

Macromolecular Research

Volume 11, Number 2 April 30, 2003

Copyright 2003 by The Polymer Society of Korea

Fatigue Crack Growth Behavior of NR and HNBR Based Vulcanizates with Potential Application to Track Pad for Heavy Weight Vehicles[†]

Wonho Kim* and Minyoung Kim

Department of Chemical Engineering, Pusan National University, Busan 609-735, Korea

Young-Wook Chang

Department of Chemical Engineering, Hanyang University, Ansan 425-791, Korea

Jung-Eun Shin

SK Chemicals, Suwon-si, Kyunggi-do 440-745, Korea

Jong-Woo Bae

Korea Institute of Footwear and Leather Technology, Busan 614-100, Korea

Received Aug. 16, 2002; Revised Mar. 20, 2003

Abstract: Generally, field performance of elastomeric track pad components has been poor, especially for the medium to heavy tonnage tracked vehicles, which are operated on the hilly cross-country course. The service life of these track pad, is affected not only by the terrain and environmental conditions but also by the speed, cornering, braking, weight of the vehicle, and the track tread design. In this research, modulus, tearing energy, and the rate of crack propagation of vulcanizates are evaluated by changing base materials to improve the service time of track pad. By increasing the contents of carbon black, modulus, tearing energy, and fatigue crack growth resistance of vulcanizates improved. Compared with the NR vulcanizate, the HNBR vulcanizate had a higher value of tearing energy. The rate of crack propagation of vulcanizates using smaller size carbon black was slower than that using larger size carbon black. When the HNBR was blended with the ZSC, the tearing energy of the vulcanizates was a little reduced because of the high modulus but the crack propagation rate was reduced significantly. In the relation between the crack propagation rate and the strain energy release rate, though up to 100% strain were applied to specimens, the slope on the log scale (β) varied between 1.72 and 2.3 with the kind of elastomer.

Keywords: track pad, NR, HNBR, ZSC, crack propagation rate.

[†]Dedicate to Prof. Won-Jei Cho on the occasion of his retirement.

*e-mail : whkim@pnu.edu

1598-5032/04/73-07©2003 Polymer Society of Korea

Introduction

Installed in the region that touches the ground, the elastomeric track pad of heavy weight vehicles generates large amount of heat by hysteresis, and the accumulated heat causes temperature rise in the pad. The modulus E , the tearing energy G_c , and the crack propagation rate of rubbery materials become deteriorated by the increased temperature. Accordingly, the service life of pad decrease more severely.^{1,2} The temperature rise by the heat generated in the rubber pad can be presumed by the following equation.³

$$\Delta T \propto E'' \varepsilon^2 \tag{1}$$

Where, E'' and ε refer to the loss modulus and the strain of the rubber pad, respectively.

To reduce such a rise, both values of E'' and ε should be low. According to Hooke's law ($\sigma = E\varepsilon$), in order for ε to be low, the value of E (Young's modulus) to the fixed external-stress (σ), that is, the load of heavy weight vehicles, should be high.

A track pad gets torn by a crack propagated from a flaw formed by an external stress from both the heavy weight of the vehicles and sharp objects on the road. Therefore, in order to increase the service life of the pad, tearing energy also should be increased, which is required when the pad is torn by the external stress.

Enhancing the resistance to fatigue crack growth of vulcanizates could increase the life span of the track pad of heavy weight vehicles. The fatigue crack propagation rate (dc/dn) and the strain energy release rate (G) have the relationship shown in the equation below.⁴

$$dc/dn \propto G^\beta \tag{2}$$

Where β is an exponent which values are dependent on the type of elastomer. In order for the crack propagation rate to be low, the values of G and β should be small.

In Figure 1, stress-strain curves of material 1 and 2 are shown. High modulus material is represented by the line 1

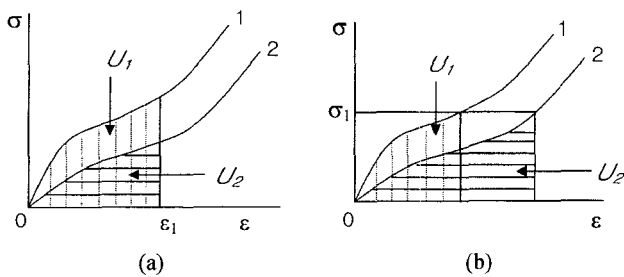


Figure 1. Hypothetical stress-strain curves for material 1 and 2, showing the strain energy density U_1 and U_2 for (a) a displacement-controlled application and (b) a load-controlled application.⁴

and low modulus material by the line 2. U_1 and U_2 , the area of vertical lines and horizontal lines, represent the strain energy density of material 1 and 2, respectively. As shown in Figure 1(a), in the strain-control-mode which has a fixed strain ε_1 , the value of U and, therefore, that of G in eq. (3) become small if the modulus of material is low, i.e. like the material 2. During operation, the rubber track pads are positioned under the weight of vehicles, as a result, the rubber pads are in the load-control-mode. Therefore, as shown in Figure 1(b), the material 1 of a high modulus has a low value of U in the load-control-mode. As a corollary, in eq. (3), the value of G for the material 1 is small, and the crack propagation rate (dc/dn) is rendered to be low.⁴

$$G = Uh_0 \tag{3}$$

Here, h_0 refers to the specimen's height. For a linear elastic material in tension, the Youngs modulus (E) describes the stress-strain behavior:

$$E = \sigma/\varepsilon \tag{4}$$

Therefore, the value of U in the strain domain can be calculated by the equation shown below.³

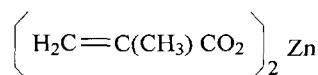
$$U = 1/2 E\varepsilon^2 \tag{5}$$

From the above, it can be said that the rubber track pads of heavy weight vehicles require properties such as higher moduli for lower heat generation, higher tearing energy, and lower crack propagation rate. In this study, to enhance the service life of the rubber track pad, the modulus, tearing energy, and the rate of fatigue crack growth of vulcanizates are evaluated by changing carbon black contents and rubbery materials. Also, large strain, i.e. up to 200%, is applied for the evaluation of fatigue crack growth rate to imitate large local deformation of the rubber pads.

Experimental

Materials. In manufacturing the natural rubber (NR) vulcanizates, SMR 20, which shows high strength and good resistance to tear and fatigue, was used. For the hydrogenated acrylonitrile-butadiene rubber (HNBR) vulcanizates which is highly resistant to thermal aging and shows good mechanical properties, Zetpol 1020 of Nippon Zeon Co. was used, which has the ACN (acrylonitrile) content of 44% and the Mooney viscosity (ML_{1+4} 100) of 78. Both peroxide curing and sulfur curing can be used for Zetpol 1020. Zetpol 2020, which has the ACN content was 36% and the Mooney viscosity of 78, was used for HNBR/ZSC (Zeon Super Composite) blends. Zeon Super Composite (ZSC 2295) of Nippon Zeon Co. is a rubber in which ZDMA (zinc dimethacrylate) is highly dispersed into HNBR (Zetpol 2020).

ZDMA is a chemical compound of zinc oxide and methacrylic acid, which has the following molecular formula.⁵



ZDMA is excellent in its compatibility with HNBR and has a high crystallinity. ZSC is superior to HNBR in strength and modulus because the size of the chain segment of the poly-ZDMA (about 2 nm) is far smaller than that of HNBR (20 to 30 nm). As a result, ZSC possesses excellent properties such as heat resistance, hardness, modulus, and abrasion resistance.⁵ Furnace blacks which consist of N110 (SAF), N220 (ISAF), and N330 (HAF), were used as the carbon black. *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylene diamine (KUMANOX, Kumho-Monsanto Co., Korea) is used as an antioxidant. *N*-Cyclohexylbenzothiazole-2-sulfenamide (CBS, Monsanto Co., USA) is used as a cure accelerator.

The basic formulations for the vulcanizates are shown in Table I.

Preparation of Vulcanizates. The preparation of vulcanizates consisted of the following steps. First, a master batch of the carbon black was manufactured by pre-mixing the rubber and carbon black at 80°C in a two-roll mill for 15 min. Then, additives or rubber were added to the master batch. After being given a final blending in the kneader or the two-roll mill, the compound was vulcanized in a hot press for the appropriate time measured with the curometer (Zwick, Model; Torsional Thrustvulcameter).

Measurement of Physical Properties. In order to estimate whether the produced vulcanizates have properties required for the track pad of heavy weight vehicles, first, the tearing

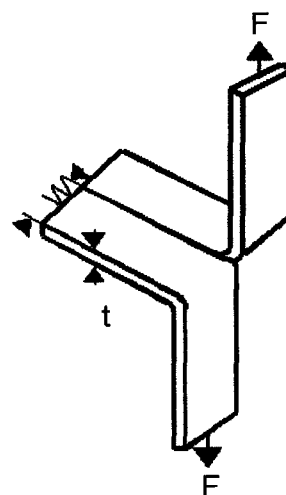


Figure 2. The geometry of a trouser tear test for measuring tearing energy.

energy was measured by a trouser tear test⁴ Universal Testing Machine (Model: Instron 8516, USA) was used, and the specimen was elongated at the speed of 5 mm/min with a load cell of 200 N. The tearing energy was calculated by eq. (6), which includes the forces to tear the specimen, shown in Figure 2, in which a pre-cut is made in the middle of a specimen, then the cut is lined with two cotton strips, and thereby makes the crack proceed in one direction.⁶

$$G_c = 2F/t \quad (6)$$

Here, G_c , F , and t refer to tearing energy, applied force, and the thickness of the specimen, respectively.

Second, to measure the modulus of the vulcanizates, specimens were manufactured according to ASTM D412, then, they were elongated at the speed of 500 mm/min by the above-mentioned Universal Testing Machine with a load cell of 2000 N. The value of G (the strain energy release rate) was calculated by eq. (3).³

Third, the crack propagation rate (dc/dn) was obtained in the following way. As shown in Figure 3(a), a 75 mm pre-cut (c) was made in the middle of the rubber specimen with a length of 150 mm, a height (h_0) of 25 mm, and a thickness (t) of 1 mm. Then, the specimen was given 25~200% strain by a fatigue tester at room temperature, as illustrated in Figure 3(b). It was then stretched, up and down, by an actuator, crossing the pre-cut, 10,000 times at the speed of 60 rpm (1 Hz). After that, to estimate crack propagation rate, the length of the crack propagation was measured, then divided by 10,000, the number of repeated stretching.⁷

Results and Discussion

Effects of Carbon Black. As shown in Figure 4(a), the tearing energy changed by the content of carbon black and it

Table I. Formulations of Various Vulcanizates

Materials	Amount(phr*)			
NR (SMR20)	100	-	-	-
HNBR (Zeptol 1020 or 2020)	-	100	100	0~90
ZSC2295	-	-	-	10~100
Carbon black (SAF, ISAF, HAF)	0~60	0~40	0~30	30
ZnO	5.0	3.0	3.0	3.0
Stearic acid	2.0	1.0	1.0	1.0
Antioxidant	2.0	2.0	2.0	2.0
Sulfur	1.8~2.6	1.5~2.4	-	-
DCP	-	-	1.5~5.0	3.0
Accelerator	0~2.2	0~1.8	-	-
TAIC (Triallylisocyanurate)	-	-	DCP/3	DCP/3

*parts per hundred resin.

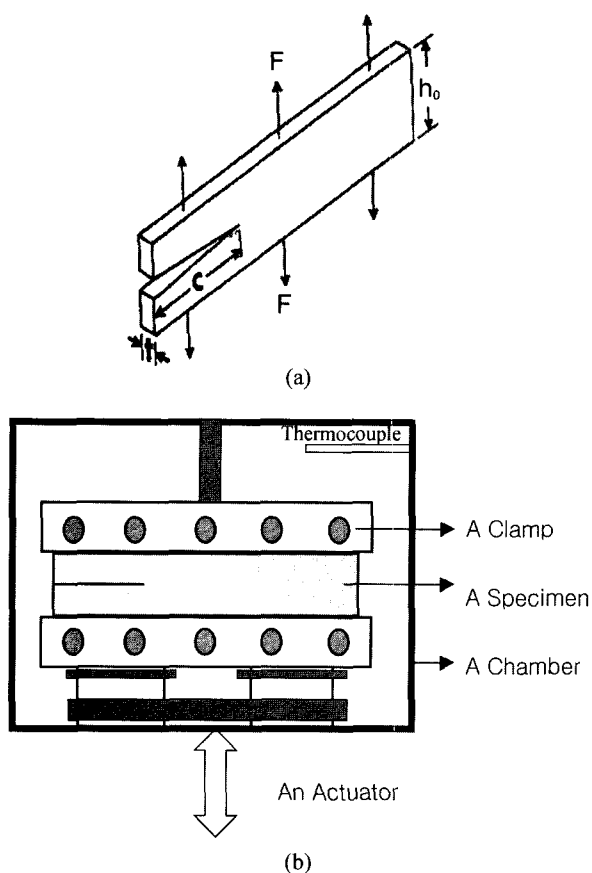


Figure 3. (a) The geometry of a pure shear test specimen for measuring the strain energy release rate (G) and (b) the design of a fatigue tester; an arrow means the direction of applied load (F).

was the highest when the content was between 40 and 50 phr. Also it increased, as the size of the carbon black became smaller. For example, the tearing energy for SAF and ISAF, whose particle sizes were 18~22 and 19~29 μm , respectively, was greater than that of HAF, whose particle size was 26~30 μm . This might be explained that the vulcanizates filled with small-sized carbon black have larger interface areas and thereby the crack path become more irregular. However, when more than 50 phr of the carbon black was added, the tearing energy decreased as the particle size became smaller. This is due to that when carbon black particles become smaller, the carbon blacks are not dispersed well under the same processing conditions.

Figure 4(b) shows tearing energy as a function of the modulus for the specimens which were used to show the Figure 4(a). As the amount of carbon black increased, the modulus became higher and the tearing energy linearly proportion to modulus when the carbon blacks were well dispersed.

Figure 5 shows the value of G (the strain energy release rate) and the crack propagation rate (dc/dn) obtained by changing the strain of the pure shear test specimen from 50 to 200%,

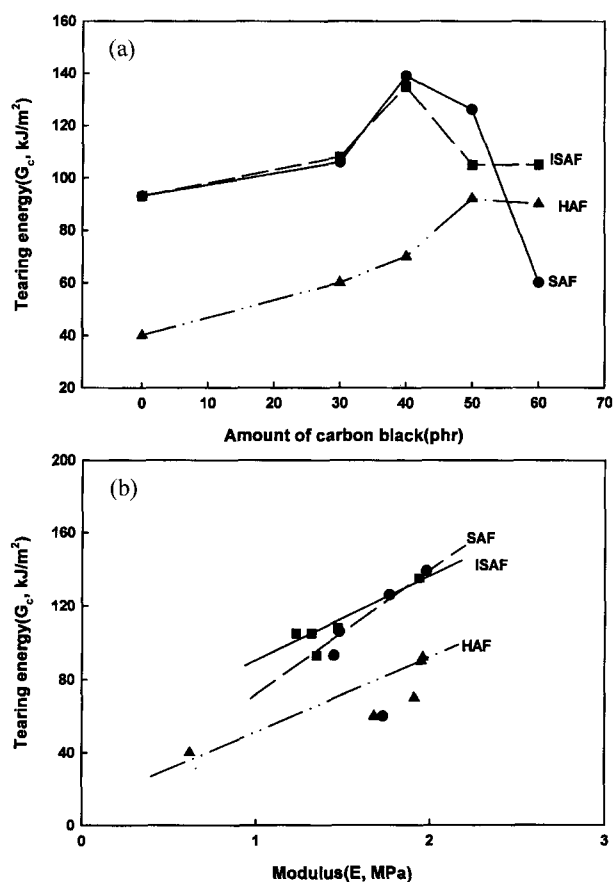


Figure 4. Tearing energy as a function of the amount of carbon black (a) and modulus (b) for natural rubber vulcanizates.

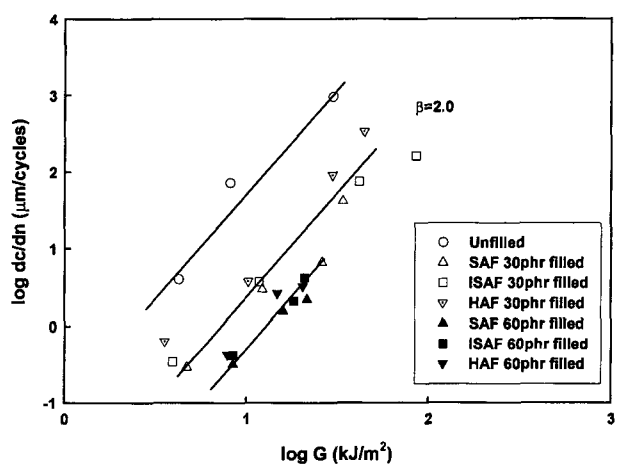


Figure 5. The rate of crack growth as a function of the strain energy release rate (G); unfilled and various type of carbon black filled NR vulcanizates.

according to the type and content of the carbon black.

The crack propagation rate of filled specimen is less than those of unfilled specimen. This is due to the irregular crack

path of carbon black-filled vulcanizates and the reduce stress magnification at the tip of inherent flaws.⁸ It is known that the crack propagation rate of finer particle-filled vulcanizates is low, in general.⁴ In our experiment, the rate of SAF (N110)-filled specimen, whose particle was the smallest among the carbon blacks, was also relatively low. When G and dc/dn are illustrated, on a log scale, as shown in Figure 5, though the values of G , i.e., 10,000~40,000 J/m², are 10 fold higher compared with the results from other experiments,⁴ the slope (β) is as usual, i.e., approximately 2.0 regardless of the types of the carbon black. When the content of carbon black increases to 60 phr, the crack propagation rate decreased to 1/90 compared to the unfilled vulcanizates and did not much affected by the particle size of carbon blacks.

Effects of Vulcanization System. To study the effects of vulcanization system, the NR compound was filled with 50 phr of ISAF, and the HNBR compound was filled with 30 phr of ISAF.

Figure 6 illustrates the modulus and the tearing energy measured by changing the content of the vulcanizing agent of the NR and HNBR vulcanizates. As Figure 6 indicates, the modulus and tearing energy are inversely proportional, on the log scale.

That is, when the modulus becomes higher due to the increase of the content of the vulcanizing agent, the tearing energy diminishes.⁶ The slope of HNBR vulcanizates is less than that of NR vulcanizates. This means that the reduction of tearing energy of vulcanizates by increased modulus is small for HNBR vulcanizates. Also, for an identical modulus, the tearing energy of the sulfur-vulcanized HNBR is little higher than that of the DCP-vulcanized HNBR. This is because the former consists largely polysulfidic groups, which has low bond strength. The polysulfidic crosslinks break before breaking of the main backbone chain under the high stress around the crack tip. The stress is therefore redistributed over the larger volume of material. This effect

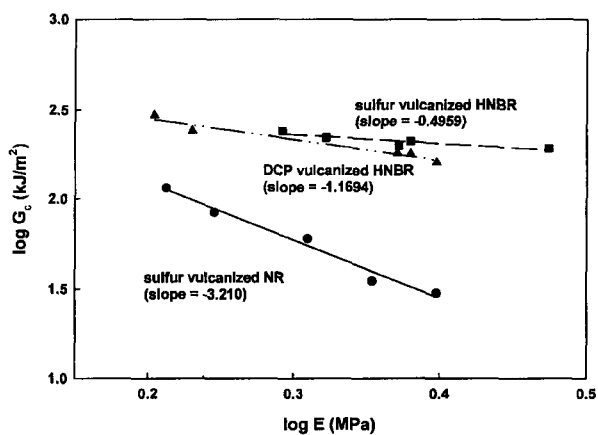


Figure 6. Tearing energy as a function of modulus for NR and HNBR vulcanizates; modulus was controlled by changing the contents of vulcanization agent.

is presumably absent in the case of carbon-carbon crosslinks, which are relatively strong. By considering the resistance to thermal aging, DCP curing is selected for the vulcanizates of HNBR/ZSC blend.

The HNBR vulcanizates were comparatively higher in tearing energy than that of NR vulcanizates. The tearing energy of natural rubber is known to be higher than that of other synthetic elastomers, because its strength is reinforced by strain-induced crystallization while it is being torn.⁹⁻¹¹ However, its tearing energy in this study was lower than that of HNBR, which is excellent in strength and elongation.

HNBR/ZSC Blend. For the vulcanization of HNBR/ZSC blends, the basic formulations are shown in Table I. Figure 7 shows the changes in the modulus of the vulcanizates at 100% strain according to the amount of the ZSC in the HNBR/ZSC blends. The modulus markedly increased when more than 50 phr of ZSC was added. This is due to the crystals of zinc dimethacrylate.

Figure 8 illustrates on a log scale the tearing energy

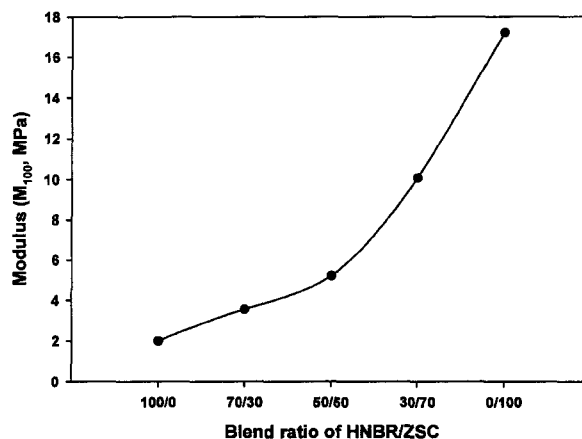


Figure 7. The modulus according to the ratio of HNBR/ZSC blend; at 100% strain.

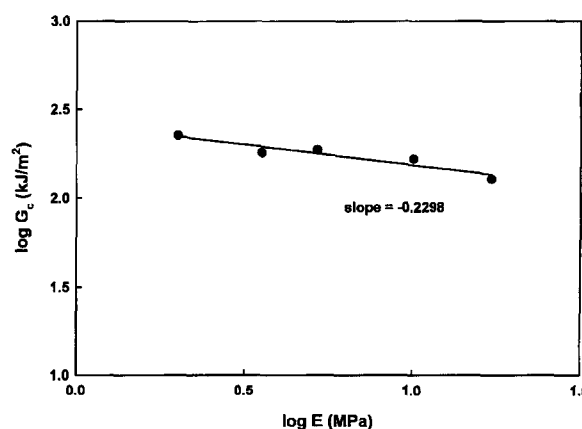


Figure 8. Tearing energy as a function of modulus for HNBR/ZSC blends.

generated by the amount of ZSC of the HNBR/ZSC blend as a function of the modulus, which are shown in Figure 7. The illustration indicates that the tearing energy decreases linearly, as the modulus increases, due to the increased amount of the ZSC. When more than 50 phr of the ZSC is added as shown in Figure 7, the modulus showed a marked rise, while the decrease rate of tearing energy, that is, the slope of the graph, is -0.2298, a numerical value which is much smaller than the rate shown in Figure 6 (-1.1694) of the DCP-vulcanized HNBR by the increase of the modulus.

The relationship of crack propagation rate (dc/dn) and strain energy release rate (G) is shown in Figure 9. Here, the applied strain on the specimens was 25, 50, 75, 100, and 200%. Up to 100% strain, i.e., the values of strain energy release rate (G) are 28,000, 35,000, and 44,000 J/m² for the vulcanizates of HNBR, NR, and HNBR (70)/ZSC (30) blend, respectively, no transition point at which the propagation rate increase rapidly appeared. For the vulcanizates of HNBR/ZSC blend, the value of 1.72 for the slope β on a log scale was smaller than those of NR and HNBR, i.e., 2.17 and 2.3, respectively. For NR, up to the values of 35,000 J/m² of strain energy release rate, the value of β is, still, very close to 2.0. When the crack propagation rate is compared at the same value of G , the rate of the vulcanizates was as follows; HNBR/ZSC blend < NR < HNBR. For the case of HNBR/ZSC blend, though the amount of carbon black was half compared to the case of NR, the value of crack propagation rate was low. This may be due to the crystals formation by ZDMA which were more effective to the resistance of crack propagation than that of carbon black. For the case of HNBR, no crystals formed during stretching, so the crack propagation rate was high compared to other vulcanizates.

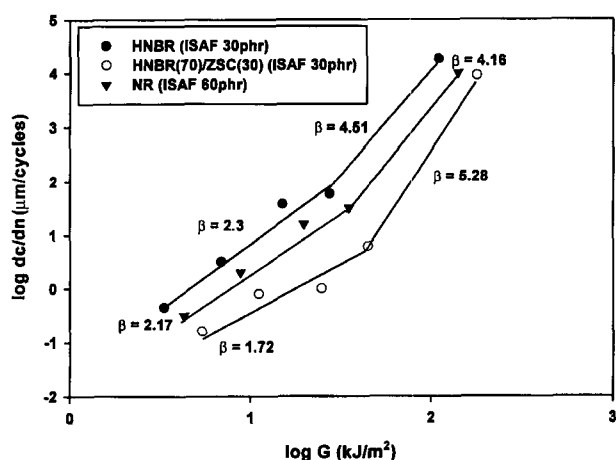


Figure 9. The rate of crack growth according to the type of the elastomer.

Conclusions

Tearing energy of NR vulcanizates was increased by reducing the size of carbon black, and was linearly increased as a function of modulus when the amount of carbon black was increased.

At the same values of modulus, tearing energy of HNBR vulcanizates was higher than that of NR vulcanizates. When the modulus of NR and HNBR vulcanizates was increased by increasing the amount of vulcanizing agents, the modulus and tearing energy are inversely proportional, on the log scale. The reduction slope of tearing energy by increased modulus was small for HNBR vulcanizates.

For NR vulcanizates, up to 100% strain which corresponds to 35,000 J/m² of strain energy release rate (G), the value of slope β on a log scale was as usual, i.e., approximately 2.0. For the case of HNBR/ZSC blend, though the amount of carbon black was half compared to the case of NR, i.e., 30 and 60 phr, respectively, the value of crack propagation rate of vulcanizates was quite low. The crystals formed by ZDMA should be more effective to the resistance of crack propagation than carbon black.

As the amount of ZSC was changed from 0 to 100 phr, the vulcanizates of HNBR/ZSC blend show high values of modulus, i.e., 2~16.6 MPa at 100% strain, high values of tearing energy, i.e., 223~126 KJ/m², and slow reduction rate of tearing energy, i.e., -0.2298 according to the increased modulus. For the vulcanizate of HNBR/ZSC (70/30) blend show low values of crack propagation rate compared to NR and HNBR vulcanizates. So the vulcanizates of HNBR/ZSC blend is preferable to the NR and HNBR for the track pad of heavy weight vehicles.

Acknowledgements. This project was funded by a research grant from the '99 Regional Consortium Project of Pusan National University (PS-10) supported by the Small & Medium Business Administration. Also this work was supported by Pusan National University Research Grant, 1999.

References

- (1) C. G. Pergantis, T. Murray, J. L. Mead, R. J. Shuford, and A. L. Alesi, *Rubber World*, **200**, 31 (1989).
- (2) P. Touchet, U.S Patent 4,843,114 (1989).
- (3) A. N. Gent and K. W. Scott, *Dynamic Mechanical Properties*, in *Engineering with Rubber*, A. N. Gent, Ed., Hanser Publishers, New York, 1992, Chap.4, pp 67.
- (4) A. N. Gent and K. W. Scott, *Mechanical Fatigue*, in *Engineering with Rubber*, A. N. Gent, Ed., Hanser Publishers, New York, 1992, Chap.6, pp 129.
- (5) Sachio Hayashi, Latest Technical Report No.10, *Structure and Mechanical Properties of HNBR/Zinc Dimethacrylate*,

Fatigue Crack Growth Behavior of NR and HNBR Based Vulcanizates

- Zeon Corporation, 1997.
- (6) A. N. Gent and R. H. Tobias, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 2051 (1982).
- (7) G. J. Lake and O. H. Yeoh, *Int. J. Fracture*, **14**, 5 (1978).
- (8) G. R. Hamed, *Rubber Chem. Technol.*, **64**, 493 (1991).
- (9) I. R. Gelling and M. Porter, *Strength Properties of Rubber*, in *Natural Rubber Science and Technology*, A. D. Roberts, Ed., Oxford, New York, 1988, Chap.15, pp 732-739.
- (10) D. G. Young and M. J. Doyle, *Proceedings of the ANTEC'92*, 1211 (1992).
- (11) W. W. Chung and Y. W. Chang, *Korea Polym. J.*, **9**, 319 (2001).