

# Effect of Mount Pinatubo Volcanic Ash on the Mechanical Properties of Styrene–Butadiene Rubber Vulcanizates

Elinor L. Bedia,<sup>1</sup> Yutaka Kasai,<sup>2</sup> Yuko Ikeda,<sup>3</sup> Shinzo Kohjiya<sup>2</sup>

<sup>1</sup>Industrial Technology Development Institute, Bicutan, Taguig, Metro-Manila, Philippines

<sup>2</sup>Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

<sup>3</sup>Faculty of Engineering and Design, Kyoto Institute of Technology, Kyoto 615-0825, Japan

Received 16 October 2003; accepted 14 April 2004

DOI 10.1002/app.20801

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Mt. Pinatubo volcanic ash, collected from Porac, Pampanga, was screened at 32 mesh screen, wet-ground in a pot mill for 3, 5, and 7 days, and dried. The volcanic ash was characterized and compounded with styrene–butadiene rubber (SBR) vulcanizates. Mineralogical investigation of the volcanic ash showed the presence of feldspar, hornblende, quartz, mica, and magnetite. The particle size of the volcanic ash ground for 3, 5, and 7 days ranged from 1440 to 4, 720 to 2, and 640 to 2  $\mu\text{m}$ , respectively. The addition of volcanic ash did not significantly influence the mechanical strength of the SBR vulcanizates. Stress–strain curves of the volcanic ash–filled SBR vulcanizates showed a

slight increase from that of the pure gum. As the particle size of the volcanic ash decreased, the tensile strength and elongation at break points increased. Crosslinking sites also increased with the addition of rubber. Furthermore, it was noted that the addition of diethylene glycol hastened the curing reaction without affecting the mechanical properties of SBR vulcanizates. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 68–73, 2005

**Key words:** Volcanic ash; vulcanization; curing of polymers; crosslinking; reinforcing effect

## INTRODUCTION

Mt. Pinatubo is situated in the southwest side of Luzon island of the Philippines. For 450 years, the volcano was in a state of quiescence and suddenly erupted in 1991, unleashing about 7 billion cubic meters of volcanic ash that were deposited along its slopes. During rainy seasons, the volcanic ejecta along with the rain water formed mudflows called lahar and were deposited in low-lying areas around Pinatubo Volcano.<sup>1,2</sup>

The composition and possible uses of the volcanic ash were extensively investigated by the Industrial Technology Development Institute of the Department of Science and Technology.<sup>3</sup> According to these studies, volcanic ash is composed of feldspar, hornblende, quartz, mica, and magnetite. Successful research works undertaken using volcanic ash were unsaturated polyester composites for novelty wares,<sup>4</sup> low melting temperature glasses for fashion accessories,<sup>5</sup> alumino-silicate glass ceramics,<sup>6</sup> ceramic bricks,<sup>7</sup> self-

glazed ceramics,<sup>8</sup> D-I-Y lahar blocks,<sup>9</sup> calcium mica–bioglass ceramics,<sup>10</sup> cement tiles,<sup>11</sup> calcium silicate blocks,<sup>12</sup> magnetic separation,<sup>13</sup> ceramic tiles,<sup>14</sup> and float glass making.<sup>15</sup>

In the rubber industry, the incorporation of fillers to rubber vulcanizates is extremely important for improving their physical properties and service life (reinforcing fillers), or to make them economically feasible (nonreinforcing fillers). The most common reinforcing fillers are carbon black and silica.<sup>16,17</sup> Both fillers impart significant improvement to the tensile properties, tear strength, and abrasion resistance of the rubber. However, carbon black is preferred overall because it can provide a relatively high modulus to the rubber. Recently, silica has increasingly been used in the tire industry, in combination with a few silane coupling agents, especially those containing polysulfide bonds.<sup>18,19</sup> Other fillers such as clays, calcium carbonate, magnesium carbonate, and talc can also be used where a high reinforcement is not required. In this case, the fillers act as an extender to reduce the production cost.

Volcanic ash can be a good source of mineral filler of rubber vulcanizates because of its feldspathic/siliceous composition and abundance as a natural resource. Hence, an attempt was made to use the volcanic ejecta as filler for styrene–butadiene rub-

Correspondence to: E. Bedia (elinor@dost.gov.ph).

Contract grant sponsor: JSPS-Japan-DOST RONPAKU Programme.

TABLE I  
Formulation of SBR Vulcanizates

Component	SBR-0	SBR-3	SBR-5	SBR-7	SBR-7D
SBR	100	100	100	100	100
ZnO	5.0	5.0	5.0	5.0	5.0
Stearic acid	1.5	1.5	1.5	1.5	1.5
MSA-G <sup>a</sup>	1.5	1.5	1.5	1.5	1.5
Sulfur	1.0	1.0	1.0	1.0	1.0
Volcanic ash	0	30 <sup>b</sup>	30 <sup>c</sup>	30 <sup>d</sup>	30 <sup>d</sup>
DEG <sup>e</sup>	0	0	0	0	3.0
Curing time, min	56	51	48	46	13

<sup>a</sup> *N*-Oxydiethylene-2-benzothiazoylsulfenamido.

<sup>b</sup> 3 days' milling.

<sup>c</sup> 5 days' milling.

<sup>d</sup> 7 days' milling.

<sup>e</sup> Diethylene glycol.

ber. The effect of this filler on the mechanical properties of the rubber was studied by static and dynamic methods.

## EXPERIMENTAL

### Materials

Volcanic ash of Mt. Pinatubo, obtained from Porac, Pampanga, was screened at 32 mesh to remove the large particles from the ash. Representative samples of the screened ash were taken for investigation as raw material and for wet-grinding, using a pot mill for 3, 5, and 7 days. Each sample of ground ash was dried at 150°C for 2 h just before being mixed into rubber.

Styrene-butadiene rubber (SBR) used was JSR SBR-1502, supplied by JSR Corp. (Tokyo, Japan). This SBR is a cold-type, nonstaining product with bound styrene and Mooney viscosity of 23.5% (mass) and 52 (ML<sub>1+4</sub> 100°C), respectively.

### Preparation of SBR vulcanizates

Formulations of the SBR vulcanizates are shown in Table I. The SBR masterbatch was first prepared by blending SBR with zinc oxide, stearic acid, *N*-oxydiethylene-2-benzothiazoylsulfenamido (MSA-G), and sulfur using a chilled two-roll mill. A representative sample of the masterbatch was taken and blended with volcanic ash ground for 3, 5, and 7 days and the vulcanizates were coded as SBR-3, SBR-5, and SBR-7, respectively. SBR-7D had the same formulation as that of SBR-7 but diethylene glycol (DEG) was added to control the probable absorption of MSA-G, a vulcanization accelerator, on the filler surface. A pure gum, SBR-0, without any filler, served as a reference material.

The rubber vulcanizates of SBR were prepared by curing at 150°C under a pressure of 100 kg/cm<sup>2</sup> using

a hot-press machine. The curing time for each formulation was determined using a JSR Curelaster III.

### Curemeter measurement

The curing times of the unfilled and volcanic ash-filled rubber vulcanizates were determined from the cure curve obtained by using a JSR Curelaster III. The suitable cure time was evaluated by calculating the torque,  $T_{90}$ , from the following equation:

$$T_{90} = (T_{\max} - T_{\min}) \times 0.9 + T_{\min} \quad (1)$$

where  $T_{\max}$  and  $T_{\min}$  are the time needed to reach the maximum and minimum torques, respectively.  $T_{90}$  is plotted and the distance from the  $T_{\min}$  to  $T_{90}$  is measured to obtain the curing time. Table II shows the calculated curing times for SBR-0, SBR-3, SBR-5, SBR-7, and SBR-7D from the curemeter measurements.

### Materials characterization

X-ray diffraction analysis (XRD) of raw volcanic ash was obtained using a Shimadzu X-ray diffractometer VDR-2 (Shimadzu, Kyoto, Japan) set with Cu-K<sub>α</sub> radiation at 30 kV and 20 mA.

Chemical analysis of raw volcanic ash was determined and is described elsewhere.<sup>11</sup>

Optical microscopic observation was conducted to elucidate the morphology and determine the particle size of the volcanic ash using a Nikon Polarizing Microscope Model POH 3 (Nikon, Tokyo, Japan).

Tensile strength, elongation, and the Young's modulus (the initial slope of tensile stress-strain curve) of the SBR vulcanizate were measured using a Shimadzu AGS tensile tester, which was set at a strain rate of 50 mm/min at room temperature. Test specimens were die-cut into rectangular shape with the following dimensions: 50 (L) × 5 (W) × 1 (T) mm. From the tensile stress-strain (S-S) curves, the Young's modulus (Y); moduli at 50, 100, 200, and 300% elongations ( $M_{50}$ ,

TABLE II  
Chemical Analysis of Raw Ash

Oxide	Composition (%)
SiO <sub>2</sub>	62.48
Al <sub>2</sub> O <sub>3</sub>	16.14
Fe <sub>2</sub> O <sub>3</sub>	0.55
TiO <sub>2</sub>	0.65
MnO	0.02
CaO	5.20
MgO	3.25
Na <sub>2</sub> O	4.99
K <sub>2</sub> O	1.68
LOI	1.68

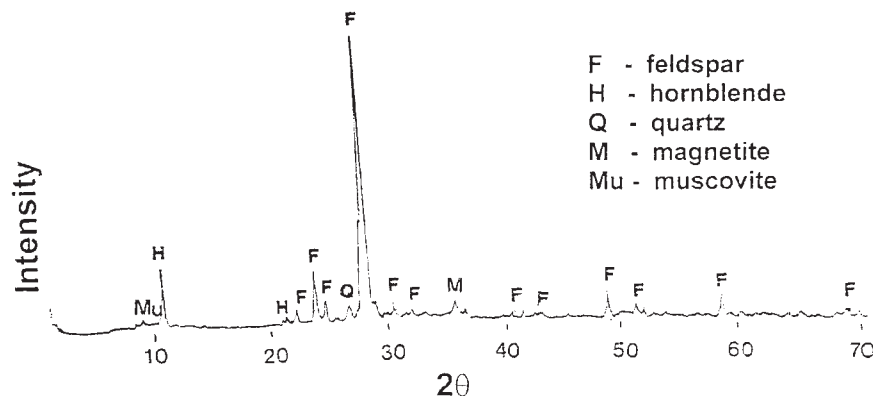


Figure 1 XRD pattern of Mt. Pinatubo volcanic ash (raw).

$M_{100}$ ,  $M_{200}$ , and  $M_{300}$ , respectively); tensile strength at break ( $T_B$ ); and elongation at break ( $E_B$ ) were calculated. Values reported in this study were based on an average of three measurements for each sample.

Dynamic mechanical analysis (DMA) was carried out using a Rheospectoler DVE-4 instrument (Rheology Co., Kyoto, Japan) at a frequency of 10 Hz and a heating rate of 2°C/min. Dynamic or complex modulus ( $E^*$ ) and loss angle ( $\delta$ ) were measured as a function of temperature. From  $E^*$  and  $\delta$ , dynamic storage modulus ( $E'$ ), dynamic loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) were calculated by the following equations:

$$E^* = E' + iE'' \quad (2)$$

$$E' = [E^*]\cos\delta \quad (3)$$

$$E'' = [E^*]\sin\delta \quad (4)$$

$$\tan\delta = \sin\delta\cos\delta = E''/E' \quad (5)$$

where  $i = -1$  and  $[E^*]$  is the absolute value of complex modulus, which is a vector. From the peak tip of the  $\tan \delta$ , the glass-transition temperature ( $T_g$ ) was obtained.

## RESULTS AND DISCUSSION

### Mineralogical analyses of Mt. Pinatubo volcanic ash

X-ray diffraction analysis of the volcanic ash confirmed the presence of feldspar, hornblende, quartz, mica, and magnetite, as exhibited in Figure 1. Table II shows the result of its chemical analysis, which indicates that the feldspar present is andesine, attributed to the ratio of CaO and Na<sub>2</sub>O, which is about 1 to 1. Hornblende and magnetite were observed under the polarizing microscope to be green-colored and opaque minerals.

Optical microscopic observation of the raw volcanic ash revealed the large particle size of the above-mentioned minerals, ranging from 2000 to 8  $\mu\text{m}$ , as shown in Figure 2(a). By pot-milling for 3, 5, and 7 days, the size of the particles was reduced and ranged from 1440 to 4, 720 to 2, and 640 to 2  $\mu\text{m}$ , respectively, as observed in Figure 2(b)–(d).

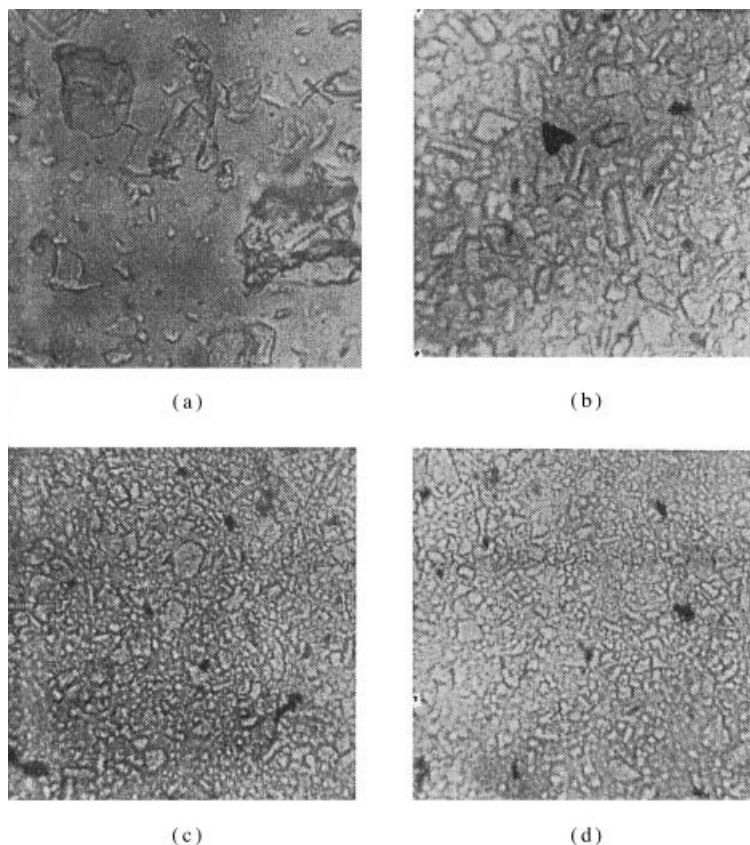
### Mechanical properties of unfilled and volcanic ash-filled SBR vulcanizates

The formulations of pure and volcanic ash-filled SBR vulcanizates are shown in Table I. The composition of the SBR masterbatch (i.e., pure gum coded as SBR-0) and the amount of volcanic ash ground for 3, 5, and 7 days added (i.e., filled vulcanizates coded as SBR-3, SBR-5, and SBR-7) are the same. The vulcanizates were cured at 150°C for approximately 50 min. When treated with DEG, the curing time of SBR-7D decreased to 13 min, which indicates that DEG is a very good activator and/or dispersing agent, enabling faster crosslinking/curing reaction.

The tensile mechanical properties of pure and volcanic ash-filled SBR vulcanizates are summarized in Table III. The pure gum exhibits  $Y$ ,  $T_B$ , and  $E_B$  values of 1.40 MPa, 1.74 MPa, and 550%, respectively. In Figure 3, the tensile S–S curves of the volcanic ash-filled vulcanizates, SBR-3, SBR-5, SBR-7, and SBR-7D, the moduli indicate a slight increase over that of SBR-0. These behaviors are similar to the moduli obtained at 50, 100, 200, and 300% elongation.

Crosslinking density ( $\nu$ ) of the rubber phase of the unfilled and filled volcanic ash SBR vulcanizates was calculated based on the classical (kinetic) theory of rubber elasticity.<sup>20</sup> According to this theory, the force per unit area  $\sigma$ , required to sustain a perfectly elastic network at a small strain ratio  $\alpha$ , is given by

$$\sigma = \nu kT(\alpha - \alpha^2) \quad (6)$$



**Figure 2** Optical micrograph of Mt. Pinatubo volcanic ash: (a) raw; and ground for (b) 3 days, (c) 5 days, and (d) 7 days.

where  $\nu$  is the number of network chains per  $\text{cm}^3$  at absolute temperature and  $k$  is the Boltzmann's constant ( $8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ ). Figure 4 shows the plot of  $\sigma$  versus  $(\alpha - \alpha^2)$ . The slope is obtained by drawing a straight line at the initial slope of the curve originating

from the small strain ratio. The value of  $\nu$  is determined by using the following equation:

$$\text{Slope} = \nu k T \quad (7)$$

**TABLE III**  
Physicomechanical Properties of Unfilled and Volcanic Ash-Filled SBR Vulcanizates

Property	SBR-0	SBR-3	SBR-5	SBR-7	SBRR-7D
$Y$ , <sup>a</sup> MPa	1.3995	1.9540	1.8797	1.8345	1.5905
$M_{50}$ , <sup>b</sup> MPa	0.5384	0.7101	0.7333	0.6685	0.6256
$M_{100}$ , <sup>b</sup> MPa	0.7009	0.8685	0.8902	0.8603	0.8027
$M_{200}$ , <sup>b</sup> MPa	0.8853	1.0058	1.0192	1.0137	0.9405
$M_{300}$ , <sup>b</sup> MPa	1.0486	1.1459	1.1365	1.1267	1.1025
$T_B$ , <sup>c</sup> MPa	1.7428	1.7824	2.1129	2.1587	2.5075
$E_B$ , <sup>d</sup> %	550	508	600	626	573
Slope <sup>e</sup>	0.3573	0.4784	0.5593	0.4190	0.3781
$\nu^f \times 10^4 \text{ mol/cm}^3$	1.4377	1.9240	2.2490	1.6850	1.5210
$E' \times 10^7$ § dyne/cm <sup>2</sup> at 20°C	2.55	4.03	3.99	4.03	3.96
$T_g$ , <sup>h</sup> °C	35.6	35.3	33.6	34.1	35.5

<sup>a</sup> Young's modulus.

<sup>b</sup> Moduli at 50, 100, 200, and 300%.

<sup>c</sup> Tensile strength at break point.

<sup>d</sup> Elongation at break point.

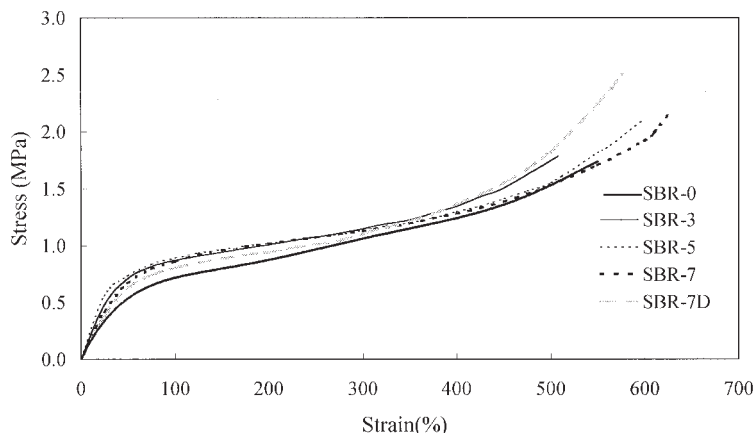
<sup>e</sup> Initial slope value at small strain ratio drawn in Figure 4.

<sup>f</sup> Crosslinking density from the classical (kinetic) theory of rubber elasticity.

§ Storage modulus at 20°C.

<sup>h</sup> Glass-transition temperature.





**Figure 3** Stress–strain curves of SBR-0, SBR-3, SBR-5, SBR-7, and SBR-7D. Plots are indicated by various lines as depicted in the inset.

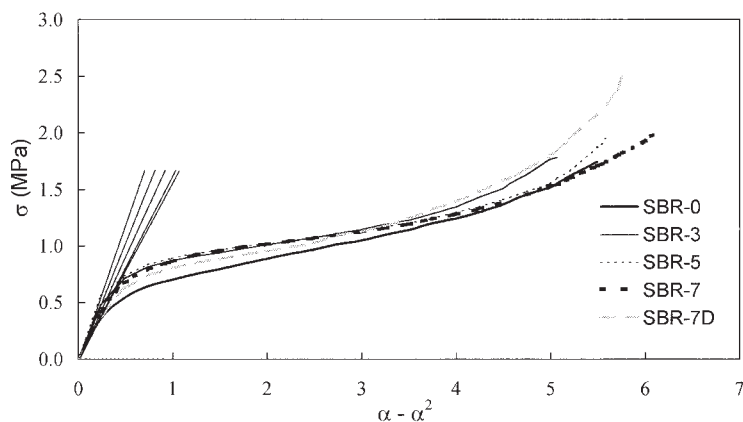
Table III shows the crosslinking densities of SBR-3, SBR-5, SBR-7, SBR-7D, and SBR-0 derived from the above procedures. SBR-0 shows the lowest crosslinking density of  $1.4377 \times 10^4 \text{ mol cm}^{-3}$ , whereas SBR-3, SBR-5, SBR-7, and SBR-7D increased to 1.9240, 2.2490, 1.6850, and  $1.5210 \times 10^4 \text{ mol cm}^{-3}$ , respectively. These suggest that the rubber filled with Mt. Pinatubo volcanic ash has better crosslinking sites.

Likewise, the results obtained from the DMA analysis further show that volcanic ash has no significant effect on SBR vulcanizates. The  $E'$  of SBR-0, which is  $2.55 \times 10^7 \text{ dyne/cm}^2$  at  $20^\circ\text{C}$ , shows only a slight increase from the values of SBR-3, SBR-5, SBR-7, and SBR-7D, which are  $4.03 \times 10^7$ ,  $3.99 \times 10^7$ ,  $4.03 \times 10^7$ , and  $3.96 \times 10^7 \text{ dyne/cm}^2$ . These are in agreement with the data of the  $Y$ ,  $M_{50}$ ,  $M_{100}$ ,  $M_{200}$ , and  $M_{300}$ . The  $T_g$  points also exhibit values similar to that of the pure gum. In Figure 5, it is also noted that the height of the  $\tan \delta$  peak of SBR-0 compounded with volcanic ash exhibits a slight decrease, which indicates that some

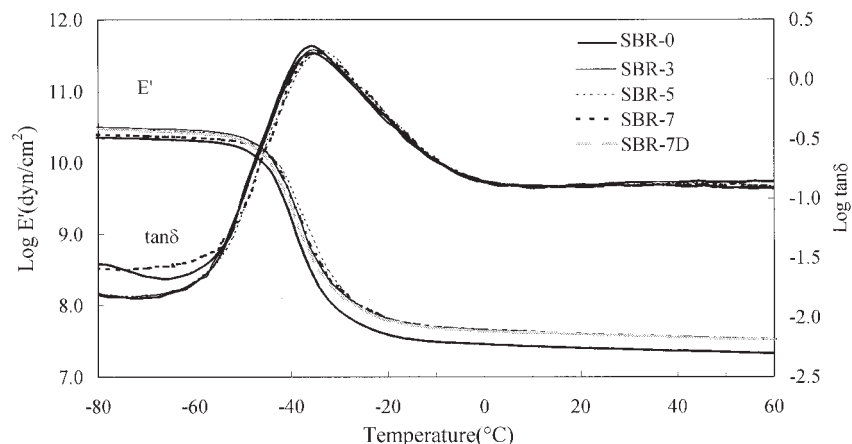
interactions could probably be present at the interface of the rubber and the filler.

## CONCLUSIONS

Mt. Pinatubo volcanic ash was collected from Porac, Pampanga, screened, and wet-ground for 3, 5, and 7 days. X-ray diffraction analysis of the volcanic ash revealed the presence of feldspar, hornblende, quartz, mica, and magnetite. When blended with SBR vulcanizates, no significant improvement on the mechanical properties was observed. Tensile tests confirm the results obtained from the DMA analysis, which indicate only a slight increase on the reinforcing effect of the volcanic ash. The values of the crosslinking densities suggest that the addition of filler increased the crosslinking sites in the rubber matrix. Furthermore, the addition of DEG hastened the speed of the curing reaction of SBR vulcanizates, with no adverse effects



**Figure 4** Stress ( $\sigma$ ) versus strain ratio ( $\alpha - \alpha^2$ ) of SBR-0, SBR-3, SBR-5, SBR-7, and SBR-7D. Plots are indicated by various lines as depicted in the inset.



**Figure 5** DMA analysis of SBR-0, SBR-3, SBR-5, SBR-7, and SBR-7D. Plots are indicated by various lines as depicted in the inset.

observed on the mechanical properties of SBR vulcanizates.

The authors sincerely thank M. Ohara, R. Cerbito, and M. Paglicawan for technical assistance in the conduct of optical analyses and preparation of the volcanic ash; P. Braganza Jr., J. Filio, E. Luis, and S. Bernardo for their valuable comments and suggestions; and to the staff of ITDI and Kyoto University, who in various ways contributed to the completion of this study. This work was financially supported by the RONPAKU (Dissertation Ph.D.) Program of DOST-JSPS Joint Scientific Cooperation Program in Japan.

## References

- Punongbayan, R. S.; Newhall, C. G.; Sabit, J.; Paladio, M.; Arboleda, M. *Pinatubo Volcano Wakes from 4 Century Slumber*; Tayag, J. C., Ed.; Philvolcs Press: Quezon City, Philippines, 1991.
- Punongbayan, R. S.; Arboleda, R. A.; Delos Reyes, P. J.; Tungol, N. M. Lahars at Pinatubo Volcano and Vicinity. *Lessons Learned and Scenarios for the Future*; NRCP-SCOPE Newsletter (Philippines), 1996; Vol. 1, p. 11.
- Bernardo, S. T.; Martinez, E. R.; Basilia, B. A.; Celorico, J. R.; Bedia, E. L.; Salvador, J. B.; Reynales, C. F.; Zambrano, C. B. In: *Characterization and Some Practical Uses of Pinatubo Pyroclastic Fall Deposits*, Proceedings of The International Symposium on Utilization Technology of Volcanic Ejecta, Tokyo, Japan, 1994.
- Bedia, E. L.; Ladines, N. B.; Paglicawan, M. A.; Monsada, A. M. *Philippine Technol J* 1999, 24, 65.
- Braganza, P. S., Jr.; Padilla, G. D.; Cabillon, S. L.; Salvador, J. B.; Gopez, G. U.; Filio, J. M.; Zambrano, C. B.; Bernardo, S. T.; Demiar, W. U.; Navarro, M. M. In: *Proceedings on the Utilization of Pinatubo Volcanic Ejecta and Other Related R&D Studies*, ITDI-PCIERD-DOST, Manila, Philippines, 1994; p. 7.
- Braganza, P. S., Jr.; Padilla, G. D.; Navarro, M. T. V.; Martinez, E.; Cabillon, S. L. In: *Proceedings on the Utilization of Pinatubo Volcanic Ejecta and Other Related R&D Studies*, ITDI-PCIERD-DOST, Manila, Philippines, 1997; p. 13.
- Reynales, C. F. In: *Proceedings on the Utilization of Pinatubo Volcanic Ejecta and Other Related R&D Studies*, ITDI-PCIERD-DOST, Manila, Philippines, 1997; p. 84.
- Samson, L. E.; Sison, F. In: *Proceedings on the Utilization of Pinatubo Volcanic Ejecta and Other Related R&D Studies*, ITDI-PCIERD-DOST, Manila, Philippines, 1997; p. 89.
- Navarro, M. M.; Develos, N. N.; Repalda, J.; De Chavez, E. In: *Proceedings on the Utilization of Pinatubo Volcanic Ejecta and Other Related R&D Studies*, ITDI-PCIERD-DOST, Manila, Philippines, 1997; p. 77.
- Braganza, K. C. S. In: *Philippine Entry to the Intel International Science and Engineering Fair*, Louisville, KY, 2002.
- Cabillon, S. L.; Kiruma, K.; Bernardo, S. T.; Visaya, A. In: *Proceedings on the Utilization of Pinatubo Volcanic Ejecta and Other Related R&D Studies*, ITDI-PCIERD-DOST, Manila, Philippines, 1997; p. 58.
- Salvador, J. B.; Bernardo, S. T.; Basilia, B. A.; Padilla, G. D. In: *Proceedings on the Utilization of Pinatubo Volcanic Ejecta and Other Related R&D Studies*, ITDI-PCIERD-DOST, Manila, Philippines, 1997; p. 93.
- Salvador, J. B. In: *Proceedings on the Utilization of Pinatubo Volcanic Ejecta and Other Related R&D Studies*, ITDI-PCIERD-DOST, Manila, Philippines, 1997; p. 1.
- Padilla, C. N.; Padilla, G. D.; Bernardo, S. T.; Braganza, P. S., Jr. In: *Proceedings of the Philippine Institute of Civil Engineers*, Manila, 2002.
- Augustin, R. G. In: *Proceedings of the 7th CAFT Convention and 22nd ASEAN Float Glass Manufacturing Conference*, Manila, Philippines, 1997.
- Kraus, G.; *Reinforcement of Elastomers*; Wiley: New York, 1965.
- Eirich, F. R. *Science and Technology of Rubber*; Academic Press: Orlando, FL, 1978.
- Wolf, S. *Rubber Chem Technol* 1996, 69, 325.
- Hashim, A. S.; Azahari, B.; Ikeda, Y.; Kohyiyu, S. *Rubber Chem Technol* 1988, 71, 289.
- Treloar, L. G. *The Physics of Rubber Elasticity*, 3rd ed.; Clarendon Press: Oxford, UK, 1975.