

# Fracture properties of silica/carbon black-filled natural rubber vulcanizates

Young Chun Ko<sup>†</sup> and Gayoung Park\*

Department of Nano-Chemical/Environmental Engineering, Daebul University, Chonnam 526-702, Korea

\*Department of Biotechnology, Chosun University, Gwangju 501-759, Korea

(Received 11 June 2007 • accepted 27 July 2007)

**Abstract**—Crack growth property of natural rubber (NR) vulcanizate with varying silica/carbon black content was examined. Tensile specimen with edge cut was used for estimating fracture properties. All filled NR specimens showed critical cut-size ( $C_{cr}$ ), which is related to abrupt decrease in tensile strength. Carbon black-filled NR, S0 (Si/N330=0/50) has higher tensile strength than equivalently loaded silica-filled NR vulcanizates, S5 (Si/N330=50/0). When the pre-cut size of specimen was less than critical cut-size, tensile strength of S1 (Si/N330=10/40) composition was the highest and that of S5 was the lowest. The critical cut-size passes through a maximum for S2 (Si/N330=20/30) and then decreases gradually with silica loading. An interesting result was that silica and carbon black-blended compounds gave higher critical cut size than the all-carbon black compounds, S0. The inherent flaw size decreased from 246  $\mu$ m for S0 to 80  $\mu$ m for S5 as the silica content increased.

Key words: Silica, Carbon Black (N330), Fracture, Critical Cut-size, Inherent Flaw-size

## INTRODUCTION

Rubber should be used with fillers such as carbon blacks to attain the desired mechanical properties [1-4]. Recently, amorphous precipitated silica has been extensively used as a contributor to improve cutting and chipping resistance in off-the-road tires [5,6]. Although silica in truck and bus tread compounds has been used as a minor component of the overall filler loading systems, silica has emerged as a major contributor to the reduction of crack growth. Therefore, there has been great emphasis on the understanding of crack growth behaviors of silica-filled compounds [7-10].

In general, crack growth in vulcanized rubber takes place through a two-step process: cutting and chipping [11]. Cutting takes place when the tire strikes a sharp object on the surface, and the surface of tread is cut [12]. Then, chipping can follow the cutting by the effect of repeated traction force or other forces, causing tearing of a compound at 90° to the direction of the cut until catastrophic failure. According to the fracture mechanics, crack propagation follows a path in the perpendicular direction to the applied deformation [13]. However, crack deviation at the tip region can occur because of strength anisotropy. Cook and Gordan proposed that primary crack deviation would occur if the interface energy,  $G_{ad}$ , was less than one-fifth of the cohesive fracture energy,  $G_{co}$  of the bulk specimen (Eq. (1)) [14]:

$$G_{co} \geq 5 G_{ad} \quad (1)$$

Crack deviation effectively eliminates the stress concentration at the tip and tensile strength is greatly enhanced. It is known that polymer type, carbon black, and labile cross-links are also important factors for controlling crack growth properties [15].

Although much work has been done on crack properties in carbon black-filled rubber, crack properties in silica/carbon black-filled

**Table 1. Formulations of rubber compound recipes**

| Compound entry no.        | S0  | S1  | S2  | S3  | S4  | S5  |
|---------------------------|-----|-----|-----|-----|-----|-----|
| SMR 5CV                   | 100 | 100 | 100 | 100 | 100 | 100 |
| N330 (HAF) <sup>a</sup>   | 50  | 40  | 30  | 20  | 10  | 0   |
| Coupsil 8108 <sup>b</sup> | 0   | 10  | 20  | 30  | 40  | 50  |
| ZnO                       | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Stearic acid              | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Sulfur                    | 2.6 | 2.6 | 2.6 | 2.6 | 2.6 | 2.6 |
| TBBS <sup>c</sup>         | 1.4 | 1.4 | 1.4 | 1.4 | 1.4 | 1.4 |

<sup>a</sup>LG carbon company, Inc.

<sup>b</sup>Silica: Nipsil VN3, Degussa.

<sup>c</sup>TBBS: *t*-butyl benzothiazole sulfonamide, Monsanto.

\*Fill factor of internal mixer=0.83.

rubber have not been examined thoroughly [6]. Here we report the crack growth properties of silica/carbon black NR vulcanizates.

## EXPERIMENTAL

### 1. Formulation and Mixing

The rubber compound recipes used in this work are summarized in Table 1. S means silica and the numbers, 0, 1, 2, 3, 4, and 5 represent silica content ( $\times 10$ ) in silica and carbon black-filled compounds. The vulcanizing system was a conventional cure system (TBBS: 1.4 phr and sulfur: 2.6 phr) of natural rubber (SMR-5CV) containing silica/HAF(N330), 0/50, 10/40, 20/30, 30/20, 40/10, and 50/0. Compounds were prepared by a two-step process that includes the preparation of a masterbatch in 1,500 mL BR Banbury mixer, followed by curative addition on a two-roll mill. The fill factor was determined to be 0.83.

### 2. Edge-cut

Tensile strips were cut from the vulcanized sheets. For simple edge cut test, pre-cuts of varying length were introduced perpen-

<sup>†</sup>To whom correspondence should be addressed.

E-mail: ycko@mail.daebul.ac.kr

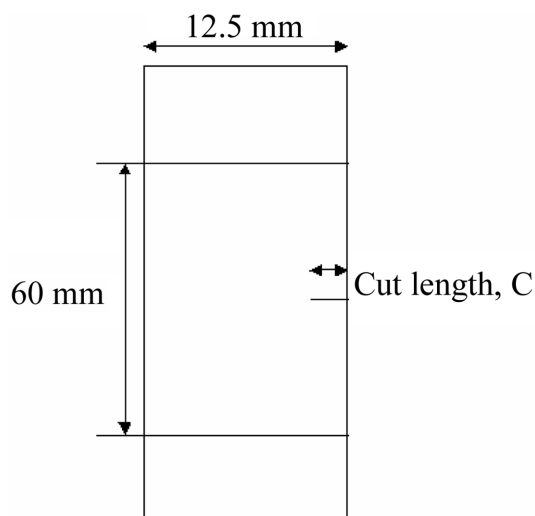


Fig. 1. Specimens of tensile strips with an edge cut of length,  $C$ .

pendicular to the specimen length at the midpoint edge by using a razor blade which had been dipped in a soap solution. Specimen dimensions and shapes are shown Fig. 1. The depth of an edge cut was determined with a traveling microscope. Cut growth testing was

carried out with Instron (Model 6021) testing machines. Specimens were extended at a strain rate of  $0.833 \text{ min}^{-1}$ . In order to analyze the effect of pre-cut on the tensile properties of carbon black/silica filled samples, the tearing energy was obtained from Eq. (2) [16]:

$$T = 2KW_bC \doteq 2(\pi/\lambda^{1/2})W_bC \quad (2)$$

Where  $T$  is the tearing energy of the sample specimen,  $W_b$  is the strain energy density which was measured from the areas under stress-strain curves corresponding to the strain of the pre-cut specimen,  $C$  is the crack length, and  $K$  is a dimensional parameter that approaches  $\pi$  at very small strain and decreases slowly with increasing strain ( $\doteq \pi/\lambda^{1/2}$ ,  $\lambda$  is the extension ratio in the body of the test piece).

## RESULTS AND DISCUSSION

### 1. Silica Loading Effect on Tensile Strength

Tensile strength was measured for silica/carbon black-filled specimens containing various pre-cut sizes ( $C$ ). The relationship between tensile strength and pre-cut size ( $C_0$ ) is shown in Fig. 2. All compositions exhibit critical cut-size ( $C_c$ ), which is related to the abrupt decrease in tensile strength. Under the fixed pre-cut size, carbon black-filled specimen, S0, possesses higher tensile strength than silica-filled sample, S5. Tensile strength was a maximum corresponding to 10 phr silica content and then decreased gradually with pre-

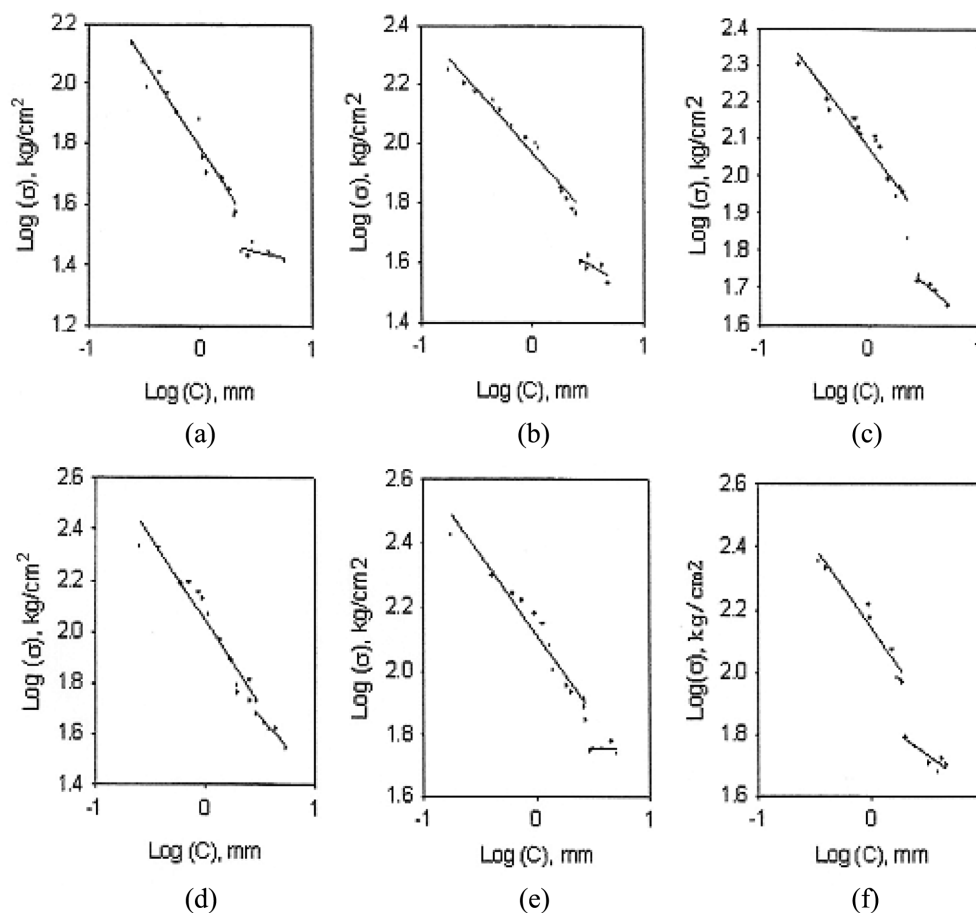
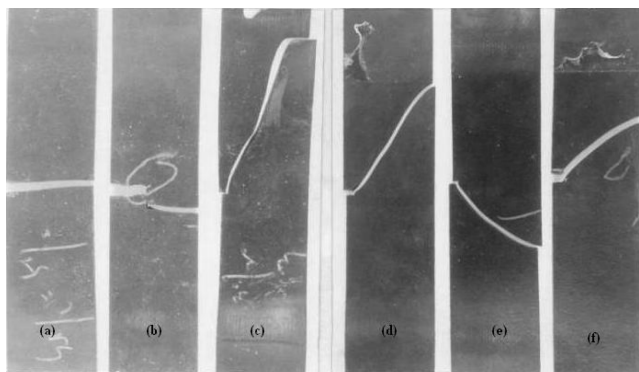
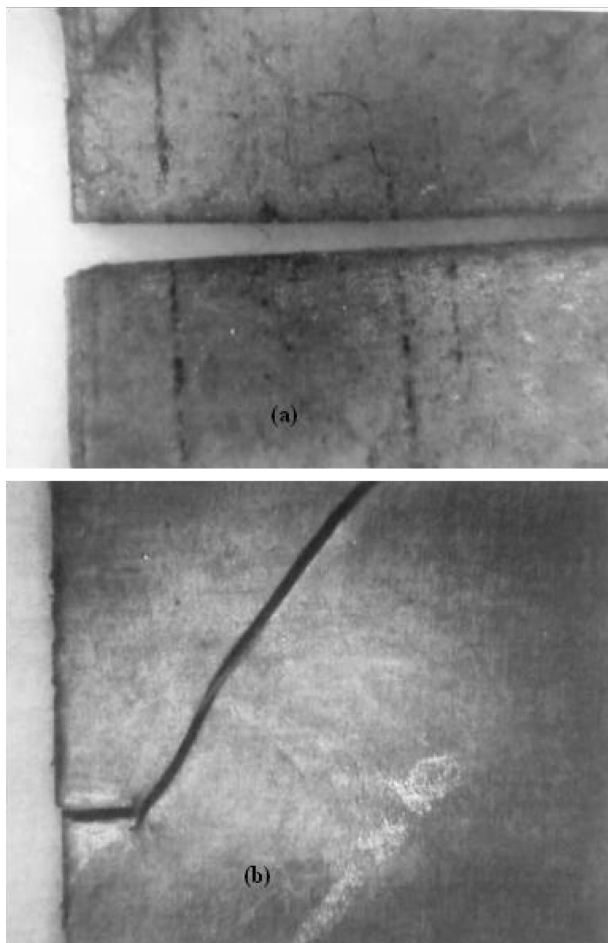


Fig. 2. Effects of pre-cut size on the tensile strength for various compositions.

(a) S5, (b) S4, (c) S3, (d) S2, (e) S1, (f) S0

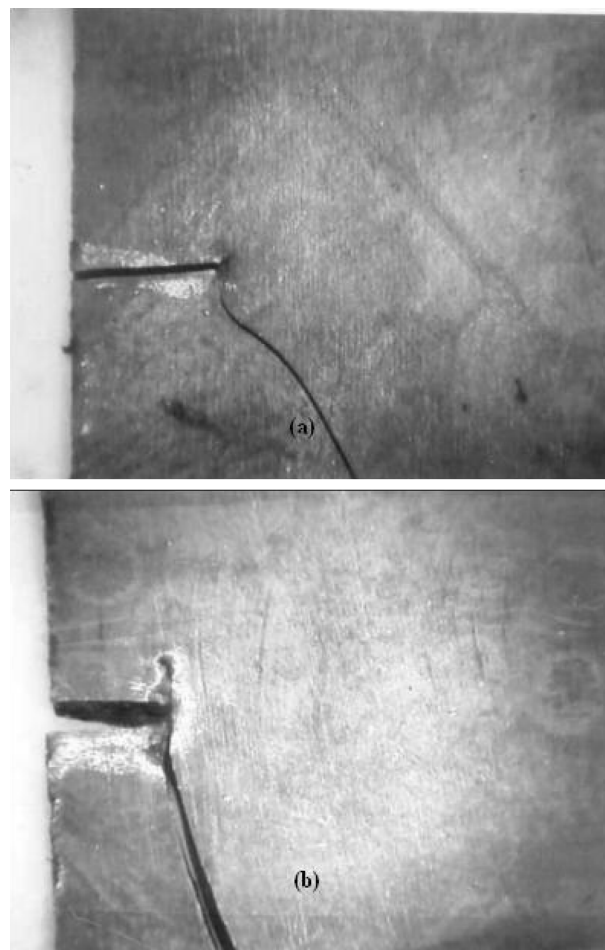


**Fig. 3.** Photomacrographs of fractured samples representing the effect of pre-cut size on crack growth paths at room temperature. (a) S5:  $C=1.08$  mm;  $\sigma=56.8$  kg/cm<sup>2</sup>,  $TE=23.7$  kJ/m<sup>2</sup>, (b) S4:  $C=1.15$  mm;  $\sigma=95.5$  kg/cm<sup>2</sup>,  $TE=44.5$  kJ/m<sup>2</sup>, (c) S3:  $C=0.85$  mm;  $\sigma=132.4$  kg/cm<sup>2</sup>,  $TE=48.7$  kJ/m<sup>2</sup>, (d) S2:  $C=1.42$  mm;  $\sigma=92.4$  kg/cm<sup>2</sup>,  $TE=65.4$  kJ/m<sup>2</sup>, (e) S1:  $C=0.96$  mm;  $\sigma=151.3$  kg/cm<sup>2</sup>,  $TE=54.9$  kJ/m<sup>2</sup>, (f) S0:  $C=1.31$  mm;  $\sigma=110.4$  kg/cm<sup>2</sup>,  $TE=53.2$  kJ/m<sup>2</sup>.



**Fig. 4.** Optical micrographs for the region near the crack tip. (a) S5:  $C=1.08$  mm;  $\sigma=56.8$  kg/cm<sup>2</sup>,  $TE=23.7$  kJ/m<sup>2</sup>, (b) S0:  $C=1.31$  mm;  $\sigma=110.4$  kg/cm<sup>2</sup>,  $TE=53.2$  kJ/m<sup>2</sup>.

cut size when  $C < C_{cr}$ . In order to investigate differences in tensile strength, the surface morphology at the crack tip region was exam-



**Fig. 5.** Optical micrographs for the region near the crack tip. (a) S1:  $C=0.96$  mm;  $\sigma=151.3$  kg/cm<sup>2</sup>,  $TE=54.9$  kJ/m<sup>2</sup>, (b) S4:  $C=1.16$  mm;  $\sigma=97.5$  kg/cm<sup>2</sup>,  $TE=45.1$  kJ/m<sup>2</sup>.

ined with an optical microscope. Crack paths of various specimens are shown in Fig. 3. There is a clear difference in crack paths with increasing silica content. The crack path for S5 sample is almost lateral to the loading direction. However, crack paths of pre-cut specimens for silica/carbon black blended samples do not proceed laterally to the loading direction, and crack paths are considerably deflected from the initial pre-cut direction. The extent of crack deviation generally decreases with increasing carbon black content. Another difference is the microcracking pattern at the tip. The S5 specimen does not show longitudinal cracking at the tip region as shown in Fig. 4. However, the S0 sample exhibits a crack deviation with secondary cracking at the tip region. Longitudinal cracking in Fig. 5 is observed above and/or below the tip, a kind of delamination for the blend systems. S1 specimen shows a deflected crack with multiple secondary cracks. On the other hand, S4 specimen had considerably deflected cracks with little developed secondary cracks at the tip region. The S1 specimen exhibits higher tensile strength (151.3 kg/cm<sup>2</sup>) than the S4 specimens (97.5 kg/cm<sup>2</sup>). Apparently, higher tensile strength is observed with longer delaminated cracks before catastrophic tearing and longer diagonal crack deflection. Hamed and co-worker reported that the reduction of stress concentration was achieved by simple energy dissipation and parabolic blunting

[11]. They also showed that crack deviation at the crack tip was responsible for the enhanced tensile strength. High orientation of NR chains at the crack tip is associated with extensive longitudinal and secondary cracking. Sufficient anisotropy at the crack tip can develop longitudinal cracks, which changes the geometry of cracking, reduces stress concentration and enhances crack growth resistance. Medalia postulated that the alignment of carbon black aggregates could be formed as the vulcanizate is stretched [17]. This forming physical barrier perpendicular to the direction of growing tear delays crack growth. One of the possible rationalizations is that both high orientations due to slippage of chain over surface of silica and strand due to strong interaction between carbon black and rubber matrix seem to be associated with extensive longitudinal cracks at the tip region. Slippage behavior of polymer chain on the surface of silica depends on the quantity of silica used. At low concentration (under 20 phr silica content), low interaction between polymer and silica is related to the enhanced orientation at the tip region during the stretching. However, at higher concentration (i.e., beyond 20 phr silica content), the stress at the tip may be too low to induce sufficient alignment of filler particles due to slippage phenomenon. Low interaction between filler and rubber molecular induces slip over the filler surface and fails to drag it into alignment.

Fracture energy against cut size for carbon black, silica, and silica/carbon black-filled NR vulcanizates is shown in Fig. 6. Here, S3 and S4 are not presented because their descriptions of the figure are complicated. High tearing energy of S0, compared to S5, is attributed to high energy dissipation due to carbon black. It is also observed that fracture energy of the silica and carbon black blend compound is similar or higher compared with that of S0 specimens and the fracture energy increases with increasing pre-cut size. At very low pre-cut size, tearing energy (TE) of S0 sample is similar to the blend compounds because it is masked by strain-induced crystallization at the crack tip. For the large pre-cut size, S1 exhibited higher fracture energy compared with S0. This implies that a small amount of silica in filled rubber seems to impart considerable advantages for improving cut and chipping resistance that cannot be obtained with carbon black alone. The tearing energy seems to be strongly influenced by microcracking at the tip region. As shown in Figs.

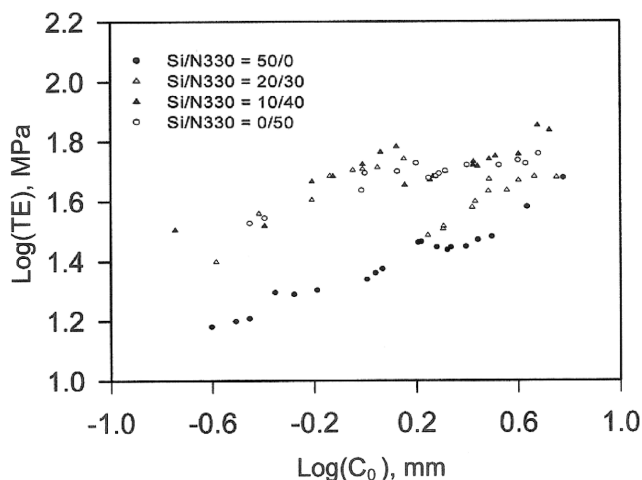


Fig. 6. Fracture energies against pre-cut size for silica/N330-filled vulcanizates.

4, 5 and 7, the high tearing energy of samples seems to be directly related with secondary cracking or highly deflected cracks before catastrophic tearing.

## 2. Critical Cut Size

The effect of silica loading on critical cut size is shown in Fig. 8.

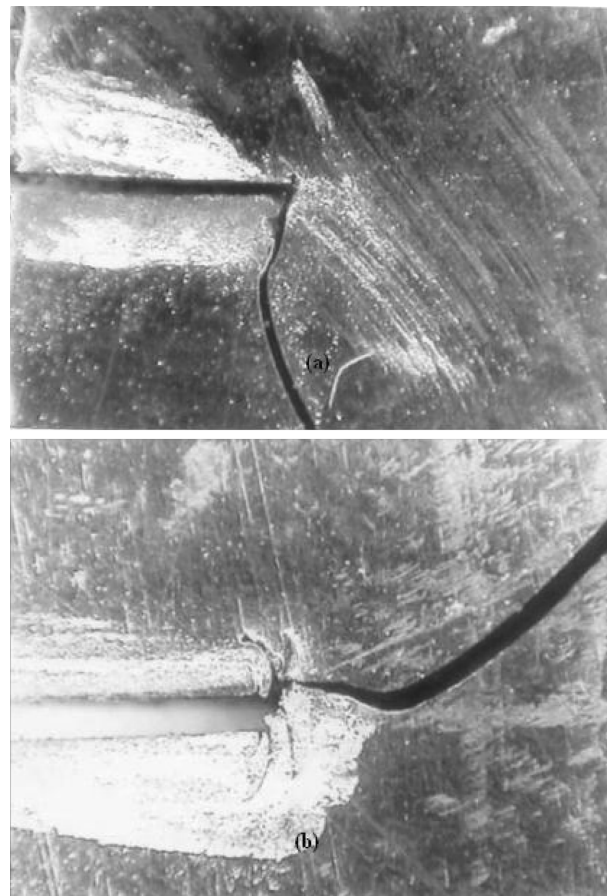


Fig. 7. Optical micrographs for the region near the crack tip. (a) S1: C=1.80 mm;  $\sigma$ =95.6 kg/cm<sup>2</sup>, TE=45.8 kJ/m<sup>2</sup>, (b) S3: C=1.75 mm;  $\sigma$ =80.3 kg/cm<sup>2</sup>, TE=40.2 kJ/m<sup>2</sup>.

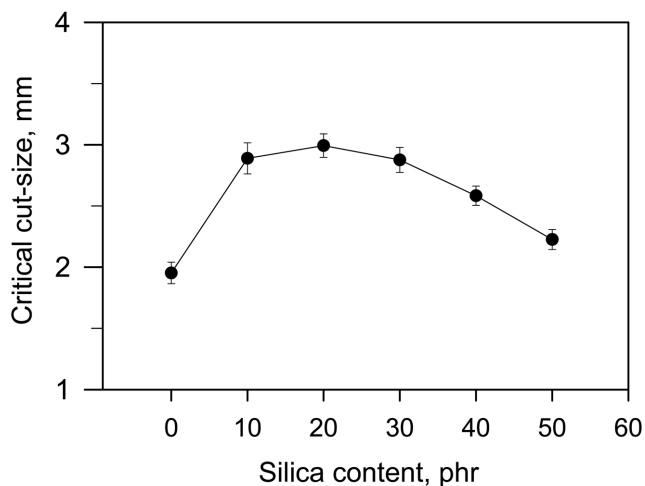


Fig. 8. Critical cut size against silica content for silica/N330-filled vulcanizates.

There are some limits to calculating the exact critical cut size with variation of silica loading because the tensile strength of pre-cut samples is closely related to crack tip pattern. In order to increase the accuracy, the experiment was carried out ten times. The critical cut size for NR is in the range of 1.95 mm to 3.00 mm, and the variation of silica loading influences the critical cut size. Test results show that maximum point of critical cut size seems to be somewhere between S1 and S3 and then decrease gradually with increasing silica loading. Thomas and Whittle observed a rapid drop of tensile strength at a critical depth of an edge cut for gum NR vulcanizates [18]. It is known that bulk crystallization occurs below the critical cut size but not above it. An interesting result is that compounds with silica gave higher critical cut size than the equivalent all-carbon black compounds. This seems to be related to the enhanced orientation at the tip region during the stretching because of low interaction energy between silica and polymer. It gives rapid crystallization, resulting in increased critical cut-size compared to that of only black-filled rubber, S0.

### 3. Intrinsic Flaw Size

The intrinsic cut-size ( $C_0$ ) of silica content for silica/N330-filled NR vulcanizates is shown in Fig. 9. Specimens always have naturally occurring flaws, entrapped impurities or edge flaws introduced by a cutter. To increase the accuracy of the intrinsic cut-size, an experiment of five specimens selected in the range of permissible 5% error was carried out. Intrinsic cut-size in which is not present intentional pre-cut is obtained from the equation of pre-cut-size vs. tensile strength by substituting tensile strength for tensile strength of no pre-cut sample when that strength is equal to this strength. The physical meaning of  $C_0$  is that an actual razor cut of length less than  $C_0$  would have no effect on strength, whereas a longer razor cut length than  $C_0$  would lower strength [19].  $C_0$  exhibited 246  $\mu\text{m}$  for S0, 184  $\mu\text{m}$  for S1, and 150  $\mu\text{m}$  for S2, respectively. For silica content above 30 phr compound, moreover,  $C_0$  showed smaller values, 107  $\mu\text{m}$  for S3, 85  $\mu\text{m}$  for S4, and 80  $\mu\text{m}$  for S5. The significance of the decrease of  $C_0$  with increased silica content is that a high content of silica in

compound has low ability to tolerate the flaws before catastrophic tearing. On the other hand, a high value of  $C_0$  for carbon black-filled rubber or for low content of silica indicates a greater ability to blunt the crack tip before catastrophic failure and hence delays fracture. It seems that a decrease of filler-polymer interaction for facilitating filler flocculation in high loading silica compounds results in low intrinsic flaw size.

## CONCLUSIONS

Silica-filled NR vulcanizates exhibit the lowest tensile strength and tear energy compared to carbon black-filled or blend compounds. In the silica/black blend vulcanizates, both tensile strength and tear energy seem to pass the maximum point corresponding 10-20 phr silica compounds. The critical cut size for silica compounds is higher than that of carbon black-filled NR. Only silica-filled NR shows the lowest tensile strength and tear energy. For a sample with only one filler, un-cut samples of carbon black and silica samples have similar tensile strength. However, for the cut samples, there are considerable differences of crack growth patterns. Apparently, silica can offer considerable advantages in some applications that cannot be obtained with carbon black alone. High fracture energies of small amount of silica-filled compounds are strongly influenced by micro-cracking at the tip region and, apparently, longitudinal cracks at the crack tips are responsible for the enhanced tensile strength.

## REFERENCES

1. A. Medalia, *J. Colloid Interf. Sci.*, **32**, 115 (1970).
2. G. Kraus, *Rubber Chem. Technol.*, **49**, 199 (1971).
3. G. S. Jeon and G. Seo, *Korean J. Chem. Eng.*, **20**, 496 (2003).
4. G. S. Jeon, M. H. Han and G. Seo, *Korean J. Chem. Eng.*, **15**, 317 (1998).
5. C. Lin, W. L. Hergenerother and A. S. Hilton, *Rubber Chem. Technol.*, **75**, 215 (2002).
6. N. Suzuki, M. Ito and F. Yatsuyanagi, *Polymer (Japan)*, **46**, 193 (2005).
7. L. A. Walker and Kautsch, *Gummi Kunstst.*, **38**, 494 (1985).
8. M. J. Wang, S. Wolff and J. B. Donnet, *Rubber Chem. Technol.*, **64**, 559 (1991).
9. S. S. Park, B. H. Park, K. C. Song and S. K. Kim, *Polymer (Korea)*, **24**, 220 (2000).
10. Q. Cao and W. Cui, *China Rubber Ind.*, **48**, 389 (2001).
11. G. R. Hamed and H. J. Kim, *Rubber Chem. Technol.*, **72**, 895 (1999).
12. J. R. Beatty and B. J. Miksch, *Rubber Chem. Technol.*, **55**, 1531 (1982).
13. R. S. Rivlin and A. G. Thomas, *J. Polym. Sci.*, **10**, 291 (1952).
14. J. Cook and J. E. Gordon, *Proc. Roy. Soc.*, **A282**, 508 (1964).
15. D. De and A. N. Gent, *J. Mater. Sci.*, **19**, 3612 (1984).
16. R. S. Rivlin and A. G. Thomas, *J. Polym. Sci.*, **10**, 291 (1953).
17. A. I. Medalia, *Rubber Chem. Technol.*, **60**, 45 (1987).
18. A. G. Thomas and J. M. Whittle, *Rubber Chem. Technol.*, **43**, 222 (1970).
19. G. R. Hamed, *Rubber Chem. Technol.*, **56**, 244 (1983).

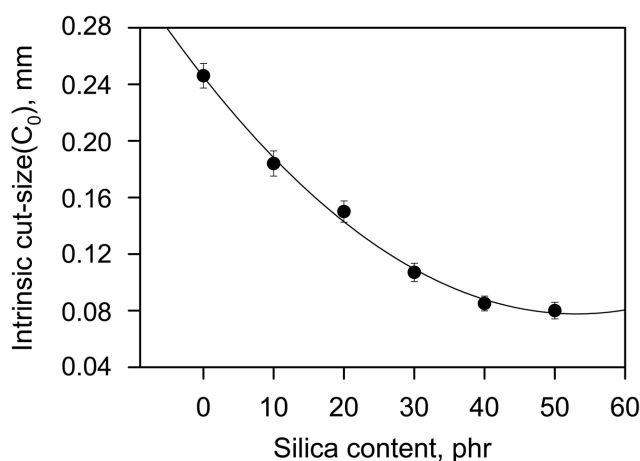


Fig. 9. Intrinsic flaw size against silica contents for silica/N330-filled vulcanizates.