

## Crystallization Behavior of Polybutadiene Containing Silica Particles

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**ABSTRACT:** The effect of silica particles (silica), which are petroleum-free products, on the isothermal and nonisothermal crystallizations of *cis*-1,4-poly(butadiene) rubber (BR) is investigated. DSC measurements reveal that silica accelerates the crystallization of BR. As a result, BR-containing silica shows crystallization even after crosslinking reaction. Because of the enhanced crystallization, the tensile modulus is much higher than that without silica in the range between the glass transition temperature and the melting point. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 1848–1853, 2013

**KEYWORDS:** crystallization; butadiene rubber; thermal properties; mechanical properties; silica

Received 22 May 2012; accepted 19 July 2012; published online 1 August 2012

DOI: 10.1002/app.38362

### INTRODUCTION

Poly(butadiene) is one of the most common synthetic elastomers, commonly known as butadiene rubber (BR), and widely used in tires. Since first synthesized in 1910, poly(butadiene) has attracted the attention of many researchers because of the low glass-to-rubber transition temperature ( $T_g$ ). Because of its semicrystalline nature, various researches<sup>1–18</sup> have been carried out to clarify the crystalline structure and crystallization kinetic. Natta et al.<sup>4</sup> revealed that there are four possible stereoisomers of poly(butadiene), which can be controlled by the catalyst type and the mechanism of polymerization reaction. Both 1,2-poly(butadiene) and *trans*-1,4-poly(butadiene) do not show elastomeric properties but exhibit crystallinity at room temperature. Therefore, among configurations of poly(butadiene), *cis*-1,4-poly(butadiene) (BR) is the only applicable one for rubber. As compared with complicated polymorphic crystalline structure of *trans*-1,4-poly(butadiene),<sup>2–4</sup> BR shows a simple monoclinic crystalline form. The melting point  $T_m$  is around 0°C<sup>1–6</sup> and heat of fusion is 157 J g<sup>-1</sup>.<sup>5</sup> However, these values are strongly dependent on the purity and synthesis method.<sup>1</sup> Recently, Lozenro studied melting behavior of BR using a temperature-modulated calorimeter and found an advanced result.<sup>7,8</sup> According to her, BR shows multiple melting peaks which will be attributed to the existence of two types of the amorphous region having different mobility.

Mitchell demonstrated that applied shear history, especially in an extruder, enhances the crystallization rate and also leads to a change of growth mechanism of the crystallization for BR.<sup>9</sup>

Cheng et al. discussed the effect of long-chain branches<sup>10</sup> and molecular weight<sup>11</sup> on the spherulite texture of BR. It was clarified that the spherulitic growth rate decreases significantly with increasing the branches, whereas the molecular weight strongly affects the spherulite form. Meanwhile, Hashimoto et al.<sup>12</sup> and Saito et al.<sup>13</sup> used small-angle and wide-angle X-ray scattering methods to determine the lamellar structure of the oriented crosslinked BR crystals. The experimental results were theoretically discussed by two asymptotic crystallization theories including equilibrium theory of crystallization in a phantom network and kinetic theory of nucleation in a system of asymmetric elements.<sup>12</sup> The nucleating ability by other materials such as carbon blacks<sup>14</sup> and clays<sup>15</sup> have been also studied. Peterman et al.<sup>16</sup> found that BR epitaxially crystallizes on polypropylene substrates. Nakajima et al.<sup>17</sup> concluded that dispersed 1,2-poly(butadiene) crystals enhance the strain-induced crystallization of BR.

It is well known that BR exhibits excellent low temperature flexibility as similar to silicon rubber. Therefore, BR is a good elastomer to improve the friction on ice of winter tires. Furthermore, due to its high resilience, BR is usually used together with another rubber to reduce heat dissipation and enhance the abrasion resistance.<sup>19–21</sup>

However, similar to other synthetic elastomers, BR shows poor mechanical properties, e.g., low strength, low elastic modulus and so on, leading to restricted applications. One way to improve the mechanical properties of elastomer is to distribute fillers. In particular, nanocomposites of rubbers have received great attention in both academic and industrial researches in

recent years.<sup>22–27</sup> Because fillers act as temporary crosslink points by the adhesion with rubber molecules, it is accepted that the addition of fillers to an elastomeric system dramatically changes the temperature dependence of modulus.<sup>19</sup> Moreover, the mechanical properties of filled rubbers are affected by size and shape of fillers, filler–filler interaction, filler–matrix interaction and dispersion state. Among conventional fillers for rubbers, silica, as a petroleum free product, is desired due to its high reinforcing capability such as enhancement of abrasion resistance, tear strength, aging resistance, and adhesion properties. Moreover, silica is also known as an eco-friendly material with good cost-performance as compared with other fillers.<sup>25–29</sup> Especially, silica has been becoming the promising material to replace carbon blacks as fillers in tire application nowadays.<sup>25–27</sup> In general, regarding to tire application, it is widely accepted that rolling resistance and wet grip performance are significantly important properties representing fuel consuming and safety, respectively. Some intensive studies revealed that elastomer/silica blends show low level of hysteresis energy around 60°C, which is typical working temperature of tires,<sup>22,27</sup> as compared with carbon black compounds. In other works, silica leads to the reduction of rolling resistance and thus the energy. In spite of the attractive properties of silica, only a few papers have been reported on the interaction between BR and silica. For the industrial application, therefore, further study on the structure and properties of BR/silica blends is required.

Besides reinforcing ability, some fillers can accelerate the crystallization of a matrix polymer. Because the degree of crystallization plays an important role on the mechanical properties, many researches have been carried out in recent years to clarify the effect of fillers on crystallization of a polymer. However, the effect of silica on the crystallization behavior of BR has not been discussed to the best of our knowledge. In this research, the effect of silica particles on the isothermal and nonisothermal crystallization behaviors of both vulcanized and unvulcanized BR is carefully investigated by DSC with the dynamic mechanical properties of the composites.

## EXPERIMENTAL

### Materials

The materials used in this research were butadiene rubber (BR) (Lanxeess, CB24) and silica particles (silica) (Zeosil, 115GR). The *cis*-content of BR is 94.8% and vinyl fraction is 0.5%. The number and weight average molecular weights are  $3.3 \times 10^5$  and  $6.5 \times 10^5$ , respectively, which were determined by a gel chromatography as a polystyrene standard. The diameter of silica is  $\sim 16$  nm.

### Sample Preparation

Composites of BR containing various amounts of silica were prepared using a 60 cm<sup>3</sup> internal batch mixer (Toyoseiki, Laboplastomil 10M100). The blade rotation speed was 40 rpm and the mixing time was 3.5 min. The temperature in the mixer was controlled at 100°C prior to mixing and then increased to 140°C by viscous dissipation. To avoid the effect of mixing history on the crystallization behavior, pure BR was also kneaded in the mixer at the same conditions.

To prepare vulcanized samples, BR and silica were mixed by a conventional two-roll mill. The blend ratio of the BR/silica was 100/70 in weight fraction, which is determined to obtain the information on the characteristics of a conventional rubber used in the industry. The content of sulfur was 1.5 phr, and the content of process oil was 10 phr. Further, two types of accelerators were added, 2 phr of *N-tert*-butyl-2-benzothiazyl-sulfenamide (Sanshin Chemical Industry, Sanceler NS-G) and 0.5 phr of 1,3-diphenyl-guanidine (Sumitomo Chemical, Soxinol). After blending, the compound was compressed and vulcanized into flat sheets with the thickness of 1 mm using a conventional compression molding machine at 160°C. Furthermore, a vulcanized BR sample without silica was also prepared following the same conditions. Vulcanization time was determined based on the curast meter as the time when the torque reaches to 95% of the equilibrium value during the vulcanization process.

### Measurements

Thermal properties of BR and BR/silica blends were analyzed using a differential scanning calorimeter (Mettler, DSC820) (DSC). Approximately 10 mg of the sample was encapsulated in a standard aluminum pan. To investigate the non-isothermal crystallization behavior, the samples were cooled from 25 to  $-80^\circ\text{C}$  at various cooling rates and then heated to 25°C at a rate of  $10^\circ\text{C min}^{-1}$ . Moreover, isothermal crystallization was performed at various crystallization temperatures ( $T_c$ ) in the range from  $-14$  to  $-22^\circ\text{C}$ .

Temperature dependence of dynamic tensile moduli was evaluated by a dynamic mechanical analyzer (DMA) (UBM, DVE3). The frequency was 10 Hz and the heating rate was  $2^\circ\text{C min}^{-1}$ .

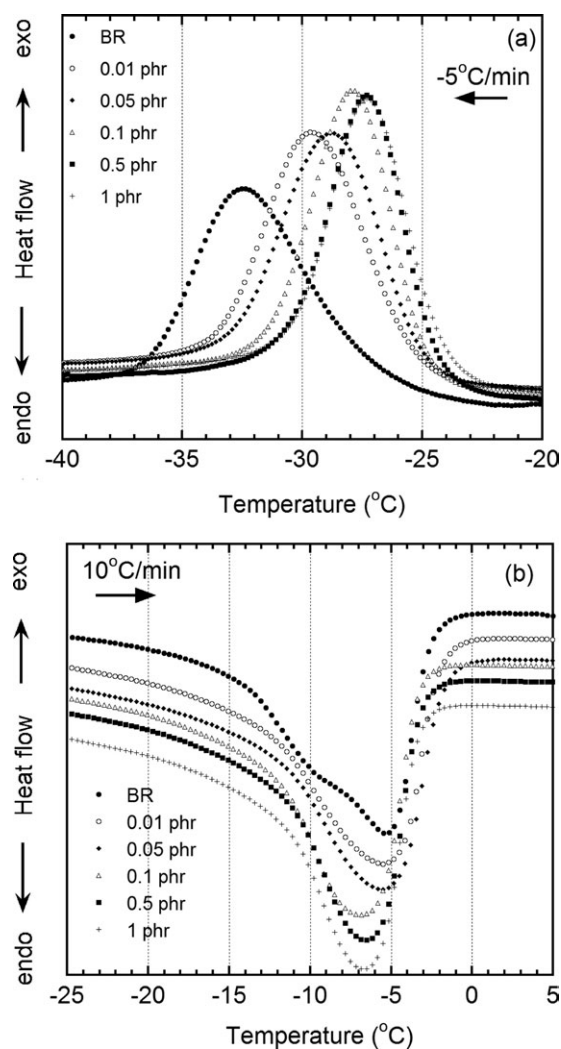
## RESULTS AND DISCUSSION

### Effect of Silica Particles on Crystallization Behavior of Unvulcanized BR

To clarify the effect of silica on crystallization behavior of BR, nonisothermal crystallization at a cooling rate of  $5^\circ\text{C min}^{-1}$  from room temperature was conducted in DSC for the unvulcanized BR and BR/silica blends. In this study, the same processing history is applied to pure BR to omit the effect of flow history on the crystallization.

The cooling and heating DSC curves are shown in Figure 1. Because all samples are cooled at the same rate, the difference between onset temperature ( $T_o$ ) and crystallization peak temperature ( $T_{cp}$ ) can be used to evaluate the nonisothermal crystallization rate as shown in Table I. It is clarified that the onset and crystallization peaks are drastically shifted to higher temperature by addition of silica, indicating that BR crystallization is enhanced even with a small amount, e.g., 0.01 phr, of silica.

In general, crystallization rate is determined by two factors, i.e., the number of nuclei and the linear growth rate. The addition of fillers usually does not enhance the molecular diffusion (rather retards the diffusion due to prolonged relaxation time). Therefore, the linear growth rate is not enhanced. Although it is known that residual strain caused by the flow history can accelerate the crystallization due to enhanced molecular orientation, the effect can be ignored at the present experiment. This is reasonable, because the measurements are performed without flow



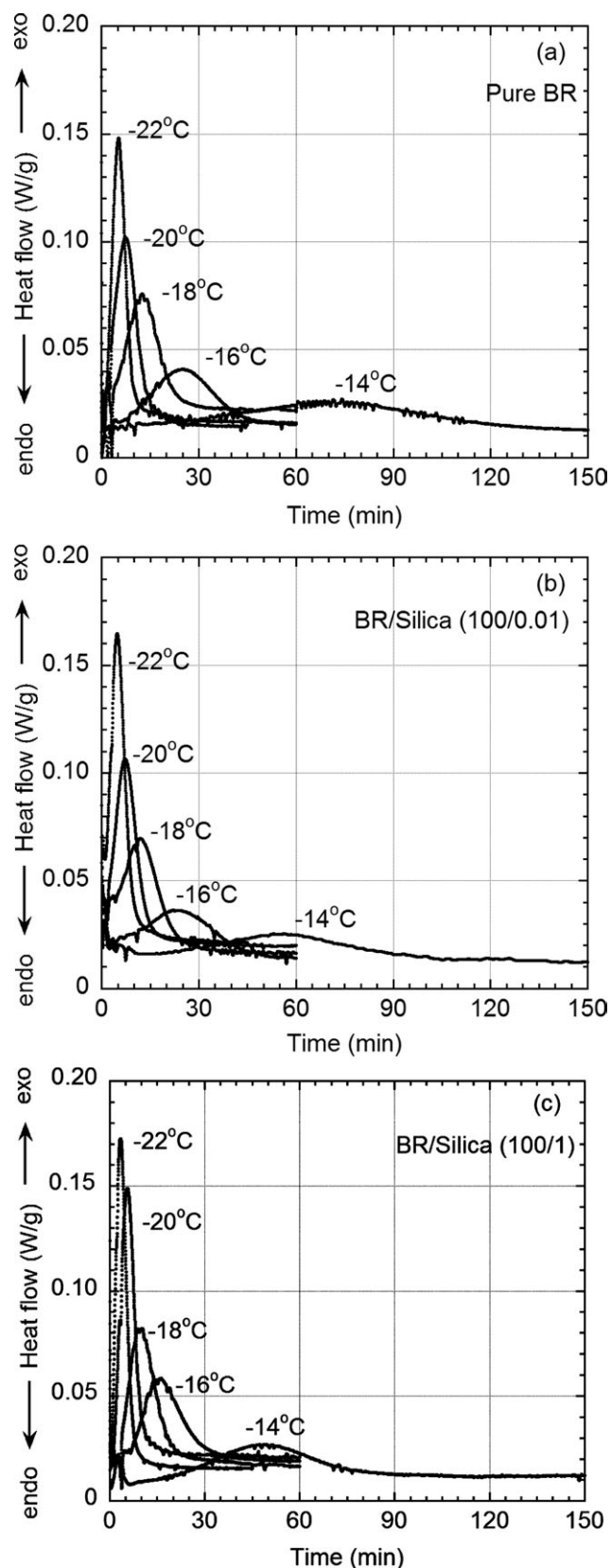
**Figure 1.** Nonisothermal DSC curves for pure BR and BR/silica blends: (a) cooling and (b) heating.

field. Moreover, rheological properties, i.e., molecular diffusion, in the molten state are unchanged by the small addition of silica. These results demonstrate that the number of nuclei increases by addition of silica.

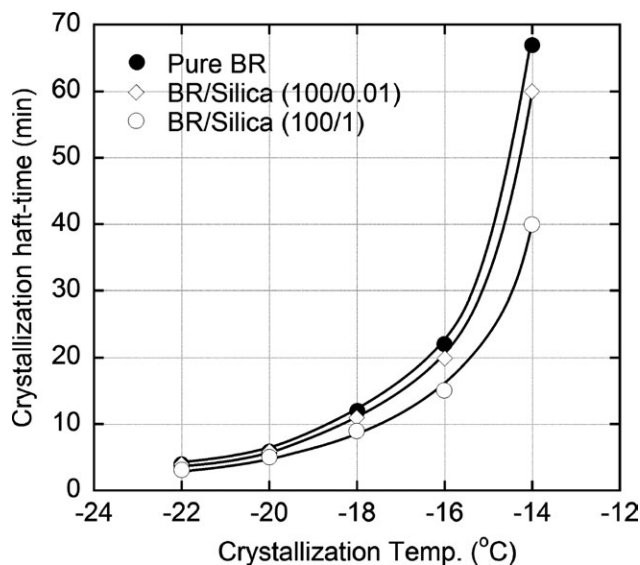
The shift of the crystallization temperature is pronounced with the content of silica. When the content is around 0.5–1 phr, however, the peak temperature is almost the same. It suggests that the effect of silica is saturated around at 0.5 phr.

**Table I.** Nonisothermal Crystallization Parameters of BR and BR/silica Blends

Sample	$T_o$ ( $^{\circ}\text{C}$ )	$T_c$ ( $^{\circ}\text{C}$ )	$\Delta H$ ( $\text{J g}^{-1}$ )
Pure BR	-24.5	-33.0	44.5
BR/Silica (100/0.01)	-21.0	-29.5	48.0
BR/Silica (100/0.05)	-20.7	-29.0	49.5
BR/Silica (100/0.1)	-20.5	-28.0	50.5
BR/Silica (100/0.5)	-20.3	-27.5	51.5
BR/Silica (100/1)	-20.0	-27.5	51.5



**Figure 2.** Isothermal DSC curves at various crystallization temperatures for (a) pure BR, (b) BR/silica (100/0.01), and (c) BR/silica (100/1).



**Figure 3.** Relation between crystallization temperature and crystallization half-time for (closed circles) pure BR, (open diamonds) BR/silica (100/0.01) and (open circles) BR/silica (100/1).

The pure BR shows double peaks in the heating curve [Figure 1(b)]. Presumably, the lower one is attributed to imperfect crystals, whereas the higher one is to the stable form. On the contrary, only a single peak is detected at  $-6^{\circ}\text{C}$  for BR/silica blends, suggesting that silica not only enhances the crystallization rate but also affects the crystalline structure of BR. As seen in the figure, thinner crystals, having lower  $T_m$ , decrease by the addition of silica. The result corresponds with a high value of heat of fusion  $\Delta H$ , as shown in Table I, indicating well-developed crystalline structure of BR.

To discuss the kinetics of crystallization behavior in detail, the isothermal crystallization is carried out at various crystallization temperatures employing the pure BR and BR containing 0.01 and 1 phr of silica. The time dependences of heat flow are shown in Figure 2.

The figure shows that crystallization peaks of all samples are shifted to longer time with increasing the crystallization temperature. Furthermore, the peak time is shortened by addition of silica, which is pronounced for the blend containing 1 phr of silica. The crystallization half time, which is defined as the time required to show the half of the peak area, is evaluated and shown in Figure 3 for all samples. It is apparent from the figure that the crystallization half-time is reduced by the addition of silica. The figures demonstrate that only 0.01 phr of silica has marked effect on the BR crystallization.

The Avrami equation,<sup>30</sup> using the relative crystallinity  $X_{\text{rel}}$  defined by eq. (1), is widely used to describe the kinetics of isothermal crystallization process.

$$X_{\text{rel}} = \frac{X_t}{X_T} = \int_0^t \frac{dH(t)}{dt} dt / \int_0^{\infty} \frac{dH(t)}{dt} dt \quad (1)$$

where  $X_t$  and  $X_T$  are the degree of crystallinity at time  $t$  and at the end of the crystallization, and  $H(t)$  is enthalpy of crystallization.

**Table II.** Avrami Parameters for BR and BR/silica (100/1) at Various Crystallization Temperatures

Samples	$T_c$ ( $^{\circ}\text{C}$ )	$n$	$k$
Pure BR	-22	2.40	$8.32 \times 10^{-6}$
	-20	2.50	$1.79 \times 10^{-6}$
	-18	2.45	$1.32 \times 10^{-6}$
	-16	2.58	$2.24 \times 10^{-7}$
	-14	2.55	$1.20 \times 10^{-7}$
BR/Silica (100/1)	-22	2.35	$1.99 \times 10^{-5}$
	-20	2.25	$4.42 \times 10^{-6}$
	-18	2.30	$1.58 \times 10^{-6}$
	-16	2.33	$1.00 \times 10^{-6}$
	-14	2.40	$3.47 \times 10^{-7}$

The overall crystallization kinetics can be further described by the following equation;

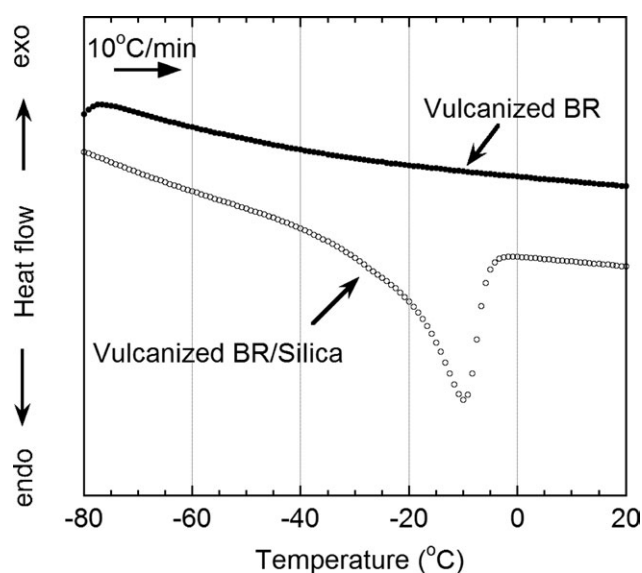
$$1 - X_{\text{rel}} = \exp(-kt^n) \quad (2)$$

where  $k$  is the parameter to express the overall crystallization rate and  $n$  is the Avrami index.

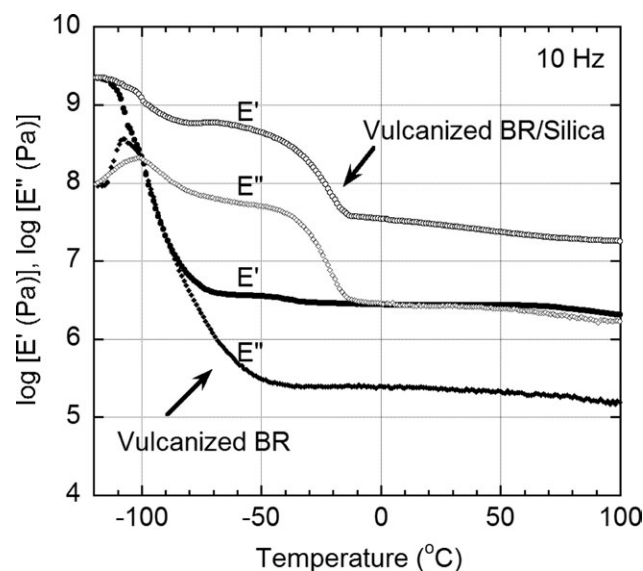
$$\log[-\ln(1 - X_{\text{rel}})] = n \log t + \log k \quad (3)$$

It is confirmed (but not presented here) that the Avrami plot is applicable to the present experimental results, and the kinetic parameters such as  $n$  and  $k$  are summarized in Table II.

The results show that all  $n$  values of both samples are in the range from 2 to 3, indicating that the crystal form is not a perfect spherulite but a mixture of lamellae and spherulites. As similar to Figure 3, the  $k$  values of all samples decrease with increasing  $T_c$ . Furthermore, it is confirmed that the  $k$  values of



**Figure 4.** DSC heating curves for (closed) vulcanized BR (open) vulcanized BR/silica (100/70).



**Figure 5.** Temperature dependence of (circles) tensile storage modulus  $E'$  and (diamonds) loss modulus  $E''$  at 10 Hz for (closed symbols) vulcanized BR and (open symbols) vulcanized BR/silica (100/70).

BR/silica are higher than those of BR, which corresponds with Figure 1.

#### Crystallization Behavior and Mechanical Properties of Vulcanized BR

Further experiments are carried out employing vulcanized samples. Figure 4 shows the DSC heating curves of vulcanized BR and BR/silica blend after cooling at a rate of  $5^{\circ}\text{C min}^{-1}$ . The endothermic peak at  $-10^{\circ}\text{C}$  ascribed to the fusion of BR crystals is detected only for the BR/silica blend. The heat of fusion is about  $13.7\text{ J g}^{-1}$ . Because the heat of fusion of perfect crystals is known to be  $157\text{ J g}^{-1}$  for BR,<sup>5</sup> the degree of crystallization for BR is 8.5%. On the contrary, vulcanized BR without silica does not show any melting peak.

The temperature dependence of dynamic tensile moduli for vulcanized BR and BR/silica blend is plotted together in Figure 5. Although these results are roughly predicted by the DSC data, the quantitative characterization of the modulus enhancement can be carried out from the figure.

The figure shows that both storage and loss moduli of the BR/silica blend are greatly higher than those of the BR in the temperature range between  $T_g$  ( $-100^{\circ}\text{C}$ ) and melting point ( $T_m$ ) of BR crystals ( $-10^{\circ}\text{C}$ ). Because of the crystallization during cooling process in the DMA machine, the moduli of the BR/silica blend are remarkably enhanced. Moreover,  $T_g$  of BR is shifted to higher temperature by the addition of silica. This is reasonable because crystallites of BR, which is enhanced by silica, restrict the mobility of amorphous chains of BR even after crosslinking.

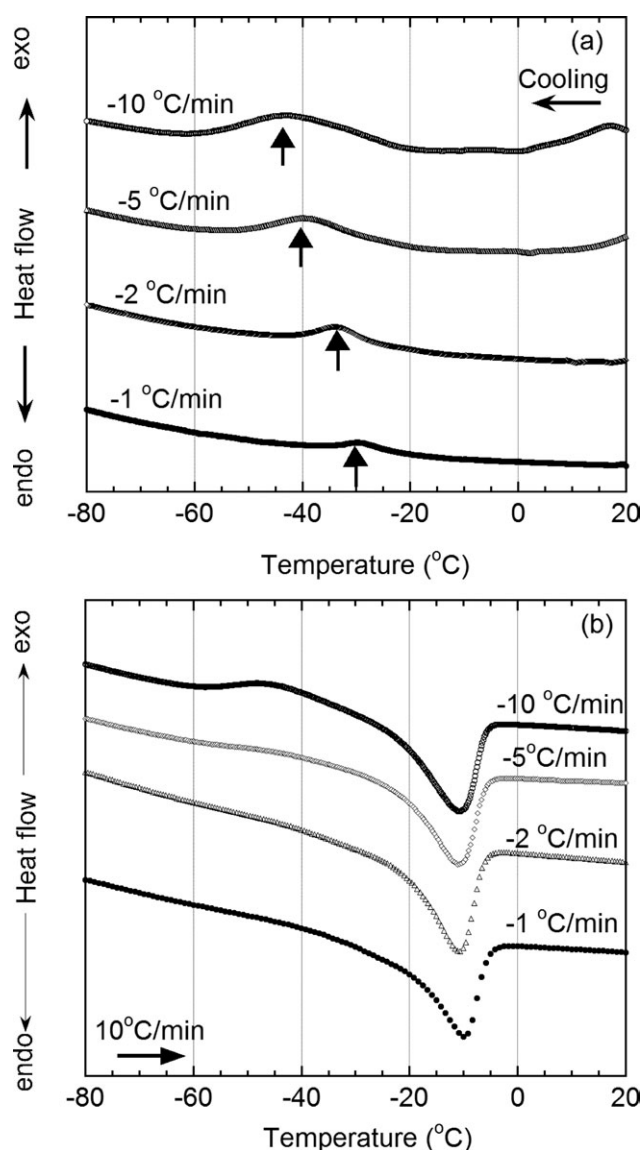
The moduli beyond the melting point are still higher for the BR/silica. One reason of the modulus enhancement is the filling effect of silica. This phenomenon is basically described by the

Kerner equation proposed for a polymer composite system containing spherical fillers<sup>31,32</sup>;

$$E = E_m \left[ 1 + \frac{15(1-\alpha)\varphi}{8-10\alpha} \frac{\varphi}{1-\varphi} \right] \quad (4)$$

where  $\varphi$  is the volume fraction of fillers,  $\alpha$  is the Poisson's ratio of a matrix,  $E$  and  $E_m$  are the moduli of a composite and a matrix, respectively.

Following the equation, the modulus of BR/silica is predicted to be 2.75 times higher than that of BR, which is significantly lower than the experimental results. Presumably, the absorption of rubber molecules onto the surface of fillers, called "bound rubber,"<sup>19,33,34</sup> is also responsible for the modulus enhancement. In other words, silica acts as crosslink points for BR.



**Figure 6.** Nonisothermal DSC curves for vulcanized BR/silica (100/70): (a) cooling at various rates and (b) heating at  $10^{\circ}\text{C min}^{-1}$  for vulcanized BR/silica (100/70).

The effect of cooling rate on the nonisothermal crystallization behavior of the vulcanized BR/silica blend is also investigated by DSC (Figure 6). In this experiment, all samples are cooled directly from room temperature to  $-80^{\circ}\text{C}$  at various cooling rates to clarify the crystallization behavior. As seen in Figure 6(a), cooling curves exhibit a single exothermal peak at any cooling rate. As a cooling rate increases from  $1$  to  $10^{\circ}\text{C min}^{-1}$ , the temperature of exothermal peaks decreases from  $30$  to  $-43^{\circ}\text{C}$ . Moreover, DSC heating curves are also evaluated after cooling as shown in Figure 6(b).

In the heating process, however,  $T_m$  is located at around  $-10^{\circ}\text{C}$  irrespective of the cooling rate. The sample cooled at a rate of  $10^{\circ}\text{C min}^{-1}$  shows a weak and broad exothermal peak at  $-43^{\circ}\text{C}$ , which will be ascribed to the crystallization. Considering the slopes of the curves, a similar very weak peak exists for the sample cooled at  $5^{\circ}\text{C min}^{-1}$ . Because of the rapid cooling, crystallization will not occur sufficiently during the cooling process.

## CONCLUSION

Isothermal crystallization and non-isothermal crystallization behaviors of BR and BR/silica blends are investigated by DSC. All of the experimental results reveal that silica enhances the crystallization of BR even with a small amount. The crystallization temperature at the cooling process increases greatly with increasing the content of silica when the amount of silica is lower than  $0.5$  phr. Moreover, the pronounced crystallization by silica is detected even after vulcanization. Because of the crystallization, the oscillatory tensile moduli of vulcanized BR/silica are higher than those of vulcanized BR without silica in the temperature range between  $T_g$  and  $T_m$ .

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