

# Effect of Low Molecular Weight Polybutadiene as Processing Aid on Properties of Silica-Filled Styrene–Butadiene Rubber Compounds

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**ABSTRACT:** Because silica has strong filler–filler interactions, a silica-filled rubber compound shows a poor filler dispersion compared to a carbon black-filled one. Improvement of the filler dispersion in silica-filled styrene–butadiene rubber (SBR) compounds was studied using low molecular weight polybutadiene (liquid PBD) with the high content of 1,2-unit. By adding the liquid PBD to the silica-filled SBR compound, the filler dispersion and flow property are improved. The cure time and cure rate become faster as

the 1,2-unit content of the liquid PBD increases for the compounds containing the liquid PBD. The crosslink density increases linearly with increase in the 1,2-unit content of the liquid PBD. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3135–3140, 2003

**Key words:** silica-filled SBR compound; liquid polybutadiene; dispersion

## INTRODUCTION

For a silica-filled rubber compound, the filler dispersion is a critical problem to solve to make good compounds. A good dispersibility in a silica-filled rubber compound improves tensile strength, elongation at break, abrasion resistance, and fatigue resistance.<sup>1</sup> Silica has a number of hydroxyl groups on the surface, which results in strong filler–filler interactions and adsorption of polar materials by hydrogen bonds. Because silica has the strong filler–filler interactions, the filler dispersion of a silica-filled rubber compound is generally worse than that of a carbon black-filled one. The polar surface of silica makes hydrogen bonds with polar materials in a rubber compound. Because the silica surface is acidic, it forms a strong hydrogen bond with basic materials. The adsorption of curatives by silica results in delay of the scorch time and reduction of the delta torque. In general, a silane coupling agent such as bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) is used to improve the filler dispersion and to prevent adsorption of curatives on the silica surface.<sup>2–4</sup> The silane coupling agent reacts with silanol on the surface of silica and a siloxane bond is formed. The silane molecule is bound to the silica surface.

In the previous work,<sup>5</sup> it was found that properties of a silica-filled styrene–butadiene rubber (SBR) compound were improved by adding acrylonitrile–butadiene rubber (NBR). Because NBR has basic nitrile groups (—CN), it can make a hydrogen bond with silica. The adsorbed NBR on the silica surface prevents adsorption of curatives. Because silica is polar, it is more compatible with polar materials than nonpolar ones. SBR consists of the four components of styrene, *cis*-1,4-, *trans*-1,4-, and 1,2-units. The 1,2-unit is more interactive with silica than the other components.<sup>6–8</sup> Polybutadiene (PBD) can have three different components of *cis*-1,4-, *trans*-1,4-, and 1,2-units. Low molecular weight PBD (liquid PBD) with high content of the 1,2-unit improves the filler dispersion in silica-filled SBR compounds.<sup>9</sup> In this study, influence of the liquid PBDs having different 1,2-unit contents on properties of silica-filled SBR compounds was investigated. Five liquid PBDs with different 1,2-unit contents were employed. In general, for the preparation of a filled rubber compound, rubbers are premixed before adding filler and processing aids are compounded after loading filler. In the present work, to use the liquid PBD as a processing aid, the liquid PBD was compounded after loading silica.

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## EXPERIMENTAL

TABLE I  
Formulation (phr)

Compound no.	1	2	3	4	5	6
SBR1500	100.0	100.0	100.0	100.0	100.0	100.0
Z175	60.0	60.0	60.0	60.0	60.0	60.0
Si69	4.8	4.8	4.8	4.8	4.8	4.8
Ricon 131	0.0	4.0	0.0	0.0	0.0	0.0
Ricon 134	0.0	0.0	4.0	0.0	0.0	0.0
Ricon 142	0.0	0.0	0.0	4.0	0.0	0.0
Ricon 150	0.0	0.0	0.0	0.0	4.0	0.0
Ricon 153	0.0	0.0	0.0	0.0	0.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0
ZnO	4.0	4.0	4.0	4.0	4.0	4.0
HPPD	2.0	2.0	2.0	2.0	2.0	2.0
Wax	2.0	2.0	2.0	2.0	2.0	2.0
TBBS	1.6	1.6	1.6	1.6	1.6	1.6
Sulfur	1.4	1.4	1.4	1.4	1.4	1.4

SBR1500: styrene-butadiene rubber with 23.5% of styrene content.

Ricon 131: liquid polybutadiene (PBD) with 28% of 1,2-unit and  $M_n$  of 4500.

Ricon 134: liquid polybutadiene (PBD) with 28% of 1,2-unit and  $M_n$  of 8000.

Ricon 142: liquid polybutadiene (PBD) with 55% of 1,2-unit and  $M_n$  of 3900.

Ricon 150: liquid polybutadiene (PBD) with 70% of 1,2-unit and  $M_n$  of 3900.

Ricon 153: liquid polybutadiene (PBD) with 85% of 1,2-unit and  $M_n$  of 4700.

Z175: silica

Si 69: silane coupling agent, bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT).

HPPD: *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine.

TBBS: *N*-*tert*-butyl-2-benzothiazole sulfenamide.

coupling agent (Si69, TESPT), cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), and curatives (TBBS and sulfur). Five type liquid PBDs with different 1,2-unit contents, Ricon 131, Ricon 134, Ricon 142, Ricon 150, and Ricon 153 of Sartomer Co., were employed. Their 1,2-unit contents are 28, 28, 55, 70, and 85%, respectively. Their average molecular weights ( $M_n$ ) are about 4500, 8000, 3900, 3900, and 4700, respectively. Z 175 (pH = 6.9, BET = 175 m<sup>2</sup>/g) of Kofran was used as silica. The formulations were given in Table I. Mixing of the compounds was performed in a Banbury type mixer at a rotor speed of 40 and 30 rpm for the master batch (MB) and final mixing (FM) stages, respectively. The initial temperatures of the mixer were 110 and 80°C for the MB and FM stages, respectively. The MB compounds were prepared as follow. (1) The SBR was loaded into the mixer

and premixed for 0.5 min. (2) The silica and silane coupling agent were compounded into the rubber for 2.0 min. (3) The liquid PBD and other ingredients (cure activators and antidegradants) were mixed for 2.0 min and the compounds were discharged. The FM compounds were prepared by mixing the curatives with the MB compounds for 2.0 min.

Mooney viscosities and Mooney cure times of the compounds were measured at 100 and 125°C, respectively, using a Mooney MV 2000 viscometer of Alpha Technologies. Contents of bound rubber were determined by extracting unbound materials such as ingredients and free rubbers with toluene for 7 days and *n*-hexane for 1 day and drying for 2 days at room temperature. Weights of the samples before and after the extraction were measured and the bound rubber contents were calculated. Die swell was measured with a Monsanto processability tester at 100°C. The capillary diameter was 1.4 mm (Length/Diameter = 10/1) and the piston rate was 12.7 mm/min. Die swell ratio (%) = 100 × ( $D_e - D_o$ )/ $D_o$ , where  $D_e$  and  $D_o$  are diameters of the extrudate and capillary, respectively.

The vulcanizates were prepared by curing at 160°C for 40 min. Crosslink densities of the samples were measured by a swelling method. Organic additives in the samples were removed by extracting with THF and *n*-hexane for 3 and 2 days, respectively, and they were dried for 2 days at room temperature. The weights of the organic material-extracted samples were measured. They were soaked in *n*-decane for 2 days and the weights of the swollen samples were measured. Physical properties of the vulcanizates were measured with a universal testing machine (Instron 6021).

## RESULTS AND DISCUSSION

Contents of bound rubber in filled rubber compounds are important because they affect physical properties of the vulcanizates.<sup>10,11</sup> The bound rubber contents were summarized in Table II. Bound rubber contents of the compounds containing the liquid PBDs are lower than that of the compound without the liquid PBD. This implies that the liquid PBD prevents the SBR from contacting the silica because it is more compatible than the SBR. There is no big difference in the bound rubber contents depending on the type of liquid PBD.

TABLE II  
Bound Rubber Content and Viscosity

Compound no.	1	2	3	4	5	6
Bound rubber content (%)	29.94	27.09	27.91	27.92	27.97	26.04
Mooney viscosity (ML1+4 at 100°C)	117.4	104.2	110.9	106.7	111.1	105.2

**TABLE III**  
MPT Test Results

Compound no.	1	2	3	4	5	6
Die Swell (%)	53	49	50	48	46	49
Stress (MPa) <sup>a</sup>	35.0	31.8	32.8	31.7	31.8	31.3

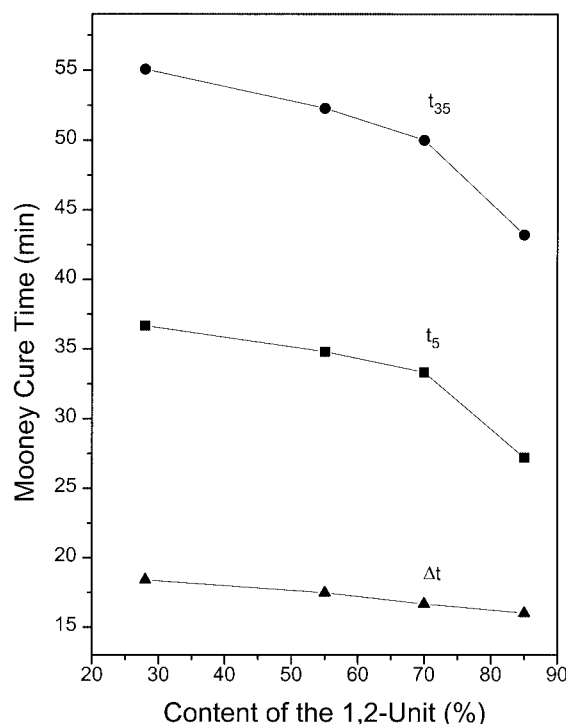
<sup>a</sup> Apparent stress at piston rate of 12.7 mm/min.

In the previous work,<sup>12</sup> improvement of the filler dispersion in silica-filled SBR compounds using liquid PBDs was investigated. Because the liquid PBDs were used as rubber, not a processing aid, the compounds were prepared by simultaneous loading of the liquid PBD and silica (the simultaneous load, the simultaneous loading compound). Bound rubber content of the compound prepared by the simultaneous load decreases with increasing the 1,2-unit content of liquid PBD.<sup>12</sup> In the present work, the liquid PBD was compounded after loading the silica (the separate load, the separate loading compound). Bound rubber contents of the separate loading compounds are higher than those of the simultaneous loading ones. For the separate loading compounds containing Ricon 131, Ricon 142, and Ricon 150, the bound rubber contents are 27.1, 27.9, and 28.0%, respectively, while those of the simultaneous loading compounds are 26.2, 25.9, and below 5%, respectively. This may be due to the longer contact time between the SBR and silica for the case of separate load. The 1,2-unit is much more interactive with silica than the *cis*-1,4-, and *trans*-1,4-, and styrene units.<sup>6-8</sup> Thus, for the simultaneous load, it is harder and harder for the SBR to contact with the silica and to form bound rubber as the 1,2-unit in the liquid PBD increases. However, for the separate load, the SBR has a sufficient time to contact with the silica (2.0 min) and to form bound rubber.

Viscosity of a rubber compound is a very important property in manufacturing of rubber goods. Filled rubber compounds should have proper viscosity levels to maintain the good extrusion and calendaring properties. Viscosities of the compounds containing the liquid PBD are lower than that of the compound without the liquid PBD by about 6–13 MU (Mooney unit) as listed in Table II. Variation of the viscosity with the 1,2-unit content does not show a specific trend. For the compounds containing the liquid PBD with the same 1,2-unit content and the different molecular weight (Ricon 131 and Ricon 134), viscosity of

**TABLE IV**  
Mooney Cure Times at 125°C

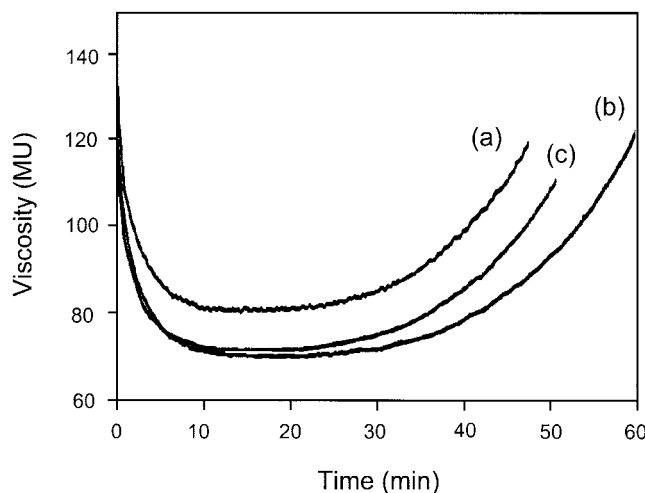
Compound no.	1	2	3	4	5	6
$t_5$ (min)	30.67	36.67	35.20	34.80	33.33	27.20
$t_{35}$ (min)	46.53	55.07	52.27	52.27	50.00	43.20
$\Delta t$ (min)	15.86	18.40	17.07	17.47	16.67	16.00



**Figure 1** Variation of the Mooney cure times as a function of the 1,2-unit content in the PBD.

the compound containing the higher molecular weight liquid PBD is higher than that of the compound containing the lower one.

Die swell ratios of the compounds containing the liquid PBD are smaller than that of the compound without the liquid PBD (Table III). This can be explained with the cavity existed between the silica and SBR. For the MPT test, pressure is applied to the sample in the reservoir to extrudate through the capillary, which can be converted to apparent stress.



**Figure 2** Rheological behaviors for measuring the Mooney cure times. (a), (b), and (c) are the Compounds 1, 2, and 5, respectively.

**TABLE V**  
Crosslink Density (Reciprocal Swelling Ratio,  $1/Q$ )

Compound no.	1	2	3	4	5	6
Before Aging	1.826	1.690	1.734	1.729	1.751	1.769
After Aging <sup>a</sup>	2.111	1.954	1.963	1.973	2.033	2.034

<sup>a</sup> 90°C for 3 days.

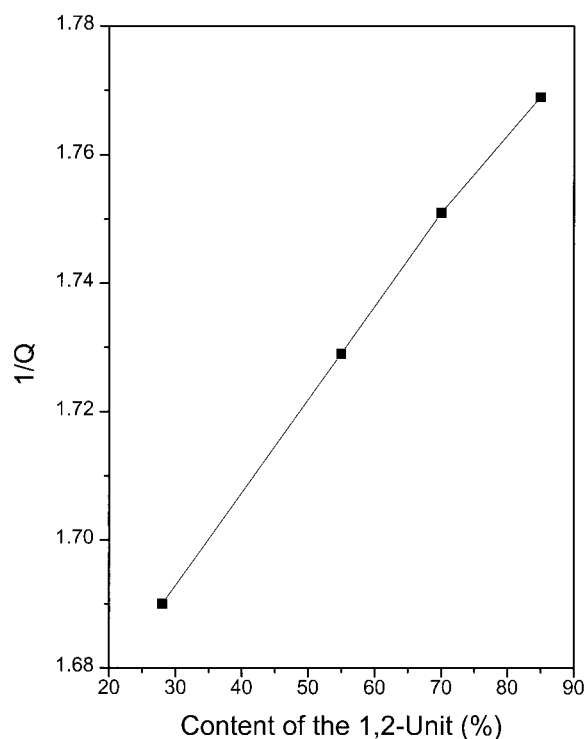
When the compound is pushed into the capillary by the piston, voids in the compound may be filled up with materials by the force. When the compound exits the capillary, the applied pressure is released and the compound is relaxed. After extruding, the deformed rubber is stabilized and some of compulsorily filled voids will be recovered. This may be a cause of the die swell. Thus, the die swell ratio will be higher for a compound with the larger void volume compared with a compound with the smaller one. The void volume will be bigger when rubber is not compatible with filler.

Mooney cure times,  $t_5$  (Mooney scorch time),  $t_{35}$ , and  $\Delta t$  (cure rate index), were measured at 125°C to investigate the cure characteristics. The  $t_5$  and  $t_{35}$  mean the times taken for the viscosity to reach from the minimum point to increases of 5 and 35 MU, respectively. The  $\Delta t$  is the difference between the  $t_{35}$  and  $t_5$ . The reciprocal of the  $\Delta t$  is used as a cure rate. The bigger the  $\Delta t$ , the slower the cure rate. By adding the liquid PBD, the  $t_5$ ,  $t_{35}$ , and  $\Delta t$  become slower (Table IV). This may be due to the much lower molecular weight of the liquid PBD compared to the SBR and the prevention of crosslinking reactions between the SBRs or between the SBR and silica by the liquid PBD. The liquid PBD molecules between the SBRs can prevent the crosslinking reactions between SBRs. The silane coupling agent reacts with silica and rubber to form a crosslink between them. The liquid PBD molecules around silica prevents the SBR molecules from contacting with silica; thus, the crosslinking reactions between SBR and silica through the silane coupling agent will be prevented. Cure times of the separate loading compounds are faster than those of the simultaneous ones. The  $t_5$  of the separate loading compounds containing Ricon 131, Ricon 142, and Ricon 150 are 36.67, 34.80, and 33.33 min, respectively, while those of the simultaneous ones<sup>12</sup> are 37.47, 35.20, and 37.60 min, respectively. This implies that the crosslinking reactions are prevented less for the separate load than for the simultaneous load.

For the compounds containing the liquid PBD, the cure times become faster with increasing the 1,2-unit content. To investigate this trend more clear, variation of the cure times was plotted in Figure 1 except the compound containing Ricon 134, because the  $M_n$  of Ricon 134 is much larger than the other PBDs. Figure 1 shows clear the decreased trend of the cure times

with the 1,2-unit content. Especially, the cure rate,  $\Delta t$ , decreases linearly with increasing the 1,2-unit content. The linear curve fitting equation for the  $\Delta t$  variation is  $y = -0.0424x + 19.658$  (correlation coefficient =  $-0.995$ ). This means that the cure rate decreases by 0.4 min for every 10% increase of 1,2-unit content. The cure time and cure rate of the compound containing the higher molecular weight PBD (Ricon 134) are faster than those of the compound containing the lower one (Ricon 131) when the 1,2-unit content is the same (Table IV).

Choi studied the filler–filler interaction of silica using abnormal rheological behaviors.<sup>13,14</sup> In general, filled rubber compounds show smooth rheological behaviors in the measurement of Mooney viscosity or Mooney scorch time. The compounds filled with high content of silica show abnormal rheological behaviors, which the viscosity increases suddenly and then decreases at a certain point during the measurement.<sup>14</sup> Figure 2 gives variation of the rheological behaviors during the measurement of Mooney scorch time. Figure 2(a) is the compound without the liquid PBD and Figure 2(b) and (c) shows the compounds containing the liquid PBD. The compound without the liquid PBD shows clearly abnormal rheological behaviors. The viscosity increases suddenly and then decreases, and this behavior is repeated. This is due to the poor filler dispersion resulting from the strong filler–filler interaction. This abnormal rheological behavior is di-



**Figure 3** Variation of the reciprocal swelling ratio ( $1/Q$ ) as a function of the 1,2-unit content in the PBD.

TABLE VI  
Physical Properties

Compound No.	1	2	3	4	5	6
Before aging						
Hardness (Shore A)	73.0	71.0	72.0	72.0	73.0	73.0
50% Modulus (kg/cm <sup>2</sup> )	20.5	18.4	19.5	19.5	19.6	19.7
100% Modulus (kg/cm <sup>2</sup> )	32.4	27.8	31.1	30.3	30.1	31.2
200% Modulus (kg/cm <sup>2</sup> )	76.3	61.1	71.5	69.4	69.4	73.3
300% Modulus (kg/cm <sup>2</sup> )	139.5	108.8	127.2	123.0	125.5	132.7
Tensile strength (kg/cm <sup>2</sup> )	245.2	232.4	232.3	241.4	246.3	267.1
Elongation at break (%)	451.5	505.0	465.4	484.0	484.2	498.1
After aging <sup>a</sup>						
Hardness (Shore A)	76.0	75.0	76.0	76.0	77.0	77.0
50% Modulus (kg/cm <sup>2</sup> )	24.0	21.6	22.9	22.3	23.0	23.2
100% Modulus (kg/cm <sup>2</sup> )	42.1	36.5	40.8	27.1	41.0	39.7
200% Modulus (kg/cm <sup>2</sup> )	104.9	90.3	98.9	91.6	100.8	98.3
300% Modulus (kg/cm <sup>2</sup> )	185.2	162.2	174.1	166.8	180.1	173.7
Tensile strength (kg/cm <sup>2</sup> )	215.7	230.3	211.8	231.1	220.8	230.7
Elongation at break (%)	337.9	389.2	347.7	383.5	351.4	372.7

<sup>a</sup> 90°C for 3 days

minished by adding the liquid PBD. This implies that the liquid PBD improves the silica dispersion.

Crosslink densities of the vulcanizates before and after the thermal aging for 3 days at 90°C are listed in Table V. The swelling ratio was calculated:  $Q = 100 \times (W_s - W_u)/W_u$ , where  $W_s$  and  $W_u$  are weights of the swollen and unswollen samples. The reciprocal swelling value,  $1/Q$ , was used as the crosslink density.<sup>15</sup> The crosslink densities of the compounds containing the liquid PBD are lower than that of the compound without the liquid PBD. This can be also explained with the prevention of crosslinking reactions between the SBRs or between the SBR and silica by the liquid PBD as discussed previously. The crosslink density increases after the thermal aging. This is due to the formation of new crosslinks. Free sulfur and residues of curatives react with rubbers to form new crosslinks.<sup>16-18</sup> The crosslink density increases linearly with increase in the 1,2-unit content when the PBD molecular weights are nearly the same as shown in Figure 3. The linear curve fitting equation for the crosslink density variation is  $y = 0.0014x + 1.652$  (correlation coefficient = 0.999). This means that the  $1/Q$  increases by 0.014 with increase of every 10% of 1,2-unit content. The crosslink density of the compound containing the higher molecular weight PBD (Ricon 134) is higher than those of the compound containing the lower one (Ricon 131) when the 1,2-unit content is the same.

Physical properties of the vulcanizates before and after the thermal aging are summarized in Table VI. Hardness and modulus of the vulcanizates containing the liquid PBD are lower than that of the vulcanizate without the liquid PBD. This is due to the crosslink density. Crosslink densities of the formers are lower than that of the latter as discussed previously. Modu-

lus of a rubber vulcanizate is a proportional property to the degree of crosslink density.<sup>19</sup> Elongation at break becomes longer by adding the liquid PBD. This is also due to the crosslink density. Elongation at break of a rubber vulcanizate is an inversely proportional property to the degree of crosslink density.<sup>19</sup> For the vulcanizates containing the liquid PBD with the nearly same molecular weight before the thermal aging, the modulus and tensile strength increases with increase in the 1,2-unit content. This can also be explained by the crosslink density. The crosslink density increases with increase in the 1,2-unit content, as shown in Figure 3. The hardness and modulus increase after the thermal aging, while the tensile strength and elongation at break decrease. This is due to the increased crosslink density during the thermal aging.

## CONCLUSIONS

Filler dispersion of the silica-filled SBR compound is improved by adding the liquid PBD. For the compounds containing the liquid PBD, the cure time and cure rate become faster as the 1,2-unit content of the liquid PBD increases. Especially, the cure rate increases linearly with increasing the 1,2-unit content. The crosslink density also increases linearly with increase in the 1,2-unit content for the vulcanizates containing the liquid PBD. The modulus and tensile strength increase with increase in the 1,2-unit content. It is found that, for the preparation of silica-filled SBR compounds containing the liquid PBD, the compounds prepared by the separate load have better properties than the compounds prepared by the simultaneous one.

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