Fracture Behavior of NR and SBR Vulcanizates Filled with Ground Rubber Having Uniform Particle Size

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ABSTRACT: The use of recycled rubber including ground scrap vulcanizates in rubber compounds was studied. When ground rubber was incorporated into rubber compounds, the physical properties, especially the tensile strength, were deteriorated compared to the virgin rubber compound. Also, incorporating ground rubber caused a change of the cure behavior via migration of sulfur or an accelerator between the virgin rubber matrix and the ground rubber vulcanizate. In this study, the fracture behavior and abrasion property of carbon black-filled SBR and NR compounds containing ground rubber vulcanizate were investigated. Also, the effect of the particle size or loading volume of ground rubber powder on those properties was studied. Four different sizes, 420–600, 177–250, 125–150, and 75–88 μm, of ambient ground rubber powder recycled from waste tire were selected and used in the compounding. The loading amounts of ground rubber powder were 10, 30, and 50 phr. The flex crack growth of SBR- and NR-based compounds was altered by the addition of ground rubber particles. More delayed crack growth was observed with an increasing loading volume and decreasing particle size of the ground rubber powders, and this behavior was more prominent in SBR than in NR compounds. Tangent delta, a direct measure of internal energy dissipation, increased with an increasing loading volume of the ground rubber particles. The abrasion rate of ground rubber-filled compounds was more dependent on the size of the abrasion pattern than on the loading level or particle size of the ground rubber powders. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2491–2500, 2002

Key words: ground rubber; particle size; SBR; NR; crack growth; abrasion

INTRODUCTION

Recycling waste tire is very much required nowadays, not only for the minimization of environmental impacts but also for the preservation of natural resources.

The recycling of waste tire can be divided into three categories: its use as heat by incineration, as the original shape, and as ground powder. Among them, ground tire rubber powder obtained by grinding and pulverizing waste tire has relatively wide applications. To improve the characteristics of ground waste tire powder and to find new application fields, the pulverization of waste tire,[1–5] the surface modification of ground rubber particles,[6–8] the standardization of quality evaluation,[9,10] and the devulcanization method[11,12] have been studied. The application of recycled rubber, including ground scrap vulcanizates, in rubber compounds has been reported.[13–16] When ground rubber was incorporated into rubber compounds, the physical properties, especially the tensile strength, was deteriorated compared to the virgin rubber compound. Also, incorporating

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Table I Compound Recipe and Physical Properties

Ingredients/Physical Properties	Compound Recipe #1	#2	#3	#4	#5	#6	#7	#8
SBR-1502	100	100	100	100	100	100	100	100
Zinc oxide	3	3	3	3	3	3	3	3
Stearic acid	1	1	1	1	1	1	1	1
Carbon black (N330)	50	50	50	50	50	50	50	50
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
NS (TBBS)[a]	1	1	1	1	1	1	1	
Ground rubber powder								
30–40 mesh		30						
60–80 mesh			10	30	50			
100–120 mesh						10	30	
170–200 mesh								30
Mooney viscometer								
Male + 4 at 125°C (lbs in.)	66.0	80.0	64.0	76.0	84.0	68.0	77.0	79.0
Scorch time ($t5$, min)	30.8	21.2	25.3	22.9	20.0	27.7	22.3	22.5
Rheometer at 160°C								
$T40$ (min)	8.1	6.4	6.4	5.9	5.4	6.5	5.5	5.7
$T90$ (min)	15.9	15.0	13.6	13.7	12.5	13.6	12.3	13.0
T_{max} (lbs in.)	54.0	43.0	49.0	45.0	42.0	50.0	46.0	46.0
Tensile tests								
Hardness (Shore A)	68	66	68	67	67	68	67	67
100% modulus (kg/cm^2)	30	22	28	23	23	29	25	25
Tensile strength (kg/cm^2)	269	157	220	195	180	250	236	242
Elongation at break (%)	418	421	408	465	456	430	470	487

[a] *N-t*-Butyl-2-benzothiazole sulfenamide.

ground rubber caused a change of the cure behavior via the migration of sulfur or an accelerator between the virgin rubber matrix and the ground rubber vulcanizate.[17,18]

In this study, the fracture behavior and abrasion property of carbon black-filled SBR and NR compounds containing ground rubber vulcanizates were investigated. Also, the effects of the particle size or loading volume of ground rubber powder on those properties were studied.

EXPERIMENTAL

Materials

Four different sizes, 420–600, 177–250, 125–150, and 75–88 μm, of ambient ground rubber powder recycled from waste tire were selected and separated precisely via passing through sieves with corresponding mesh sizes of 30–40, 60–80, 100–120, and 170–200, respectively. The loading amounts of ground rubber powder were 10, 30, and 50 phr. The compound formulations are listed in Tables I and II.

Preparation of Specimen

Mixing was performed using an internal mixer (Farrel 82-BR, USA). The ground rubber powder was premixed with rubber and then the ingredients were incorporated. This was for better dispersion of the ground rubber powder on the rubber matrix. The total mixing time was about 6 min. The specimen was cured on a hot press at 160°C. The cure time was determined by a rheometer (Monsanto-R100).

Measurements

The crack growth rate was measured using the De Mattia flex cracking (DMFC) test by the

Table II Compound Recipe and Physical Properties

Ingredients/Physical Properties	Compound Recipe #1	#2	#3	#4	#5	#6	#7	#8
SMR-CV60	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
Carbon black (N330)	35	35	35	35	35	35	35	35
Sulfur	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25
NS (TBBS)[a]	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Ground rubber powder								
30–40 mesh		30						
60–80 mesh			10	30	50			
100–120 mesh						10	30	
170–200 mesh								30
Mooney viscometer								
Male + 4 at 125°C (lbs in.)	47.0	56.0	55.0	60.0	64.0	54.0	60.0	59.0
Scorch time ($t5$, min)	20.1	18.1	15.7	15.2	14.2	17.5	17.8	16.6
Rheometer at 160°C								
$T40$ (min)	4.4	4.0	3.8	3.6	3.7	3.9	3.8	3.6
$T90$ (min)	7.2	6.8	6.5	6.3	6.5	6.7	6.5	6.4
T_{max} (lbs in.)	43.0	41.0	43.0	41.0	39.0	43.0	39.0	42.0
Tensile tests								
Hardness (Shore A)	57	59	59	58	57	58	58	59
100% modulus (kg/cm^2)	22	23	24	22	21	24	21	23
Tensile strength (kg/cm^2)	312	193	280	251	242	289	269	270
Elongation at break (%)	577	470	537	517	535	539	558	543

[a] *N-t*-Butyl-2-benzothiazole sulfenamide.

ASTM D813 test method. The cut length was measured at frequent intervals to determine the cut growth rate. The initial cut was made by a specially shaped chisel. The initial cut length was 1.2 mm, the flexing speed was 300 cycles/min, and the test temperature was 50°C. The abrasion rate was measured using a PICO abrasion tester (blade-type abrader, ASTM D2228) and was represented by the weight loss per revolution of the specimen. The abrasion rate was measured when the weight loss reached a steady state, and the sliding direction of the abrader (knife) was unidirectional. A 25 N of normal load was applied constantly during the test. Also, the surface morphology of the specimen obtained after the DMFC test or the abrasion test was observed through an image analyzer (KH-2200, Mitsubishi, Japan). The pattern spacing was measured on a photograph. Each pattern of the central region of the worn surface was measured and average values were determined. Dynamic viscoelastic properties (elastic modulus, loss modulus, tangent delta) were obtained by a Qualimeter (Eplexor-150N, Gabo, Germany) under the tensile mode with a strain of 0.13% at 11 Hz.

RESULTS AND DISCUSSION

Cure Behavior

As seen in Figure 1, the scorch time ($T40$) and maximum torque (T_{max}) on the rheometer curve for the SBR compounds decreased with an increasing loading amount of ground rubber powders. These results agree well with previous observations, showing a decrease in the scorch time and maximum torque when ground rubber vulcanizates were added to the SBR compounds.[17] According to Gibala and Hamed,[17] torque reduction could be explained by the migration of sulfur from the matrix rubber to the ground vulcanizate and

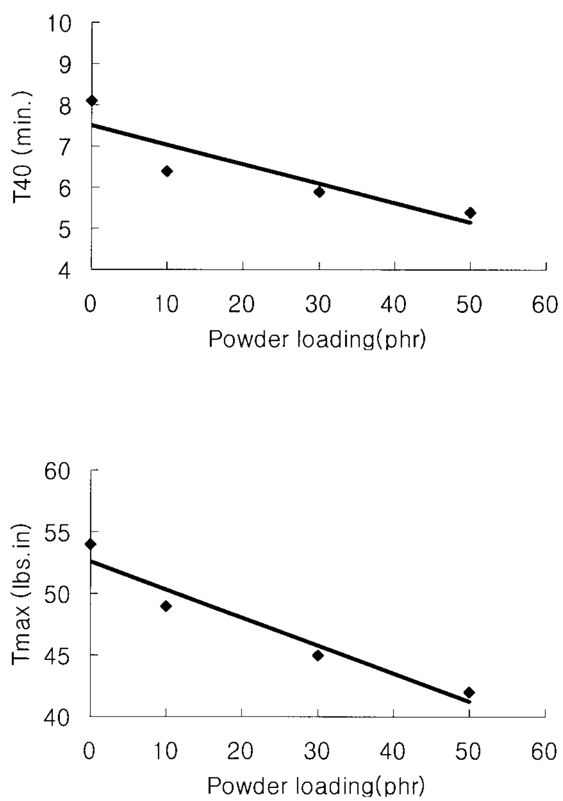


Figure 1 Cure behavior of SBR compounds with varying loading amounts of ground rubber powders: $T40$: scorch time; T_{max}: maximum torque.

the decreased scorch time by the migration of accelerator fragments from the ground vulcanizate to the matrix.

Tensile Properties

The tensile properties, tensile strength, and modulus decreased with an increasing loading volume and particle size. These results are in a good agreement with previous works.[13,14] Especially, such a trend was more prominent in the tensile strength than in the modulus as shown in Figures 2 and 3.

Fracture Behavior

Figures 4 and 5 show the test results of the DMFC test for filled SBR compounds containing ground rubber powders. As seen in Figures 4 and 5, crack growth was delayed with a decreasing average particle size and increasing loading volume of the ground rubber powder. These results show a good agreement with the morphology of

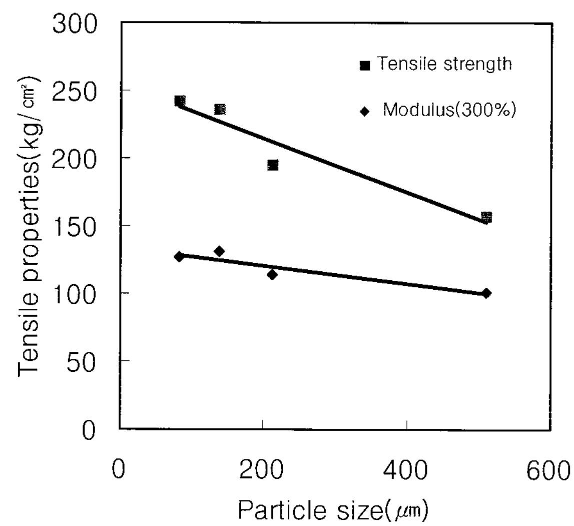


Figure 2 Tensile properties of SBR compounds with varying particle sizes of ground rubber powder (loading amount of powder = 30 phr).

the fracture surface observed after the DMFC test. As seen in photographs of Figure 6, the fracture surfaces of SBR compounds without any ground rubber particles appeared to be smooth, whereas those compounds containing ground rubber powders became relatively rough. It appears that the ground rubber particles interrupt the path of the crack growth direction, so crack growth is resisted and delayed. According to the

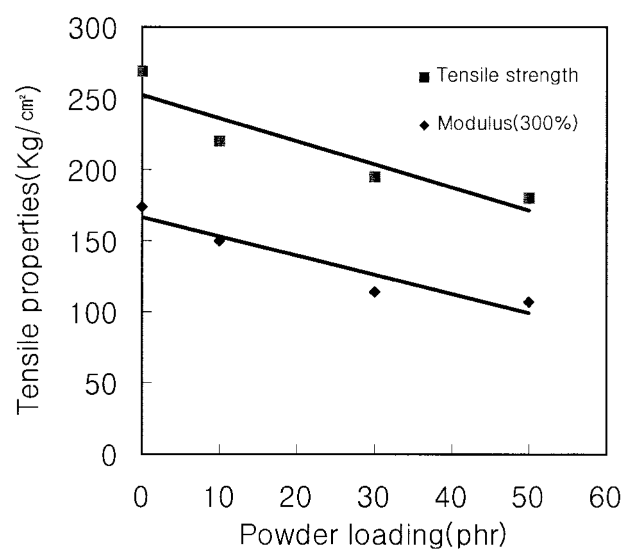


Figure 3 Tensile properties of SBR compounds with varying loading amounts of ground rubber powder (particle size of powder = 177–250 μm).

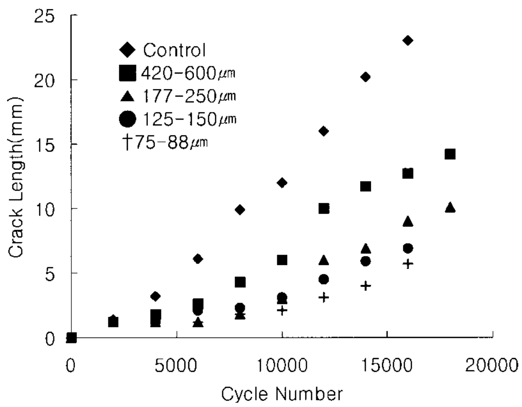


Figure 4 Crack growth rate of SBR compounds with varying particle sizes of ground rubber powder (loading amount of powder = 30 phr).

literature,[19] the increase in tear strength by fillers has been known to be of two kinds: an increase in intrinsic strength due to enhanced energy dissipation or a major increase due to a deviation of the tear path; it may reflect the anisotropy of stress around the crack tip.

The fracture behavior of NR compounds including ground rubber powders was also investigated. As shown in Figures 7 and 8, the effect of ground rubber particles on the fracture behavior of NR compounds was less compared to the case of SBR compounds. This lessened tendency was also observed on the fracture surface of the NR compounds. As seen in Figure 9, there was no conspicuous difference on the fracture surface between the ground rubber-filled compound and the

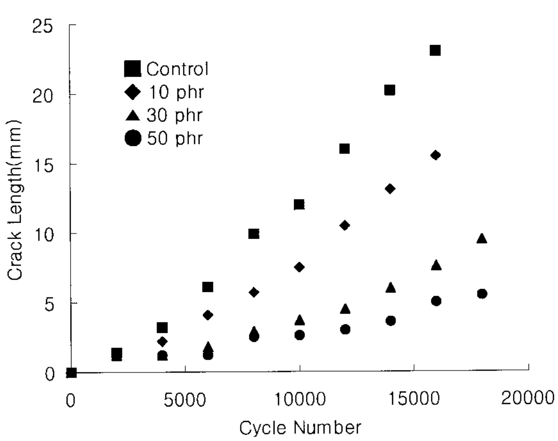
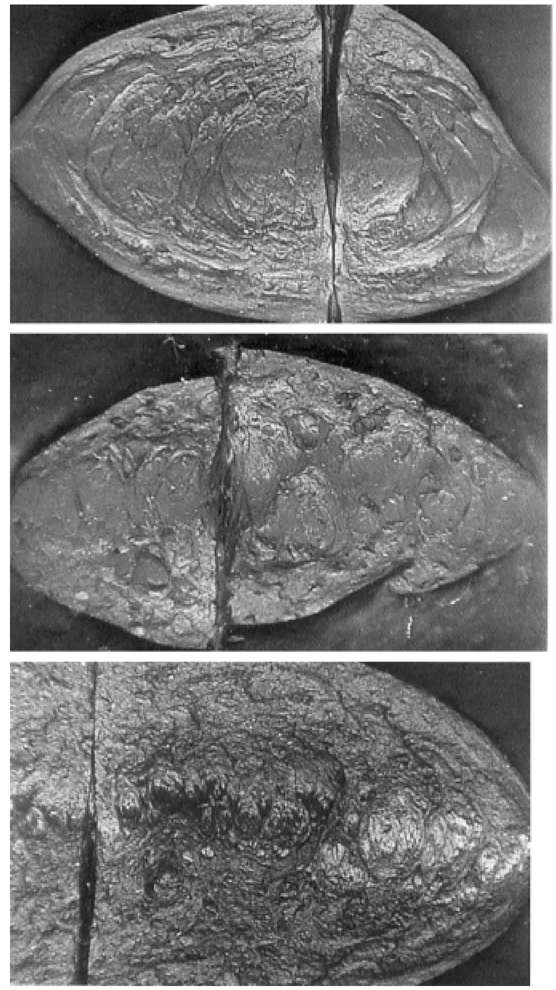


Figure 5 Crack growth rate of SBR compounds with varying loading amounts of ground rubber powder (particle size of powder = 177–250 μm).



A

B

C

Figure 6 Fracture surface after DMFC test for filled SBR compounds: (A) without ground rubber powder; (B) with ground rubber powder (particle size = 420–600 μm; loading = 30 phr); (C) with ground rubber powder (particle size = 125–150 μm; loading = 30 phr).

pure compound. However, the tendency of a decrease of the crack growth rate with a decreasing average particle size and with an increasing loading volume of ground rubber powders also was seen (Figs. 7 and 8). Even though SBR-based compounds had a lower crack growth resistance compared to the NR-based compounds, the crack growth rates of the SBR and NR compounds were similar when ground rubber particles were incorporated into the matrix compounds. Figures 10 and 11 well illustrate this phenomenon.

According to Lake and Lindley,[20] the fatigue crack growth rate of NR compounds is lower than that of SBR compounds, which can be represented by the equation

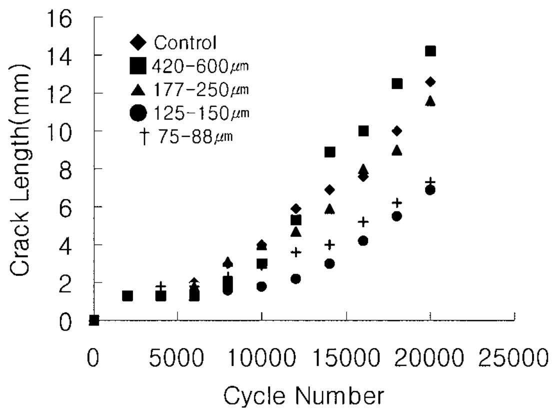


Figure 7 Crack growth rate of NR compounds with varying particle sizes of ground rubber powder (loading amount of powder = 30 phr).

$$\Delta c = BG^{\alpha}; \quad \alpha = 2 \text{ for NR} \quad \text{and} \quad \alpha = 4 \text{ for SBR}$$

where $\Delta c(dc/dn)$ is the crack growth step per stress application (crack growth rate); B, the crack growth constant; and G, the tearing energy. Such a higher strength of the NR compound is explained by that strain-induced crystallization occurred *in situ* the crack tip.

However, in this study, when the ground rubber particles were incorporated into the NR rubber matrix, the advantage of NR over the corresponding SBR compounds was not found. It can be attributed to the fact that some advantages of NR, such as a strain-induced crystallization, are not likely to occur due to the depression effect by the ground rubber particle present *in situ* the crack tip.

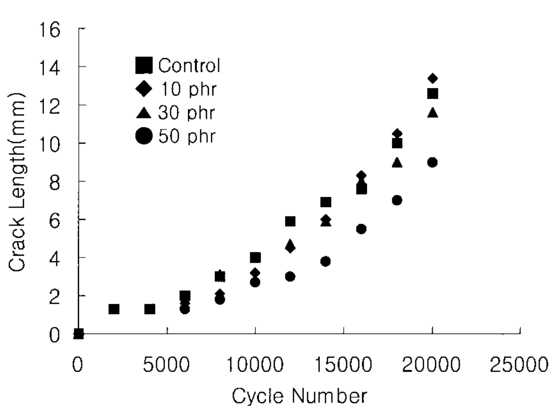


Figure 8 Crack growth rate of NR compounds with varying loading amounts of ground rubber powder (particle size of powder = 177–250 μm).

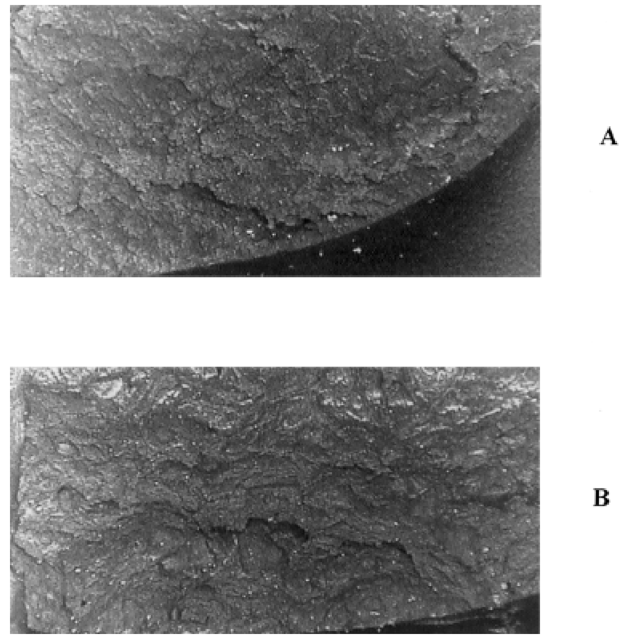


Figure 9 Fracture surface after DMFC test for filled NR compounds: (A) without ground rubber powder; (B) with ground rubber powder (particle size = 420–600 μm; loading = 30 phr).

In addition, the fatigue life was measured using a Monsanto fatigue-to-failure tester. Figures 12 and 13 show that fatigue life increased with a decreasing average particle size and with an increasing loading volume of ground rubber powders, confirming the results obtained from the DMFC test.

Incorporating ground rubber particles into the rubber matrix increased the internal energy dis-

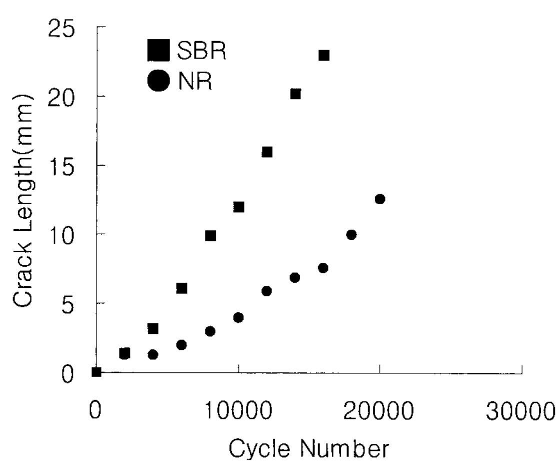


Figure 10 Crack growth rate of NR and SBR compounds without ground rubber powder.

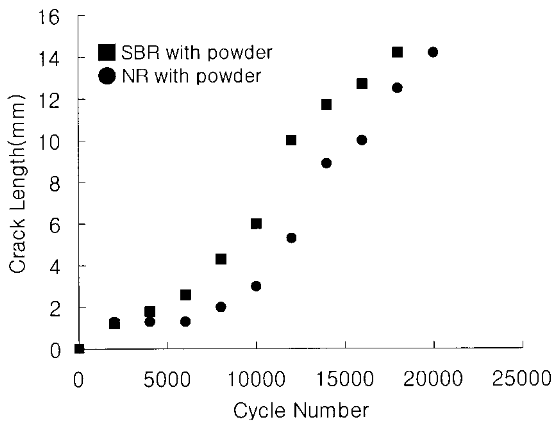


Figure 11 Crack growth rate of NR and SBR compounds with ground rubber powder (particle size = 420–600 μm; loading = 30 phr).

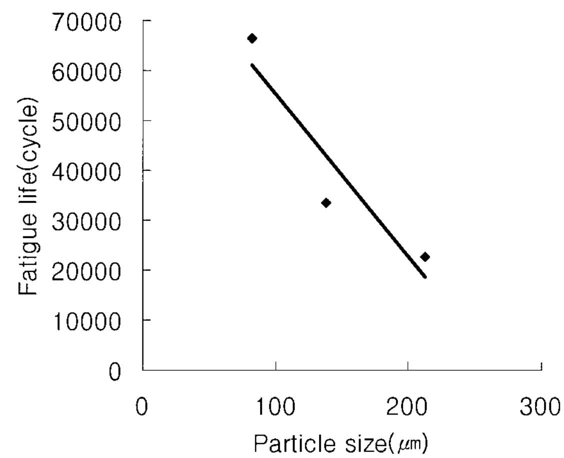


Figure 13 Fatigue life of SBR compounds with varying particle sizes of powder (loading amount of powder = 30 phr).

sipation of the rubber compounds. As seen in Figure 14, the values of tangent delta, a direct measure of energy dissipation, increased with an increasing loading volume of ground rubber particles. However, the effect of the particle size was not remarkably revealed. Consequently, the superior fracture resistance when ground rubber particles were incorporated was thought to be attributed to enhanced energy dissipation and to a deviation of the tear path by the ground rubber particles.

Abrasion Behavior

The abrasion rate of the ground rubber-filled SBR and NR compounds were measured using a PICO abrasion tester. The abrasion rates of the SBR-based compounds were lower than were those of NR-based compounds (Fig. 15), in contrast to the crack growth behavior in which the NR-based compounds showed better crack growth resistance than that of the SBR compounds (Fig. 10). These results agree with those reported previously.[21,22] As shown in Figure 15, the effect of the particle size or loading volume of ground rubber on the abrasion rate was not prominent compared to that on the crack growth rate. Figures 16 and 17 indicate that the ground rubber-filled SBR compound produced more wear loss compared to

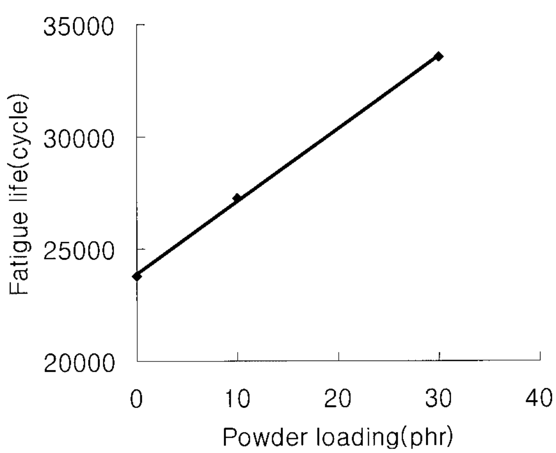


Figure 12 Fatigue life of SBR compounds with varying loading amounts of powder (particle size of powder = 125–150 μm).

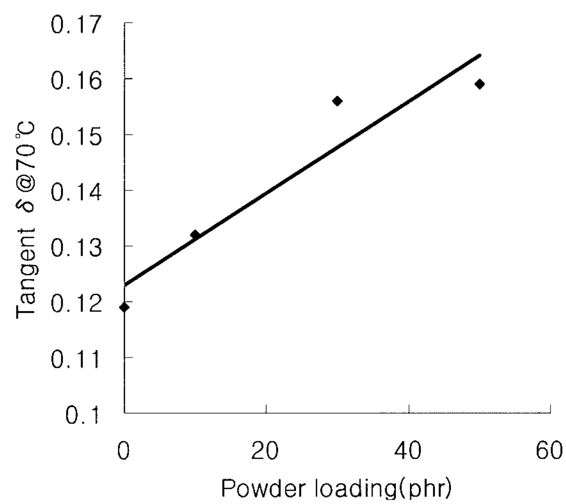


Figure 14 Energy dissipation behavior of SBR compounds with varying powder loading (particle size of powder = 125–150 μm).

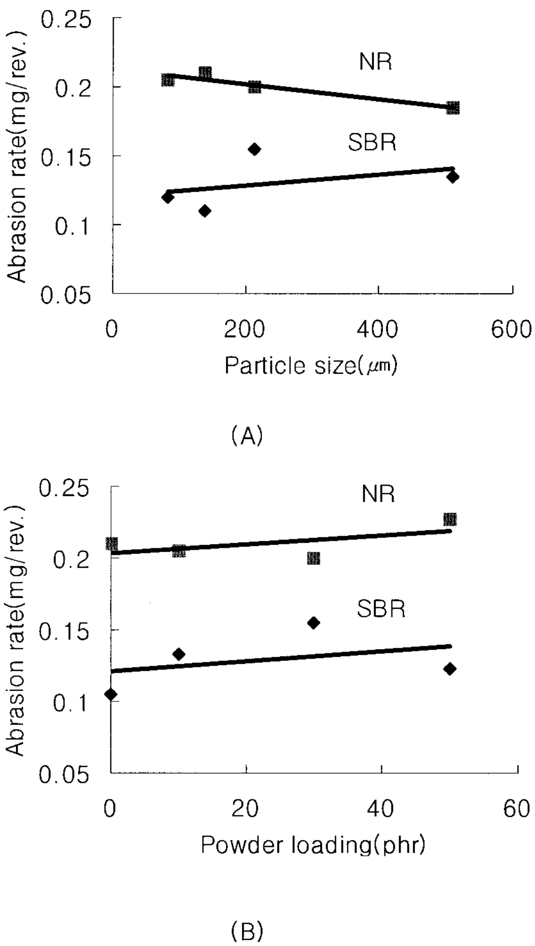
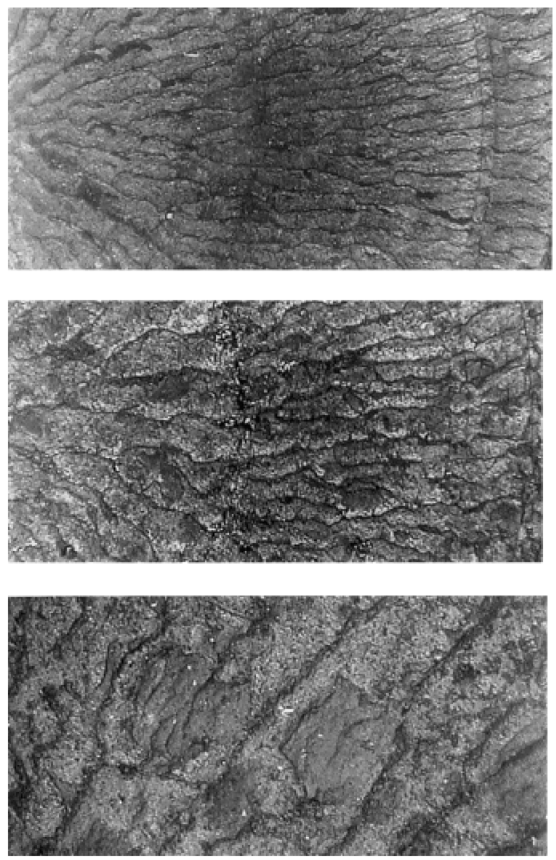


Figure 15 Abrasion rate of SBR and NR compounds with varying particle sizes and loading amounts of ground rubber powder: (A) particle size; (B) loading amount.

the pure compound, whereas, in the case of the NR compound, the ground rubber-filled compound represented less wear loss than that of the pure compound. On the other hand, the abrasion rate was proportional to the pattern spacing or modulus in both the NR and SBR compounds. The abrasion rate plotted against the pattern spacing for all SBR-based compounds is seen in Figure 18. They showed a good linear relationship between the abrasion rate and pattern spacing and between the pattern spacing and the reciprocal of the modulus (Fig. 19). It appears that the removal of ground rubber particles did not significantly contribute to the wear loss; instead, pattern spacing was closely related to the wear rate. The abrasion rate has been known to be proportional to the pattern spacing for NR or SBR compounds. Also, pattern spacing was inversely proportional to the moduli.[23,24]

CONCLUSIONS

The flex crack growth of SBR- and NR-based compounds was altered by the addition of ground rubber particles. More delayed crack growth was observed with an increasing loading volume and decreasing particle size of the ground rubber powders, and this behavior was more prominent in SBR than in NR compounds. Tangent delta, a direct measure of internal energy dissipation, increased with an increasing loading volume of the

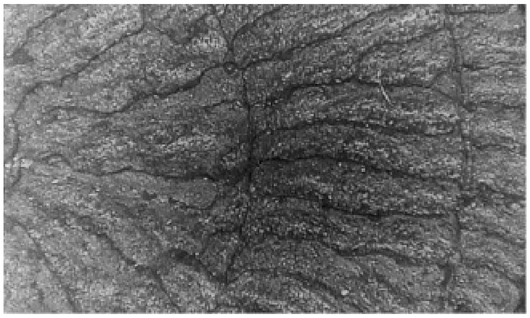


A

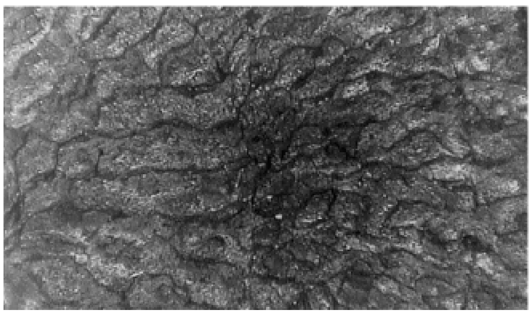
B

C

Figure 16 Top view of worn surface of filled SBR compound, showing abrasion pattern (normal load = 25 N: magnification = ×40): (A) without ground rubber powder (wear rate = 0.1 mg/rev; 100% modulus = 30 kg/cm^2; pattern spacing = 0.4 mm); (B) with ground rubber powder (particle size = 420–600 μm; loading = 30 phr; wear rate = 0.13 mg/rev; 100% modulus = 22 kg/cm^2; pattern spacing = 0.5 mm). (C) magnified view of (B) photograph.



A



B

Figure 17 Top view of worn surface of filled NR compound, showing abrasion pattern (normal load = 25 N; magnification = ×40). (A) without ground rubber powder (wear rate = 0.21 mg/rev; 100% modulus = 22 kg/cm^2; pattern spacing = 0.8 mm); (B) with ground rubber powder (particle size = 420–600 μm; loading = 50 phr; wear rate = 0.17 mg/rev; 100% modulus = 30 kg/cm^2; pattern spacing = 0.5 mm).

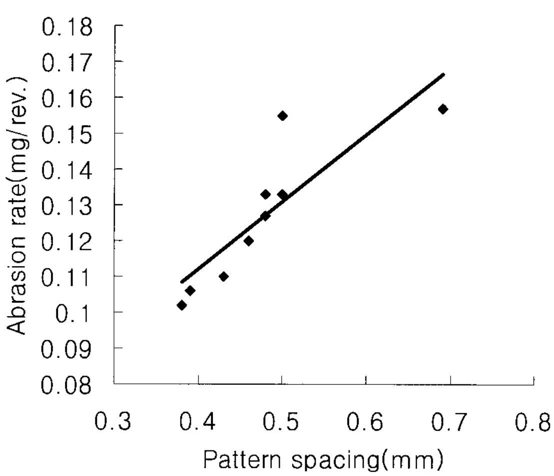


Figure 18 Abrasion rate versus pattern spacing of ground rubber-filled SBR compounds.

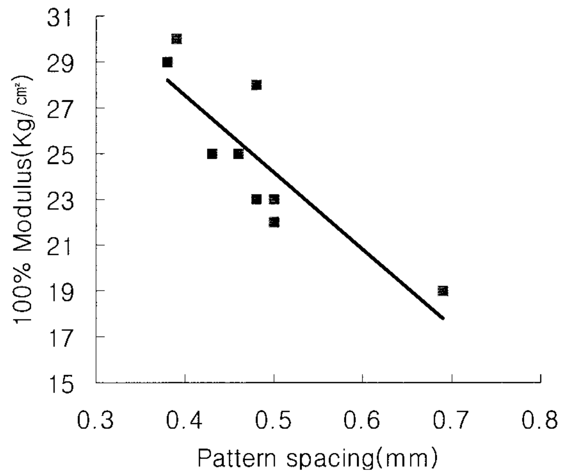


Figure 19 Modulus versus pattern spacing of ground rubber-filled SBR compounds.

ground rubber particles. The abrasion rate of ground rubber-filled compounds was more dependent on the size of the abrasion pattern than on the loading level or particle size of the ground rubber powders.

REFERENCES

1. Kohler, R. In 148th Rubber Division Meeting, ACS, 1995; Paper No. 35.
2. Astafan, C. G.; Koler, R. In 148th Rubber Division Meeting, ACS, 1995; Paper No. 40.
3. Winters, R. E. In 130th Rubber Division Meeting, ACS, 1986; Paper No. 62.
4. Smith, F. G. In 130th Rubber Division Meeting, ACS, 1986; Paper No. 63.
5. Lynch, J.; Lagrone, B. D. In 130th Rubber Division Meeting, ACS, 1986; Paper No. 64.
6. Bauman, B. D. Doc. No. DE-90015472; U.S. Dept. of Energy, 1990.
7. Stark, F. J.; Wagner, D. In 130th Rubber Division Meeting, ACS, 1982; Paper No. 67.
8. Stark, F. J. In 121th Rubber Division Meeting, ACS, 1982; Paper No. 67.
9. Holland, G. W.; Hu, B.; Holland, S. W. In 148th Rubber Division Meeting, ACS, 1995; Paper No. 34.
10. Blumenthal, M. In 148th Rubber Division Meeting, ACS, 1995; Paper No. 33.
11. Warner, W. C. Rubb Chem Technol 1994, 67, 559.
12. Isayev, A. I.; Chen, J.; Tukachinsky, A. Rubb Chem Technol 1995, 68, 267.
13. Bleyie, P. L. Rubb Chem Technol 1975, 48, 254.
14. Burgoyne, M. D.; Leaker, G. R.; Krekic, Z. Rubb Chem Technol 1976, 49, 375.

15. Swor, R. A.; Jensen, L. W.; Budzol, M. Rubb Chem Technol 1980, 53, 1215.
16. Phadke, A. A.; Chakraborty, S. K.; De, S. K. Rubb Chem Technol 1984, 53, 19.
17. Gibala, D.; Hamed, G. R. Rubb Chem Technol 1994, 67, 636.
18. Gibala, D.; Laohapisitpanich, K.; Thomas, D.; Hamed, G. R. Rubb Chem Technol 1996, 69, 115.
19. Gent, A. N. In Science and Technology of Rubber; Eirich, F. R., Ed.; Academic: New York, 1978; Chapter 10.
20. Lake, G. J.; Lindley, P. B. J Appl Polym Sci 1966, 10, 343.
21. Southern, E.; Thomas, A. G. Plast Rubb Mater Appl 1978, Nov., 133.
22. Gent, A. N.; Pulford, C. T. R. J Appl Polym Sci 1983, 28, 943.
23. Ratner, S. B.; Gul, V. E.; Klitenik, G. S. Rubb Chem Technol 1959, 32, 471.
24. Han, S. C. Ph.D. Dissertation, University of Akron, May 1997.