

# Mechanical Properties of Styrene–Butadiene–Styrene Block Copolymer Composites Filled with Calcium Carbonate Treated by Liquid Polybutadienes

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**ABSTRACT:** The factors influencing the mechanical properties of styrene–butadiene–styrene block copolymer (SBS) composites filled with liquid polybutadiene (LB)-surface-treated calcium carbonate (CaCO<sub>3</sub>) were investigated with respect to the molecular structure of the LB, the amount of the LB adsorbed on the CaCO<sub>3</sub> surface, the heat treatment conditions, and the surface treatment method. The mechanical properties, such as the modulus, tensile strength at break, tear strength, storage modulus, and tension set, of the SBS composites were improved remarkably through the filling of CaCO<sub>3</sub> surface-treated with a carboxylated LB

with a high content of 1,2-double bonds. The heat treatment of LB–CaCO<sub>3</sub> in air was also effective in enhancing such properties. When SBS, CaCO<sub>3</sub>, and LB were directly blended (with the integral blend method), secondary aggregation of CaCO<sub>3</sub> took place, and the mechanical properties of the composite were significantly lower. In the integral blend method, LB functioned as a plasticizer. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3661–3670, 2009

**Key words:** composites; elastomers; fillers; mechanical properties

## INTRODUCTION

A thermoplastic elastomer (TPE) is a rubbery material with properties and functional performance very similar to those of a conventional thermoset rubber, yet it can be fabricated in the molten state as a thermoplastic.<sup>1</sup> Presently, the transition from vulcanized rubbers to environmentally friendly TPEs is underway. However, TPEs have some disadvantages, including poor heat resistance and compression set, because the crosslinking is not chemical but physical.<sup>2</sup> Thus, the fields in which TPEs can be used as substitutes for rubber are limited. With a view toward increasing the use of TPEs, there have been numerous research reports in recent years concerning the mechanical properties of TPE composites filled with various short fibers and organoclays. When poly(ethylene terephthalate) fibers are used as fillers in styrene–butadiene–styrene block copolymers (SBSs)<sup>3,4</sup> and olefinic thermoplastic elastomers (TPOs),<sup>5</sup> the mechanical properties of the composites are improved. Similar reinforcement effects of fibers have been reported for a cellulose fiber/dynamically vulcanized TPO composite system,<sup>2</sup> a carbon fiber/SBS composite system,<sup>6</sup> an aramid fiber/styrene–

(ethylene–butylene)–styrene composite system,<sup>7</sup> and a glass fiber/TPO composite system.<sup>5</sup> In practical applications for manufacturing high-performance goods with complicated dies and molds, however, the extrusion and injection molding of TPEs filled with fibers become difficult because of the diminished fluidity and fiber orientation. Moreover, from the viewpoint of recycling, the mechanical properties become lower because of the cutting into small fibers with a low aspect ratio by shearing stress during remixing. On the other hand, organoclays have high dispersibility in the TPE matrix, and the thermal properties of TPE nanocomposites filled with organoclays are remarkably enhanced,<sup>8–11</sup> but organoclays are quite expensive, and the fabrication process is also complicated in comparison with conventional blending methods. Nowadays, a simple process for preparing a reactive filler for TPE is strongly desired.

Calcium carbonate (CaCO<sub>3</sub>) is one of the most inexpensive and recyclable natural resources with the highest reserves on earth, and it is a white filler widely used in polymer processing. However, the surface chemical activity of CaCO<sub>3</sub> is poor. Therefore, it is often used as a filler for cost reduction rather than as a reinforcing agent. To use CaCO<sub>3</sub> as a reinforcing agent, surface treatment with coupling agents<sup>12–15</sup> or organic acids<sup>16–19</sup> is absolutely necessary. Thus, there are numerous reports concerning

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TABLE I  
Structure and Properties of the SBS Matrix

Code	Density	Styrene/Butadiene (wt %)	Hardness (A)	$M_{300}$ (MPa)	Breaking	
					Strength (MPa)	Extension (%)
SBS	0.94	24/76	55	2.0	16	1040

$$-(\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\text{CH}})_a-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_b-(\underset{\text{C}_6\text{H}_5}{\text{CH}}-\text{CH}_2)_c-$$

the mechanical properties of polyolefin composites filled with various surface-treated  $\text{CaCO}_3$  particles, but there are few reports on surface treatment with an oligomer.

Liquid polybutadiene (LB) resins have high unsaturation, which is mainly present in the form of pendant vinyl groups, and they undergo reactions very similar to those of unsaturated elastomers. High-vinyl LBs cure into hard, glasslike polymers. Because they are unsaturated hydrocarbons like the majority of elastomers, however, LBs are compatible with these elastomers and can be chemically modified easily. Numerous new LBs with carboxyl, hydroxyl, and amino terminal functionalities have been developed in recent years, and they are widely used as various modifiers.

In this study, we examined LBs as surface modifiers. The influence of factors such as the molecular structure of the LB, the amount of the LB adsorbed on the  $\text{CaCO}_3$  surface, and the heat treatment conditions on the mechanical properties of SBS composites filled with LB-surface-treated  $\text{CaCO}_3$  was investigated. The modification of SBS by the integral blend method, in which an LB was directly added to a molten mixture of  $\text{CaCO}_3$  and SBS, was also investigated.

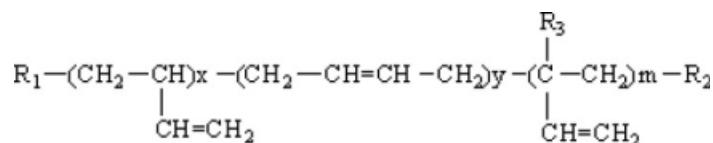
## EXPERIMENTAL

### Materials

$\text{CaCO}_3$  in the form of an agglomerate with cubic particles 50 nm in diameter (Maruo Calcium Co., Ltd., Akashi, Japan) was used. The average particle size and specific surface area of the agglomerate were 2.6  $\mu\text{m}$  and 13.2  $\text{m}^2/\text{g}$ , respectively. As a TPE, SBS (Kraton Polymers Japan Co., Ltd., Tokyo, Japan), in which styrene segments were hard domains and butadiene segments were soft domains, was used. The properties are summarized in Table I. As surface treatment agents for  $\text{CaCO}_3$ , six LBs, shown in Table II, were used. LB1, LB2, LB3, and LB4 were purchased from Nippon Soda Co., Ltd., Tokyo, Japan; LB5 was purchased from Ube Industries, Ltd., Tokyo, Japan; and LB6 was purchased from Ricon Resins, Inc. (Gand Junction, CO) The content of 1,2-double bonds in LB1, estimated by IR measurement according to the literature,<sup>20</sup> is 90.1%. LB2 is a derivative of LB1, the terminals of which are carboxylated. LB3 is a terminal-carboxylated saturated derivative of LB2 obtained by hydrogenation. LB4 is an LB2 derivative in which 2.5 maleic anhydride groups, on average, are introduced into the molecular

TABLE II  
Structural Properties of LBs Used as Surface Modifiers for  $\text{CaCO}_3$

Code	Molecular structure					Molecular weight ( $M_n$ )	Functional group number ( $\text{mol}^{-1}$ )
	End group $R_1$	X	Y	Side group $R_3$	End group $R_2$		
LBR1	$\text{CH}_3-$	90.1	9.9	—	$\text{CH}_3-$	1100	0.0
LBR2	$\text{HOOC}-$	88.7	11.3	—	$\text{HOOC}-$	1375	2.2
LBR3	$\text{HOOC}-$	0.0	0.0	—	$\text{HOOC}-$	1400	2.0
LBR4	$\text{CH}_3-$	87.2	12.8	Maleic anhydride	$\text{CH}_3-$	1400	2.5
LBR5	$\text{HOOC}-$	18.0	82.0	—	$\text{HOOC}-$	4800	2.0
LBR6	$\text{CH}_3-$	25.5	74.5	Maleic anhydride	$\text{CH}_3-$	5000	10.5



chain of LB2. There are abundant 1,4-trans double bonds in LB5, which is a terminal-carboxylated modified derivative with a molecular weight 3.5 times as high as that of LB2. LB6 is a derivative of LB5 that contains about the same number of 1,4-trans double bonds and has a similar molecular weight, but it contains 10.5 maleic anhydride groups on average.

## Methods

### Surface treatment of CaCO<sub>3</sub>

The surface treatment of CaCO<sub>3</sub> was carried out according to the following procedure:

1. Preparation of the LB treatment solution. A toluene solution of LB was prepared through the addition of 300 mL of toluene and 1–7 g of LB to a 500-mL beaker and stirring at 35°C for 30 min.
2. Surface treatment. To the LB toluene solution, 100 g of CaCO<sub>3</sub> was added, and the solution was stirred for 3 h; then, toluene was removed with an evaporator.
3. Heat treatment. LB-treated CaCO<sub>3</sub> (LB–CaCO<sub>3</sub>) was dried at room temperature for 24 h and then was heat-treated in an air oven or vacuum oven at temperatures ranging from 120 to 210°C for a period of 30–240 min.
4. Grinding and fractionation. After the heat treatment, LB–CaCO<sub>3</sub> was ground with a mortar and pestle and fractionated with a 150-mesh sieve. Particles of 150 mesh or less were used as fillers.

### Preparation of the specimens

SBS was rolled at 160°C on an open roll surface with an adjusted gap of 1 mm. Subsequently, a filler was added, and it was kneaded for 6 min; the roll gap was adjusted to 1.5 or 2.5 mm to fabricate sheets. Sheets with a thickness of 1 mm for dynamic viscoelasticity measurements and 2 mm for the measurement of the mechanical properties were formed with a press at 170°C and 1.47 kN, respectively.

### Measurement of the mechanical properties

*Tensile test and tear test.* The measurements were conducted according to JIS K 6251 and JIS K 6252 with a tensile tester (AG-10k NI, Shimadzu Corp., Kyoto, Japan) at a test speed of 500 mm/min at 23°C. The average of three results is reported.

*Test for tension set.* According to JIS K 6273, a dumbbell no. 3 test piece (stipulated in JIS K 6251) was elongated at a tensile speed of 10 mm/min to 50% strain at 23°C and kept there for 1 h. The test piece was removed from the tester and allowed to stand for 1 h, and then the tension set was measured. The average of three results is reported.

*Dynamic viscoelasticity measurement.* The dynamic storage modulus ( $E'$ ) was measured with a viscoelasticity measurement apparatus (DVE-V4 FT Rheospectra, Rheology Co., Ltd., Tokyo, Japan) with a multifrequency film-tension module. The specimens ( $1.0 \times 5.0 \times 20 \text{ mm}^3$ ) were cut from the center of the samples. The temperature range for measurement was –100 to 160°C, and the frequency, displacement amplitude, and heating rate were 110 Hz, 0.15%, and 3°C/min, respectively.

*Surface hardness test.* According to JIS K 5600, LB with a thickness of about 0.2 mm was applied to a glass plate and heated for a predefined period in an air oven or vacuum oven at a predefined temperature. The sample was allowed to stand at 23°C for 1 h, and then the pencil hardness was measured.

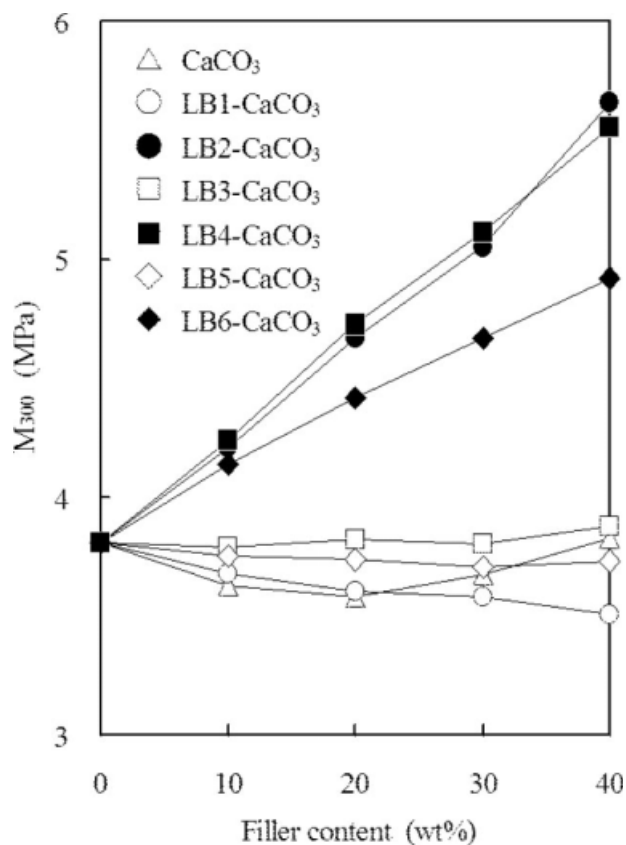
*Fourier transform infrared (FTIR) measurement.* IR absorption spectra of LB and LB–CaCO<sub>3</sub> were measured with an FTIR spectrophotometer (FT/IR-410, Jasco) by the KBr tablet method.

*Observation by scanning electron microscopy (SEM).* Tensile fracture surfaces of the composites were sputtered with gold/palladium and observed with a scanning electron microscope (S-2360N, Hitachi, Tokyo, Japan).

## RESULTS AND DISCUSSION

### Effects of the LB molecular structures

The changes in the modulus at 300% elongation ( $M_{300}$ ) due to the filler content in SBS composites filled with untreated CaCO<sub>3</sub> and CaCO<sub>3</sub> surface-treated with various LBs (LB–CaCO<sub>3</sub>/SBS) are shown in Figure 1.  $M_{300}$  of the SBS composites filled with LB1- and LB3-treated CaCO<sub>3</sub> (LB1–CaCO<sub>3</sub> and LB3–CaCO<sub>3</sub>) was almost constant with an increase in the filler content in the same way as that of the SBS composite filled with untreated CaCO<sub>3</sub> (CaCO<sub>3</sub>/SBS). The terminal methyl groups of LB1 are not reactive, and LB1 only physisorbs on the CaCO<sub>3</sub> surface. Similarly, LB3 has no double bonds in the molecular chain, and no reaction takes place with SBS. As a result, LB1–CaCO<sub>3</sub> and LB3–CaCO<sub>3</sub> did not exhibit SBS reinforcement capability. On the other hand,  $M_{300}$  of the SBS composite filled with LB2–CaCO<sub>3</sub> drastically improved with an increase in the filler content. It is thought that the reinforcing effect was displayed because the carboxyl groups introduced onto the LB2 terminals and CaCO<sub>3</sub> formed chemical bonds, and the compatibility with SBS was improved. CaCO<sub>3</sub> modified with LB4, in which maleic anhydride groups are introduced into the molecular chain, displayed an SBS reinforcing effect similar to that of LB2–CaCO<sub>3</sub>. However, LB5-modified CaCO<sub>3</sub> (LB5–CaCO<sub>3</sub>), in which LB5 contains terminal carboxyl groups like LB2, displayed very little SBS reinforcing effect. The molecular

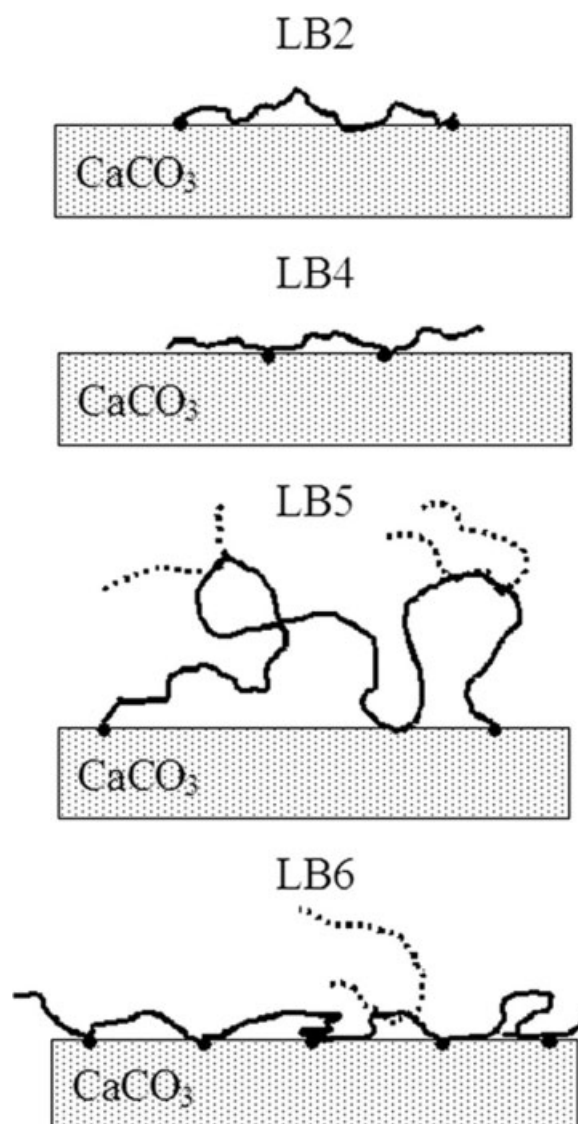


**Figure 1** Effect of the filler content and LB type on  $M_{300}$  for SBS composites filled with untreated  $\text{CaCO}_3$  and  $\text{CaCO}_3$  treated with various LBs.

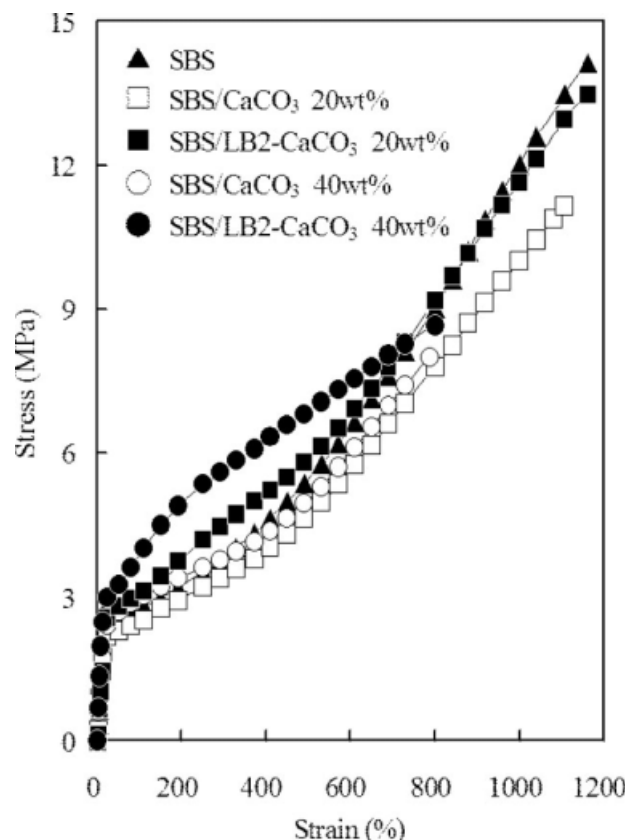
weight of LB5 is 3.4 times as high as that of LB2. Even if both terminals had reacted with calcium ions, the main chain would have formed a loose molecular loop. The loose molecular loop may have entangled with free LB5 molecules. As a result, the  $\text{CaCO}_3$  surface was covered with a thicker organic layer than in the case of LB2- $\text{CaCO}_3$ . In addition, the content of 1,2-double bonds in LB5 is small. As a result, the crosslink density of the surface organic layer was low after heating. Thus, even if LB5- $\text{CaCO}_3$  had been filled in SBS, the modulus of the composite probably would not have increased. This is supported by the high modulus of the LB6- $\text{CaCO}_3$ /SBS composite, in which SBS was filled with LB6- $\text{CaCO}_3$ . LB6 has approximately the same molecular weight as LB5 but contains about 10 maleic anhydride groups in the molecular chain. Therefore, it is believed that the carboxyl groups generated by the hydrolysis of maleic acid in the molecular chain of LB6 react with calcium ions at multiple points and that a tight organic layer is formed on the  $\text{CaCO}_3$  surface. As a result, LB6- $\text{CaCO}_3$  seemed to interact strongly with SBS. In Figure 2, the structures of  $\text{CaCO}_3$  surfaces treated with LB2, LB4, LB5, and LB6 are schematically represented. As is clear from the figure, for the improvement of the modulus of the SBS composite filled with LB-treated  $\text{CaCO}_3$ , the introduc-

tion of carboxyl groups suitable to the molecular weight of LB, which is used as a treatment agent, and the content of 1,2-double bonds are important.

Figure 3 shows stress-strain curves for the SBS composite filled with untreated  $\text{CaCO}_3$  and for the SBS composites filled with 20 or 40 wt % LB2- $\text{CaCO}_3$ . A comparison of the composites with the same filler content shows that the stress of LB2- $\text{CaCO}_3$ /SBS was significantly greater than that of  $\text{CaCO}_3$ /SBS. The stress of  $\text{CaCO}_3$ /SBS was lower than that of the matrix until the elongation at break. On the other hand, the stresses of LB2- $\text{CaCO}_3$ /SBS with filler contents of 20 and 40 wt % were larger than those of the matrix up to 900 and 780%, respectively. The stress and elongation at break of composites were dependent on the content of polymers that were able to stretch freely. The more free polymer there was, the larger the stress and elongation at break of the composite were. Therefore, a



**Figure 2** Adsorption models of LB on  $\text{CaCO}_3$ .



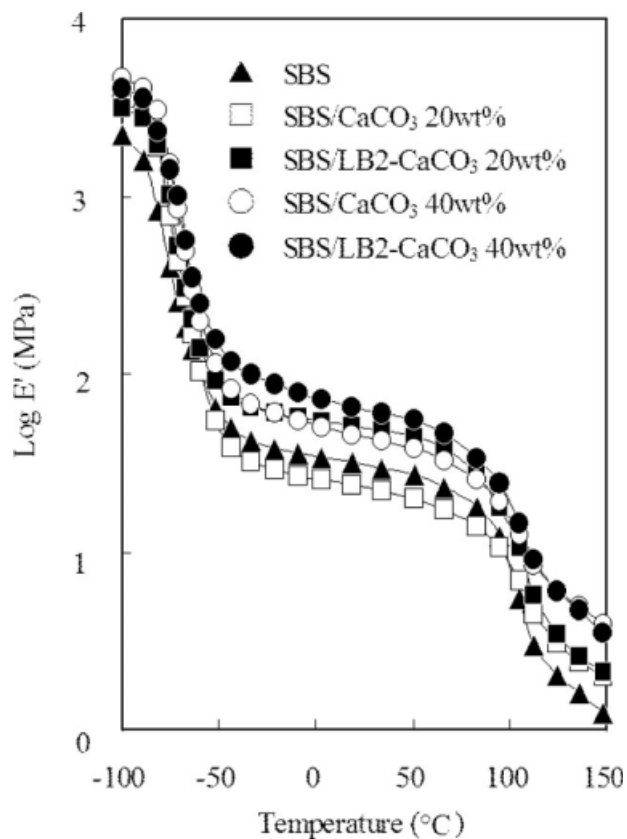
**Figure 3** Stress-strain curves for the SBS matrix and composites filled with untreated  $\text{CaCO}_3$  and treated  $\text{CaCO}_3$ .

remarkable decrease in the stress and elongation for the composite with a filler content of 40 wt % indicated that the polymer chains in the matrix were restrained with fillers.

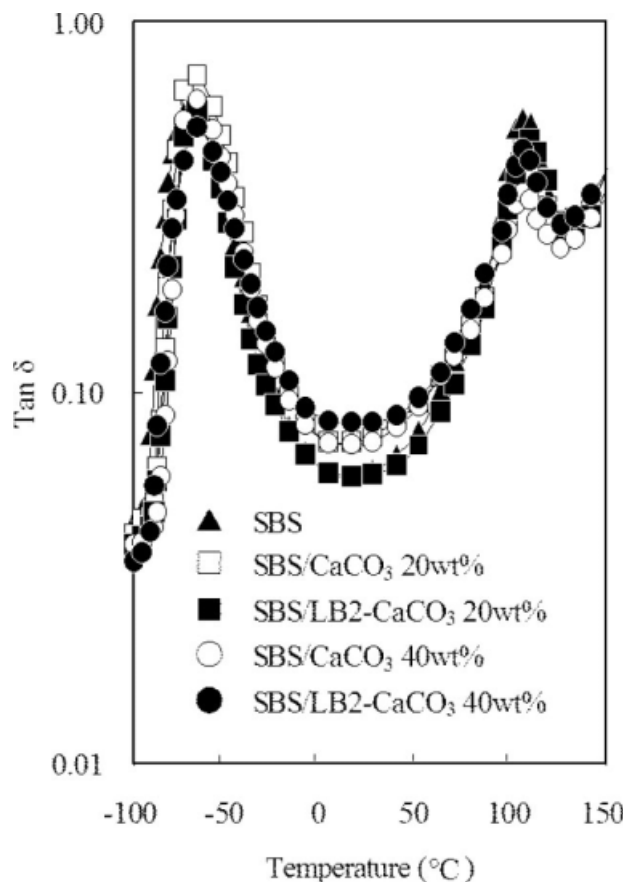
Figure 4 shows  $E'$  for the SBS matrix and the composites filled with  $\text{CaCO}_3$  and  $\text{LB2-CaCO}_3$  within the temperature range of  $-100$  to  $150^\circ\text{C}$ .  $E'$  of the composite filled with 20 wt %  $\text{CaCO}_3$  was lower than that of the matrix, but  $E'$  of the composite filled with 40 wt %  $\text{CaCO}_3$  was higher. The composites filled with  $\text{LB2-CaCO}_3$  showed an enhanced  $E'$  value in the rubbery region in comparison with the composite filled with  $\text{CaCO}_3$  with the same filler content. Comparative plots of the loss factor ( $\tan \delta$ ) against the temperature, which ranged from  $-100$  to  $150^\circ\text{C}$ , for the SBS matrix and the composites filled with  $\text{CaCO}_3$  and  $\text{LB2-CaCO}_3$  are shown in Figure 5. Because SBS is a block copolymer, two distinct glass-transition temperatures ( $T_g$ 's), one around  $-70^\circ\text{C}$  for the soft segment (polybutadiene domains: rubber phase) and another around  $106^\circ\text{C}$  for the hard segment (polystyrene domains: plastic phase), could be observed for both the neat SBS and its composites. The  $T_g$  values and the values of  $\tan \delta$  at each  $T_g$  are summarized in Table III. For  $\text{CaCO}_3/\text{SBS}$ , the  $T_g$  values shifted toward the high-temperature side compared to those of neat SBS, and the  $\tan \delta$  values at

each  $T_g$  decreased with an increase in the filler content. On the other hand,  $T_g$  for the rubber phase of  $\text{LB2-CaCO}_3/\text{SBS}$  was higher and the value of  $\tan \delta$  was further reduced in comparison with those of  $\text{CaCO}_3/\text{SBS}$ . This may be attributed to the better compatibility between the polybutadiene domains of SBS and LB2 in  $\text{LB2-CaCO}_3$  and the better dispersion of  $\text{LB2-CaCO}_3$  in the matrix. However, the  $T_g$  values for the plastic phase were almost equal to those for  $\text{CaCO}_3/\text{SBS}$  with the same filler content. Moreover, the values of  $\tan \delta$  were higher compared to those for  $\text{CaCO}_3/\text{SBS}$ . This may be due to the poor compatibility between the polystyrene domains with polarity and LB2 of  $\text{LB2-CaCO}_3$ .

Figure 6 shows a schematic representation of the surface modification mechanism of  $\text{CaCO}_3$  with LB2 and also the SBS reinforcing mechanism. On the surface of  $\text{CaCO}_3$ , adsorbed water is present. The adsorbed water reacts with  $\text{CO}_2$  in the atmosphere and forms  $\text{H}_2\text{CO}_3$ , and part of the  $\text{CaCO}_3$  surface is ionized as shown in Figure 6(a).  $\text{Ca}^{2+}$  ions and carboxyl groups of the LB2 terminals form partial neutral salts and strong bonds, as shown in Figure 6(b), because of electrostatic interactions.<sup>21</sup> Upon heating, LB2 molecules introduced onto the  $\text{CaCO}_3$  surface generate intermolecular bridges through the reaction

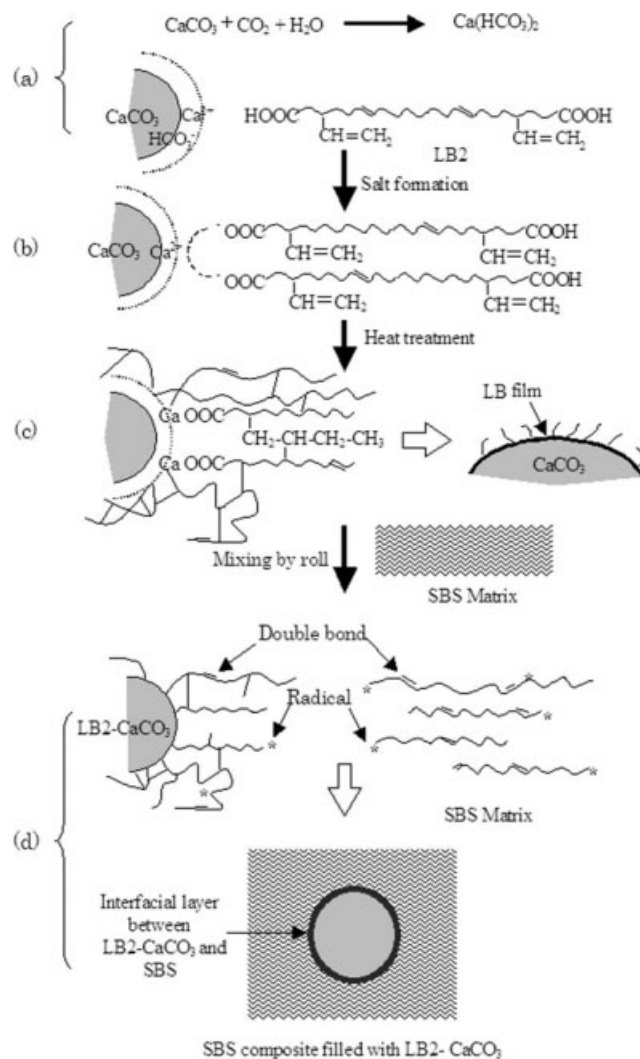


**Figure 4** Temperature dependence of  $E'$  for the SBS matrix and composites filled with untreated  $\text{CaCO}_3$  and treated  $\text{CaCO}_3$ .



**Figure 5** Comparative  $\tan \delta$  traces for the SBS matrix and composites filled with untreated  $\text{CaCO}_3$  and treated  $\text{CaCO}_3$ .

of double bonds on the side chains. Thus, a thin film (organic layer) that is highly compatible and reactive with SBS is formed on the  $\text{CaCO}_3$  surface, as shown in Figure 6(c). When LB2- $\text{CaCO}_3$  is added to SBS and kneaded, elastomer or LB2 free radicals generated through mechanical shearing react with unreacted double bonds on the LB2- $\text{CaCO}_3$  surface. Thus, chemical bonds are formed along the interface of LB2- $\text{CaCO}_3$ /SBS, as shown in Figure 6(d). As a



**Figure 6** Schematic representation of (a–c) the surface modification mechanism of  $\text{CaCO}_3$  with LB2 and (d) the interaction between SBS and LB2- $\text{CaCO}_3$ .

result, the mechanical properties of the composite are improved.

#### Effect of the amount of adsorbed LB

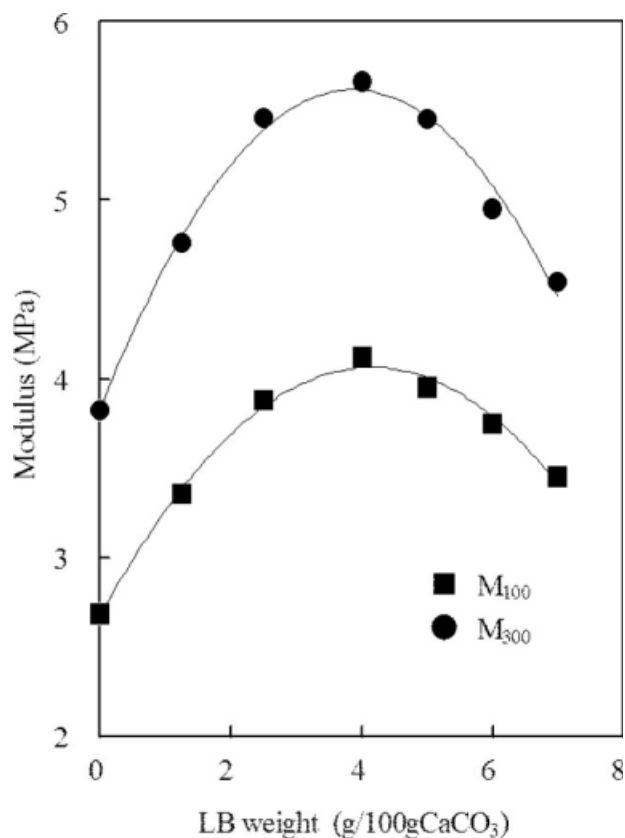
It has been reported that the amount of a surface treatment agent that adsorbs onto the filler surface has a great effect on the reinforcing effect of the filler.<sup>22</sup> In this study, the amount of LB2 in LB2- $\text{CaCO}_3$  was determined with thermogravimetry (TG) measurements. Figure 7 shows the relationship between the amount of LB2, which was used as a surface treatment agent for  $\text{CaCO}_3$ , and the moduli [modulus at 100% elongation ( $M_{100}$ ) and  $M_{300}$ ] of the LB2- $\text{CaCO}_3$ /SBS composite. Both  $M_{100}$  and  $M_{300}$  increased with an increase in the amount of adsorbed LB2. The maximum value was reached when 4 g of LB2 was added to 100 g of  $\text{CaCO}_3$ . At this point, the  $\text{CaCO}_3$  surface was considered to be

**TABLE III**

$T_g$  and  $\tan \delta$  Values for the SBS Matrix and Composites Filled with Untreated and Treated  $\text{CaCO}_3$

Sample	$T_{gB}$ (°C)	$\tan \delta_B$	$T_{gS}$ (°C)	$\tan \delta_S$
SBS	-71.6	0.67	106.1	0.55
$\text{CaCO}_3$ (20 wt %)/SBS	-67.3	0.73	108.3	0.38
LB2- $\text{CaCO}_3$ (20 wt %)/SBS	-66.0	0.57	108.4	0.49
$\text{CaCO}_3$ (40 wt %)/SBS	-67.7	0.62	107.7	0.34
LB2- $\text{CaCO}_3$ (40 wt %)/SBS	-66.0	0.52	108.0	0.45

$\tan \delta_B$  = highest loss factor corresponding to  $T_{gB}$ ;  $\tan \delta_S$  = highest loss factor corresponding to  $T_{gS}$ ;  $T_{gB}$  = glass-transition temperature of the polybutadiene segment of the system;  $T_{gS}$  = glass-transition temperature of the polystyrene segment of the system.



**Figure 7** Effect of the amount of adsorbed LB on the modulus of SBS composites filled with 40 wt % LB2-CaCO<sub>3</sub>.

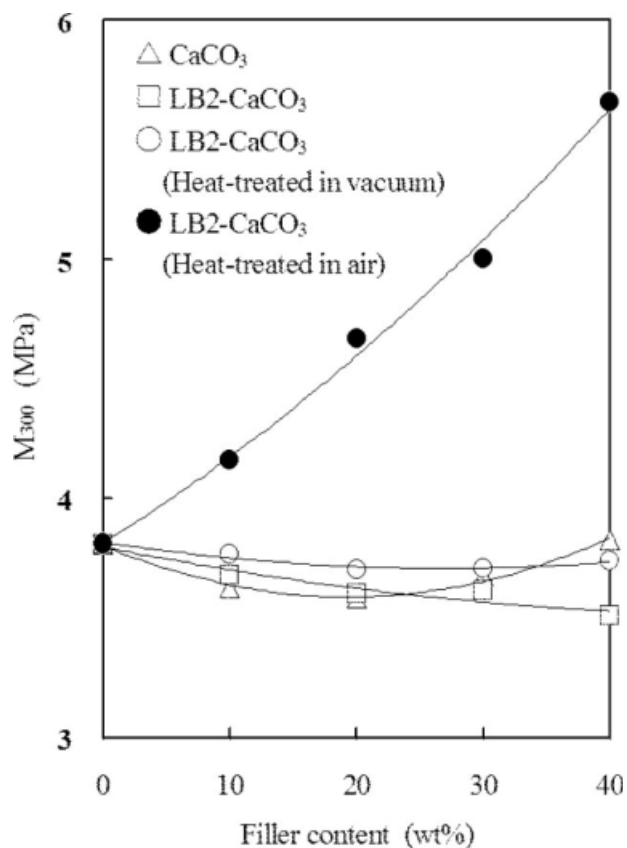
uniformly covered with LB2 molecules. Excessive addition generated multiple adsorption layers of LB2, forming a weak boundary layer and reducing  $M_{100}$  and  $M_{300}$ .

#### Effects of the heat-treatment methods

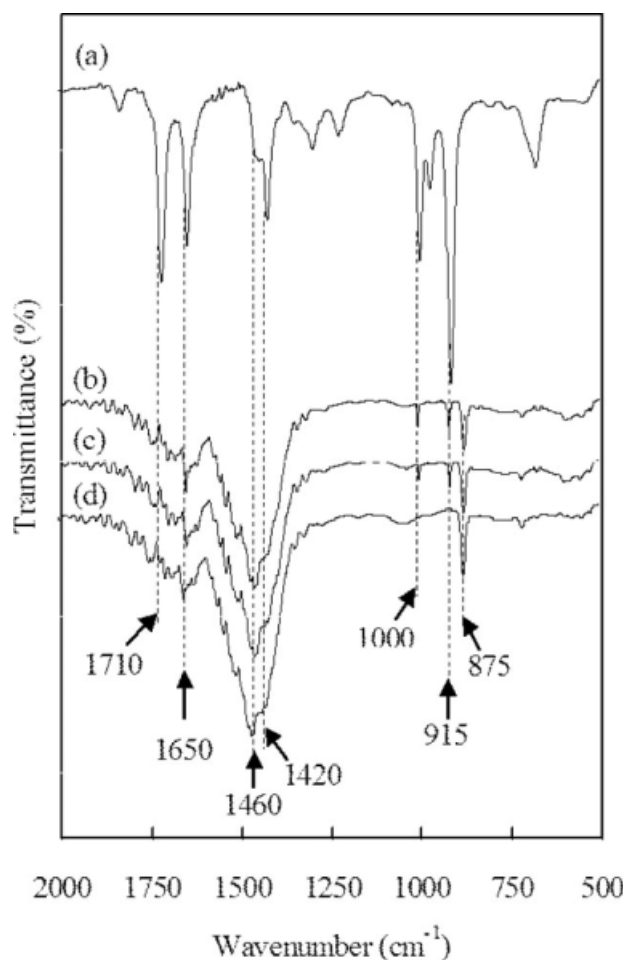
The moduli of LB2-CaCO<sub>3</sub>/SBS composites were dependent on the heat treatment method of LB2-CaCO<sub>3</sub>. Figure 8 shows  $M_{300}$  of the SBS composites filled with untreated CaCO<sub>3</sub>, non-heat-treated LB2-CaCO<sub>3</sub>, LB2-CaCO<sub>3</sub> heat-treated in a vacuum, and LB2-CaCO<sub>3</sub> heat-treated in air. Neither  $M_{300}$  of the SBS composite filled with the non-heat-treated LB2-CaCO<sub>3</sub> nor  $M_{300}$  of the SBS composite filled with LB2-CaCO<sub>3</sub> heat-treated in a vacuum increased with an increase in the filler content as in the CaCO<sub>3</sub>/SBS composite. On the other hand,  $M_{300}$  of the SBS composite filled with LB2-CaCO<sub>3</sub> heat-treated in air significantly increased with an increase in the filler content.

The cause for this was investigated from the viewpoint of the structure of LB2, which was introduced onto the CaCO<sub>3</sub> surface. Figure 9 shows IR spectra for LB2 alone and LB2-CaCO<sub>3</sub> particles subjected to different heat treatments. In the spectrum of LB2,

strong absorption peaks can be observed at 1710, 1650, 1420, 1000, and 915 cm<sup>-1</sup>. The peaks at 915 and 1000 cm<sup>-1</sup> are absorption peaks due to the 1,2-double bond, and the absorption peak at 1650 cm<sup>-1</sup> is due to the 1,4-double bond. In the spectrum of LB2-treated CaCO<sub>3</sub>, absorption peaks due to CaCO<sub>3</sub> can be observed at 1460 and 875 cm<sup>-1</sup> in addition to the absorption peaks due to LB2. The absorption peaks due to the 1,2-double bond can be observed in the spectrum of the non-heat-treated particles and in the spectrum of the particles heat-treated in a vacuum. However, these peaks cannot be observed in the spectrum of the particles heat-treated in air. The 1,2-double bond reacts with oxygen in the atmosphere and forms peroxide (—C—O—O—H), and the radicals generated by the decomposition of the unstable peroxide react and form intermolecular bridges, forming a strong organic layer. On the other hand, the absorption peak due to the 1,4-double bond was observed in all spectra, and the 1,4-double bond does not react with heat treatment. The LB2 layer on the surface of the non-heat-treated particles and the LB2 layer on the surface of the particles heat-treated in a vacuum do not form bridges and



**Figure 8** Effect of the filler content on  $M_{300}$  for SBS composites filled with untreated CaCO<sub>3</sub>, non-heat-treated LB2-CaCO<sub>3</sub>, LB2-CaCO<sub>3</sub> heat-treated in a vacuum, and LB2-CaCO<sub>3</sub> heat-treated in air.



**Figure 9** FTIR spectra of (a) LB2, (b) LB2-CaCO<sub>3</sub>, (c) LB2-CaCO<sub>3</sub> heat-treated in a vacuum, and (d) LB2-CaCO<sub>3</sub> heat-treated in air.

function as a plasticizer in the interface with the matrix. As a result, the modulus is lowered.

The reactivity of LB on the CaCO<sub>3</sub> surface for the matrix after heat treatment is very important for

**TABLE IV**  
Pencil Hardness of LB2 Films Treated Under Various Conditions and  $M_{300}$  of SBS Composites Filled with 40 wt % Heat-Treated LB2-CaCO<sub>3</sub>

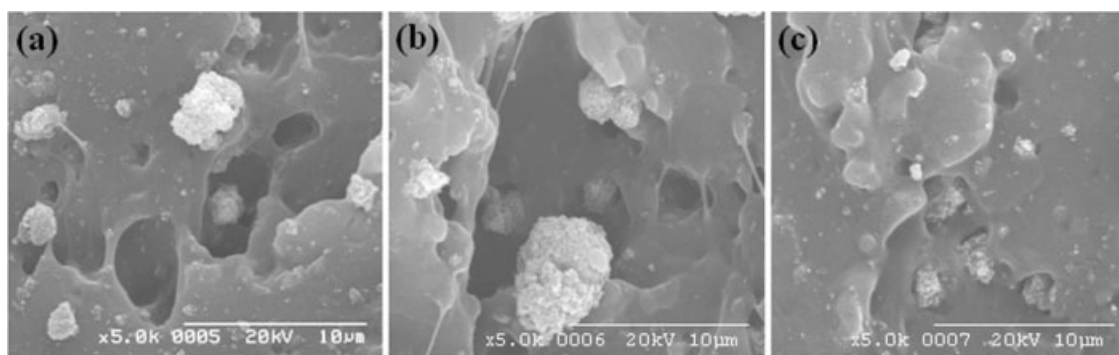
Treatment conditions		LB2 film: Pencil hardness	Composites: $M_{300}$ (MPa)
Temperature (°C)	Time (min)		
120	30	Not hardening	3.91
150	30	Not hardening	4.53
180	30	4H	5.66
240	30	Oxidized	4.01
150	60	2H	4.87
150	120	4H	5.53
150	240	Oxidized	3.87

improving the mechanical properties of composites. However, it is difficult to directly estimate parameters of reactivity, such as the double-bond content and degree of crosslinking, of an LB film on a CaCO<sub>3</sub> surface. To optimize the heat treatment conditions, an LB2 film applied to a glass plate was treated in air through changes in the heating temperature and time. The film hardness after the treatment and the modulus values for the LB2-CaCO<sub>3</sub>/SBS composites are shown in Table IV. LB2 did not cure with heating at 120 or 150°C for 30 min. However, LB2 cured when the heating time was lengthened, and it decomposed through oxidation by heating for 240 min at 150°C. The pencil hardness of the film surface became 4H with heating at 180°C for 30 min. The modulus of the SBS composite filled with LB2-CaCO<sub>3</sub> heated under this condition exhibited the maximum value. When the heating temperature was increased to 240°C, the decomposition of LB2 occurred in the same way as that with heating at 150°C for 240 min, and the modulus of the composite became lower. On the basis of these results, the best heat treatment conditions were determined to

**TABLE V**  
Effect of the Surface Treatment Method for CaCO<sub>3</sub> on the Mechanical Properties of SBS Composites Filled with CaCO<sub>3</sub>

Filler		$M_{300}$ (MPa)	Tensile strength at break (MPa)	Elongation at break (%)	Tension set (%)	Tear strength (N/mm)
Content (wt %)	Modifier					
0	Matrix	3.8 ± 0.3	14.4 ± 1.4	1179 ± 96	9.1 ± 0.6	41.3 ± 1.2
10	CaCO <sub>3</sub>	3.7 ± 0.3	12.3 ± 1.4	1149 ± 104	8.2 ± 0.4	39.6 ± 1.5
	LB2+CaCO <sub>3</sub>	3.4 ± 0.3	11.6 ± 1.2	1114 ± 112	8.8 ± 0.6	38.1 ± 1.9
	LB2-CaCO <sub>3</sub>	4.1 ± 0.2	14.2 ± 1.0	1171 ± 77	6.3 ± 0.3	45.5 ± 1.6
20	CaCO <sub>3</sub>	3.6 ± 0.2	11.1 ± 0.5	1069 ± 76	8.1 ± 0.4	42.4 ± 0.9
	LB2+CaCO <sub>3</sub>	3.1 ± 0.1	9.8 ± 0.7	1012 ± 68	9.3 ± 0.3	37.3 ± 0.6
	LB2-CaCO <sub>3</sub>	4.5 ± 0.2	13.5 ± 0.4	1142 ± 54	5.4 ± 0.3	47.7 ± 0.9
30	CaCO <sub>3</sub>	3.5 ± 0.3	9.6 ± 1.0	952 ± 59	8.2 ± 0.4	38.8 ± 1.1
	LB2+CaCO <sub>3</sub>	2.9 ± 0.2	7.8 ± 0.9	902 ± 44	9.5 ± 0.2	34.2 ± 1.0
	LB2-CaCO <sub>3</sub>	5.1 ± 0.1	11.6 ± 0.7	1006 ± 57	5.4 ± 0.3	49.6 ± 0.3
40	CaCO <sub>3</sub>	3.4 ± 0.1	8.0 ± 0.7	788 ± 35	8.6 ± 0.2	39.4 ± 0.5
	LB2+CaCO <sub>3</sub>	2.7 ± 0.2	6.5 ± 0.5	751 ± 53	10.7 ± 0.4	33.3 ± 0.2
	LB2-CaCO <sub>3</sub>	5.7 ± 0.4	8.6 ± 0.9	800 ± 41	5.3 ± 0.3	53.7 ± 1.3





**Figure 10** SEM micrographs of fracture surfaces of SBS composites filled with 20 wt % filler: (a)  $\text{CaCO}_3/\text{SBS}$ , (b)  $\text{LB2}+\text{CaCO}_3/\text{SBS}$ , and (c)  $\text{LB2}-\text{CaCO}_3/\text{SBS}$ .

be a heating temperature of  $180^\circ\text{C}$  and a heating time of 30 min.

### Integral blend method

In the actual industrial process, the integral blend method is widely used for the production of composites to simplify operations and reduce the cost of production. The integral blend method is a method for improving the mechanical properties of a composite by the direct addition of a surface modifier, such as a coupling agent, when the filler and polymer are heat-kneaded; this reduces the surface energy of both phases and improves compatibility.<sup>22</sup> We prepared a  $\text{CaCO}_3$ -filled composite ( $\text{LB2}+\text{CaCO}_3/\text{SBS}$ ) by kneading the same amounts of LB2 and  $\text{CaCO}_3$  used for the surface treatment of  $\text{CaCO}_3$  as well as SBS. In Table V, the tensile strength at break, elongation at break, tension set, tear strength, and  $M_{300}$  for the  $\text{CaCO}_3/\text{SBS}$ ,  $\text{LB2}-\text{CaCO}_3/\text{SBS}$ , and  $\text{LB2}+\text{CaCO}_3/\text{SBS}$  composites are summarized. The tear strength and  $M_{300}$  for the  $\text{LB2}-\text{CaCO}_3/\text{SBS}$  composite increased with an increase in the filler content. For all the filling contents, the tensile strength at break of the  $\text{LB2}-\text{CaCO}_3/\text{SBS}$  composite was the highest, and the tension set of the  $\text{LB2}-\text{CaCO}_3/\text{SBS}$  composite was the lowest. On the other hand, the tear strength and  $M_{300}$  of the  $\text{LB2}+\text{CaCO}_3/\text{SBS}$  composite decreased more than those of the  $\text{CaCO}_3/\text{SBS}$  composite with an increase in the filler content.

Figure 10 shows SEM micrographs of the tensile fracture surfaces of the  $\text{CaCO}_3/\text{SBS}$ ,  $\text{LB2}+\text{CaCO}_3/\text{SBS}$ , and  $\text{LB2}-\text{CaCO}_3/\text{SBS}$  composites. On the tensile fracture surface of the  $\text{CaCO}_3/\text{SBS}$  composite [Fig. 10(a)],  $\text{CaCO}_3$  aggregates were observed, as well as voids formed by the boundary separation of  $\text{CaCO}_3$  and SBS. This indicates that the compatibility of the  $\text{CaCO}_3$  particles and SBS was weak. On the fracture surface of the  $\text{LB2}+\text{CaCO}_3/\text{SBS}$  composite [Fig. 10(b)], a large aggregation of  $\text{CaCO}_3$  was observed, and no bonding trace was observed

between the  $\text{CaCO}_3$  particles and SBS. Much of the directly added LB2 is believed to have contributed to the aggregation of  $\text{CaCO}_3$  particles, and some of the LB2 is believed to have functioned as a plasticizer of SBS, resulting in the reduction of the mechanical properties of the composite. Thus, it was found that the integral blend method with the use of an oligomer-type LB was not suitable for the improvement of the mechanical properties of SBS. On the fracture surface of the  $\text{LB2}-\text{CaCO}_3/\text{SBS}$  composite [Fig. 10(c)],  $\text{CaCO}_3$  particles were adequately dispersed, with a few voids due to the boundary separation of the particles and the matrix. Thus, it was shown that the surface treatment of  $\text{CaCO}_3$  with LB2 not only suppressed the aggregation of  $\text{CaCO}_3$  particles but also improved the compatibility with SBS.

### CONCLUSIONS

The  $\text{CaCO}_3$  particles were treated with various LBs and were characterized with FTIR spectroscopy, TG measurements, and SEM and TEM observations. The factors that influenced the mechanical properties of the SBS composite filled with LB-surface-treated  $\text{CaCO}_3$  were investigated with respect to the molecular structure of the LB, the amount of the LB adsorbed on the  $\text{CaCO}_3$  surface, the heat treatment conditions, and the surface treatment method. As a result, the following were determined.

1. In the study of the molecular structure of the LB, three factors, namely, the molecular weight, the content of 1,2-double bonds, and the number of functional groups, were found to greatly influence the SBS reinforcing effect of  $\text{LB}-\text{CaCO}_3$ . Among six LBs, the LB with a molecular weight of about 1400, a 1,2-double-bond content of 88.7%, and two or more carboxyl functional groups had the highest reinforcing effect on the  $\text{LB}-\text{CaCO}_3/\text{SBS}$  composite.
2. The amount of LB adsorbed on the  $\text{CaCO}_3$  surface had a great effect on the mechanical

properties of the LB–CaCO<sub>3</sub>/SBS composite. In this study, the optimum amount of adsorbed LB was determined to be 4 g/100 g of CaCO<sub>3</sub>.

3. The most effective heat treatment method after the surface treatment was the heat treatment of LB–CaCO<sub>3</sub> in air. The best heat treatment conditions were as follows: a heating temperature of 180°C and a heating time of 30 min.
4. When LB was directly added to a molten mixture of CaCO<sub>3</sub> and SBS by the integral blend method, CaCO<sub>3</sub> aggregated, and the composite was plasticized by LB. As a result, the mechanical properties of the composite drastically decreased.

## References

1. Harper, C. A. *Handbook of Plastics, Elastomers, and Composites*, 3rd ed.; McGraw-Hill: New York, 1999.
2. Nagatani, A.; Endo, T.; Hirotsu, T.; Furukawa, M. *J Appl Polym Sci* 2005, 95, 144.
3. Ashida, M.; Guo, W. *J Appl Polym Sci* 1993, 49, 573.
4. Guo, W.; Ashida, M. *J Appl Polym Sci* 1993, 50, 1435.
5. Lopez-Manchado, M. A.; Biagiotti, J.; Kenny, J. M. *Polym Compos* 2002, 23, 779.
6. Ibarra, L.; Panos, D. *Polym Int* 1997, 43, 251.
7. Chantaratcharoen, A.; Sirisinha, C.; Amornsakchai, T.; Bualek-Limcharoen, S.; Meesiri, W. *J Appl Polym Sci* 1999, 74, 2414.
8. Liao, M.; Zhu, J.; Xu, H.; Li, Y.; Shan, W. *J Appl Polym Sci* 2004, 92, 3430.
9. Xu, H.; Li, Y.; Yu, D. *J Appl Polym Sci* 2005, 98, 146.
10. Ganguly, A.; Sarkar, M. D.; Bhowmick, A. K. *J Appl Polym Sci* 2006, 100, 2040.
11. Lai, S.; Chen, C. *Eur Polym J* 2007, 43, 2254.
12. Gonzalez, J.; Albano, C.; Ichazo, M.; Hernández, M.; Sciamanna, R. *Polym Degrad Stab* 2001, 73, 211.
13. Gonzalez, J.; Albano, C.; Ichazo, M.; Díaz, B. *Eur Polym J* 2002, 38, 2465.
14. Leong, Y. W.; Abu Bakar, M. B.; Mohd Ishak, Z. A.; Ariffin, A. *J Appl Polym Sci* 2005, 98, 413.
15. Wan, W.; Yu, D.; Xie, Y.; Guo, X.; Zhou, W.; Cao, J. *J Appl Polym Sci* 2006, 102, 3480.
16. Zuiderduin, W. C. J.; Westzaan, C.; Huétink, J.; Gaymans, R. J. *Polymer* 2003, 44, 261.
17. Osman, M. A.; Suter, U. W. *Polymer* 2004, 45, 1177.
18. Leong, W. Y.; Abu Bakar, M. B.; Mohd Ishak, Z. A.; Ariffin, A. *Polym Degrad Stab* 2004, 83, 411.
19. Yang, Y.; G'Sell, C.; Hiver, J.; Hiver, J. M.; Bai, S. L. *J Appl Polym Sci* 2007, 103, 3907.
20. Clark, J. K.; Chen, H. Y. *J Polym Soc* 1974, 12, 925.
21. Wei, H.; Shen, Q.; Wang, H.; Gao, Y.; Zhao, Y.; Xu, D. *J Cryst Growth* 2007, 303, 537.
22. Hozoji, H.; Horie, O.; Ogata, M.; Numata, S. *Kobunshi Ronbunshu* 1990, 47, 483.