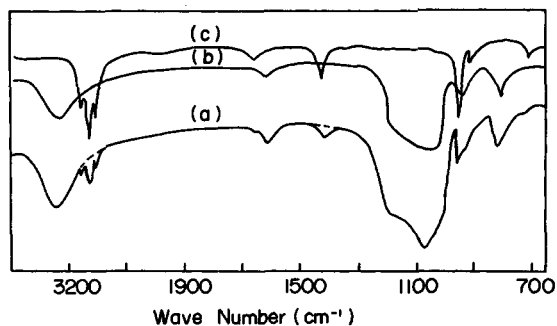


Fig. 2. Infrared spectra of the polymers: (a) silica residue of the polymer PG<sub>1</sub> after extraction; (b) silica residue of the polymer PSi after extraction; (c) the polymer PM<sub>1</sub>.

These facts suggest the presence of chemical bonding between polybutadiene and silica when living polybutadiene is reacted with chlorinated silica.

### Mechanical Properties of the Vulcanizates

Static and dynamic tests of the mechanical properties and the swelling test were carried out. The degree of swelling ( $Q$ ) was calculated as follows:

$$Q = (W - W_0)/W_0$$

where  $W_0$  = weight of the polymer when it was dry and reached constant weight after swelling and  $W$  = weight after dipping in benzene for 30 hr at 25°C. The results of tensile and swelling properties of the vulcanizates are shown in Figures 3-6. As for PG<sub>1</sub>-GSi, it is readily seen from Figures 3 and 4 that the tensile stress increased, the degree of swelling decreased, but the elongation decreased and the tensile strength stayed approximately

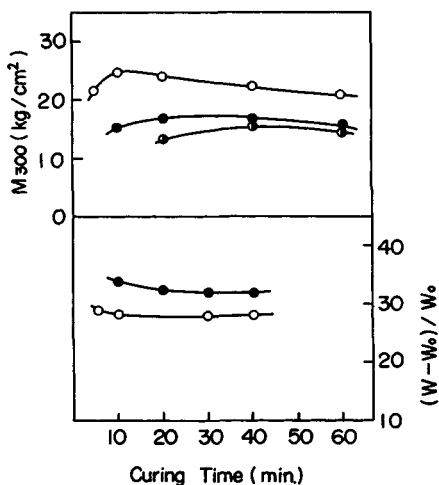


Fig. 3. Effect of curing time on 300% modulus and the degree of swelling: (○) PG<sub>1</sub>-GSi; (●) PM<sub>1</sub>-Si; (◐) PM<sub>1</sub>-ClSi.

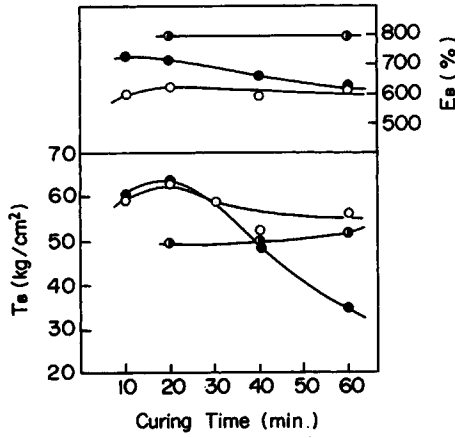


Fig. 4. Tensile strength and elongation for the polymer P-1: (○) PG<sub>1</sub>-GSi; (●) PM<sub>1</sub>-Si; (◐) PM<sub>1</sub>-ClSi.

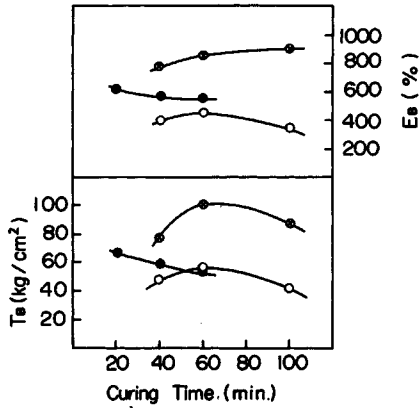


Fig. 5. Tensile strength and elongation for the polymer P-2 and BR: (○) PB-GSi; (◐) PM<sub>2</sub>-Si; (●) BR-Si.

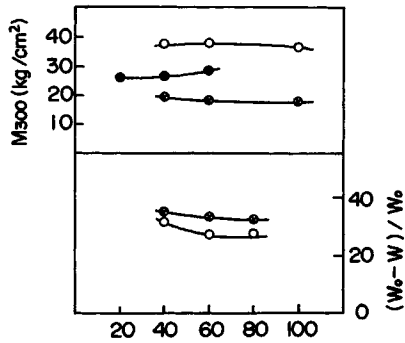


Fig. 6. Degree of swelling and 300% modulus for the polymer P-2 and BR: (○) BR-GSi; (◐) PM<sub>2</sub>-Si; (●) BR-Si.



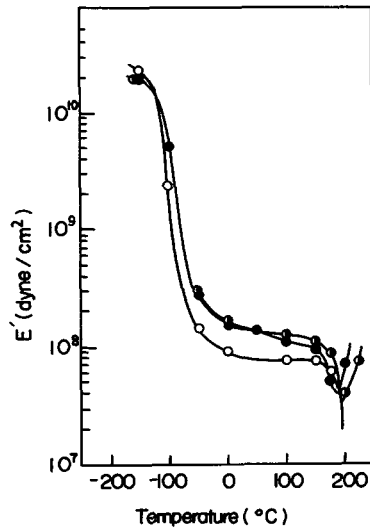


Fig. 7. Temperature dependence of dynamic modulus  $E'$  for polymer P-1: (O)  $PG_1$ -GSi; (●)  $PM_1$ -Si; (◐)  $PM_1$ -ClSi.

unchanged in the vicinity of optimum cure time as compared with the controlled sample, i.e.,  $PM_1$ -Si. BR-GSi, which is a mixture of butadiene rubber and silica grafted with polybutadiene, showed the same tendencies, except for tensile strength as seen in Figures 5 and 6. These tendencies seem to result from the presence of chemical bonding between silica and rubber. The probable reason for the tensile strength of BR-GSi to be lower than the others is the formation of some agglomerates of GSi during the chlorination of silica.

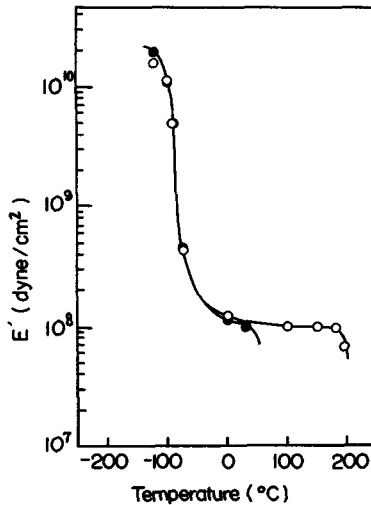


Fig. 8. Temperature dependence of dynamic modulus  $E'$  for polymer P-2 and BR: (O) BR-GSi; (●)  $PM_2$ -Si.

The dynamic property is shown in Figures 7 and 8. From Figure 7 it was found that there was no difference in the dynamic moduli of PG<sub>1</sub>-GSi, PM<sub>1</sub>-ClSi, and PM<sub>1</sub>-Si at a temperature below  $-120^{\circ}\text{C}$ , but at a temperature above  $-120^{\circ}\text{C}$ , PG<sub>1</sub>-GSi had a smaller modulus than the other two, which is a trend opposite to that of the tensile modulus. Above  $180^{\circ}\text{C}$ , PM<sub>1</sub>-ClSi and PM<sub>1</sub>-Si showed an increase in dynamic modulus, which was probably due to thermal crosslinking. This phenomenon was not found in the case of PG<sub>1</sub>-GSi at the present temperature range. Figure 8 shows that BR-GSi, which was compounded with polybutadiene-grafted silica, was able to be measured near  $200^{\circ}\text{C}$ , while PM<sub>2</sub>-Si was not measurable above room temperature, probably because of the presence of bonds of silica and polymer in BR-GSi.

### CONCLUSIONS

IR spectroscopy and elemental analysis revealed that the polymer produced by the reaction of living polybutadiene and chlorinated silica has chemical bonds between the polybutadiene chain ends and the surfaces of the silica. This explains the various differences of the physical properties of rubbers according whether they are chemically bonded to silica or not.

The authors would like to express their gratitude to Dr. Yujiro Kosaka and Mr. Shotaro Ohno of Toyo Soda Manufacturing Co. for their measurement of the dynamic properties and for discussions.

### References

1. J. Furukawa, S. Yamashita, and T. Kotani, *Nippon Gomu Kyokaishi*, **34**, 89 (1961).
2. M. Fukuda, J. Furukawa, S. Yamashita, and T. Kotani, *Nippon Gomu Kyokaishi*, **34**, 928 (1961).
3. J. Furukawa, S. Yamashita, and H. Niwa, *Nippon Gomu Kyokaishi*, **36**, 295 (1963).
4. H. Niwa, J. Furukawa, and S. Yamashita, *Nippon Gomu Kyokaishi*, **40**, 375 (1967).
5. J. Furukawa, S. Yamashita, M. Fukuda, H. Niwa, and T. Kotani, *Rev. Gen. Caout. Plast.*, **41**, 831 (1964).
6. J. V. Fusco, *Rubber World*, **147** (5), 48 (1963).
7. W. C. Smith and N. F. Newman, *Rubber World*, **153** (4), 79 (1966).
8. D. M. Schwaber and F. Rodriguez, *Rubber Plast. Age*, **48**, 1081 (1967).
9. G. W. MacDonald, *Rubber Age*, **102** (4), 66 (1970).
10. E. Papirer, N. van Tao, and J. B. Donnet, *Polym. Lett.*, **9**, 195 (1971).
11. J. B. Donnet, G. Riess, and G. Majowski, *Eur. Polym. J.*, **7**, 1065 (1971).
12. E. Papirer, J. B. Donnet, G. Riess, and V. T. Nguyen, *Angew. Makromol. Chem.*, **19**, 65 (1971).
13. Nippon Silica Co., qualification sheets on Nipsil VN-3, Tokyo, Japan, 1961.
14. H. P. Boehm and M. Schneider, *Z. Anorg. Allgem. Chem.*, **301**, 326 (1959).

Received December 27, 1972