ELSEVIER

Polymer 41 (2000) 133–140

polymer

Effect of molecular weight between cross-links on the abrasion behavior of rubber by a blade abrader

Kilwon Cho*, Daeho Lee

Department of Chemical Engineering/Polymer Research Institute, Pohang University of Science and Technology, Pohang 790-784, South Korea

Received 30 October 1998; accepted 1 February 1999

Abstract

The effect of molecular weight between cross-links on the abrasion behavior of rubber was investigated using acrylonitrile–butadiene rubber (NBR), styrene–butadiene rubber (SBR), and natural rubber (NR) with a blade abrader. The rate of abrasion was found to be almost constant irrespective of the cross-link density of rubber at low frictional input work, whereas it decreased to a minimum and increased again as frictional input work increased. For rubbers with high cross-link density, it was found that the rate of abrasion increased slowly below the critical frictional input work and increased abruptly above the critical frictional input work. A similar phenomenon was also found in the fatigue test. The values of critical input work in the abrasion test and fatigue test were very close to the fracture energies of rubber. Thus, mechanical fatigue was the major abrasion mechanism below the critical frictional input work and the abrasion mechanism changed from mechanical fatigue to direct tearing at the critical frictional input work. As cross-link density decreased, the critical point in the frictional input work was not observed due to the high fracture energy of rubber. In this range, the abrasion mechanism was the mechanical fatigue, which was confirmed by the fatigue test. However, the critical frictional input work was observed at high test-temperature due to the lowering of the fracture energy. For rubbers with very low cross-link density, a rolling-type abraded surface occurred as a result of the thin surface layer peeling away by abrasion.

Keywords: Rubber; Abrasion; Cross-link density

1. Introduction

Abrasion is defined as the removal of materials from a surface by frictional force, and the process by which materials are removed from a surface is an abrasion mechanism. The rate of abrasion is an important characteristic of rubbery articles, especially for tires, for example, because the abrasion rate is directly related to the service life. A primary characteristic feature of the abrasion of rubber is a ridge pattern, which is formed perpendicular to the direction of abrasion [1]. The debris, i.e. rubber particles removed from the surface, also forms with a ridge pattern. Many studies [2–8] have been done investigating the abrasion of rubber by various types of abraders in order to elucidate the abrasion mechanism and to predict the service life of rubbery articles with the aid of abrasion mechanisms. Over the last few decades, many abrasion mechanisms such as mechanochemical decomposition [2], mechanical fatigue [3,4], and chemical degradation [5–7] were proposed to explain abrasion behavior.

The Thomas et al. [3] investigation of the abrasion of rubber by a razor blade is particularly informative. In their studies the slope of the abrasion rate was observed to be the same as that of crack growth rate in fatigue. Mechanical fatigue was therefore suggested as an abrasion mechanism. They also proposed a mechanical model by which an abrasion rate can be calculated. Gent and Pulford [2] also investigated the abrasion of rubber by a razor blade and suggested mechanochemical decomposition as an abrasion mechanism as well as the mechanical fatigue. Recently, there was an attempt to relate the abrasion mechanism to the fracture energy of rubber by Gent and Nah [9].

In this study, an abrasion experiment was performed using a blade abrader to investigate the effect of the cross-link density of rubber on abrasion behavior, especially the relationship between the abrasion mechanism and the fracture energy of rubber.

* Corresponding author. Tel.: +82-562-279-2270; fax: +82-562-279-8269.

E-mail address: kwcho@postech.ac.kr (K. Cho)

0032-3861/00/$ - see front matter
PII: S0032-3861(99)00111-1

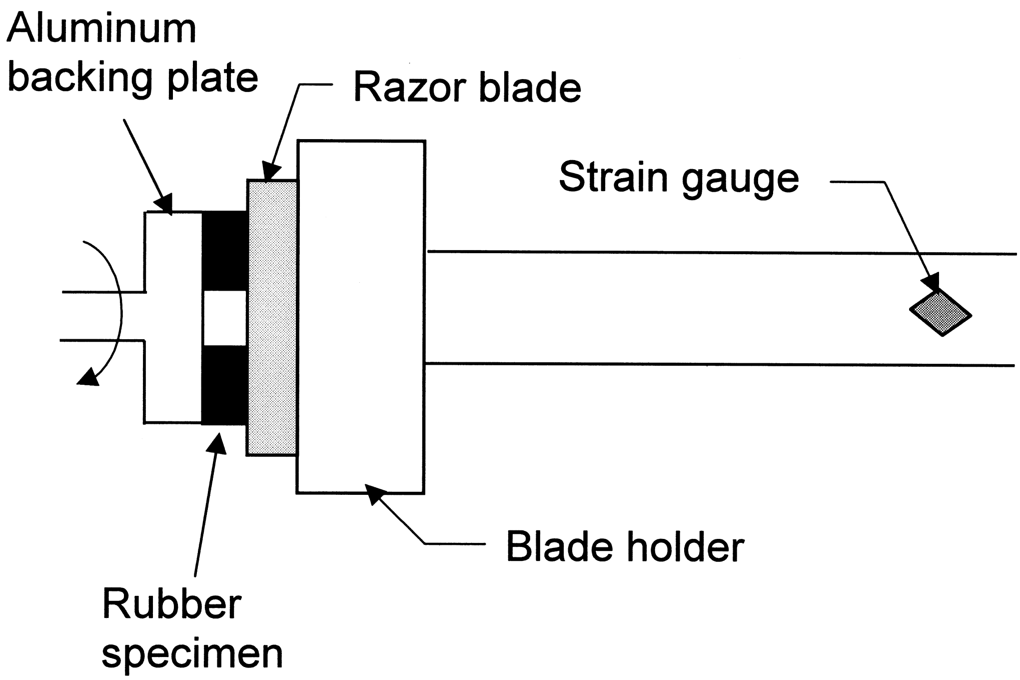

Fig. 1. Schematic diagram of the blade type abrader used in this study.

2. Experimental procedure

2.1. Material and sample preparation

The rubbers used in this study were acrylonitrile–butadiene rubber (NBR, Kumho Petrochemical Co. Korea, KNB203L, Acrylonitrile content: 35%), styrene–butadiene rubber (SBR, Kumho Petrochemical Co. Korea, SBR 1502, Styrene content: 23%), and natural rubber (NR). The rubbers were mixed with dicumylperoxide (Aldrich) as a cross-linking agent using an internal mixer with the conditions that the mixing temperature was 60°C and the mixing speed was 60 rpm for 5 min. The amount of dicumylperoxide used was varied from 0.25 phr to 3 phr to change the cross-link density of rubbers. The cross-linked sheets and specimens for the abrasion test were prepared by molding the mixtures in a cavity mold at 150°C for 1.5 h. The razor blade was obtained from Dorco Co. Ltd. (Korea) and its tip diameter was about 100 nm.

2.2. Measurement of cross-link density

Tensile strips were cut from a cross-linked sheet. Tensile stress–strain curves were obtained with tensile strips using a universal test machine(Instron 4206) with a crosshead speed of 5 mm/min. The Mooney–Rivlin coefficients, C_1 and C_2 were calculated from the tensile stress–strain curves up to 100% elongation. The average molecular weight between cross-links, M_C was calculated using Eq. (1) based on the rubber elasticity theory [10]:

$$M_C = 3\rho RT/E \quad (1)$$

where ρ is the density, R is the gas constant, T is the absolute temperature, and E is the tensile modulus taken as $6(C_1 + C_2)$.

2.3. Measurement of abrasion rate

A schematic diagram of the blade abrader used in this study is given in Fig. 1. The specimen was a cylindrical disk with 25 mm outer diameter, a 9.6 mm inner diameter, and a height of 10 mm. The rubber disk was bonded to an aluminum backing plate, held in a lathe chuck, and then rotated at 45 rev/min. The razor blade was clamped in a blade holder attached to the supporting shaft installed on a sliding bed. The razor blade was arranged so that it was positioned at the center of the rubber disk, and the razor blade was advanced against the rubber disk. The frictional torque was kept constant during each experiment by advancing the razor blade manually. The strain gauge which was used to measure the frictional torque on a rubber disk was attached to the thin steel pipe that made up part of the supporting shaft. It was confirmed that a linear relationship exists between the frictional torque and the output voltage from the strain gauge. Each razor blade was replaced by a new one at every 900 revolutions. One revolution of the rubber disk was taken as two revolutions in the calculation of the abrasion rate, because the rubber disk was in contact with a razor blade twice at each revolution of rubber disk.

Weight loss was measured at each 900 revolutions after the steady state, i.e. at about 5000 revolutions. Then loss in weight per revolution (ω) was calculated from the slope in the plot of the cumulative loss in weight against revolution.

Table 1
Molecular weight between cross-links of various rubbers

Rubber	Content of dicumylperoxide (phr)	M_C (g/mol)
NBR	3.0	2310
	1.0	4060
	0.5	5810
	0.25	7580
SBR	1.0	4650
NR	1.0	7370

Abrasion rate, i.e. loss in thickness per revolution (h), was calculated using Eq. (2):

$$h = \omega/\rho\pi(r_1^2 - r_2^2) \quad (2)$$

where ρ is the density of rubber, and r_1 and r_2 are outer and inner diameters of the specimen, respectively. The detailed method to calculate the abrasion rate and frictional input work was described elsewhere [9].

2.4. Measurement of fracture energy and fatigue test

The fracture energy, G_C, of rubber was determined by the trouser tear test using a universal test machine (Instron 4206) at a crosshead speed of 5 mm/min. The fracture energy was calculated using Eq. (3)

$$G_C = 2F/t \quad (3)$$

where F is the tear force and t is the tear path width.

The fatigue test was carried out on a dynamic testing machine using pure shear test pieces at a frequency of 150 cycles/min, and the crack growth rate was calculated by measuring the crack length with an optical microscope (Zeiss).

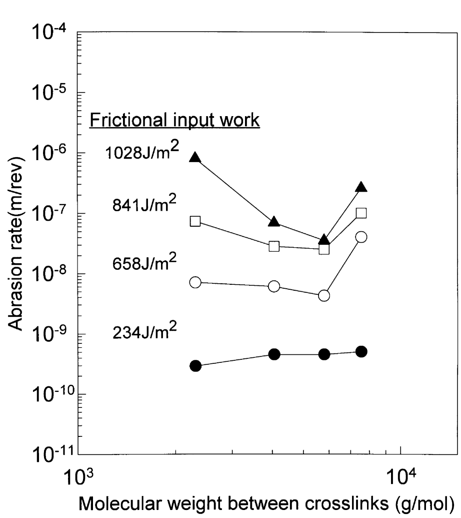

Fig. 2. Abrasion rate of NBR as a function of molecular weight between cross-links at various frictional input work.

3. Results and discussion

3.1. Effect of molecular weight between cross-links

The average molecular weight between cross-links calculated using Eq. (1) is illustrated in Table 1. As expected, molecular weight between cross-links increased as the content of dicumylperoxide decreased. Cumulative loss in weight was measured every 900 revolutions, and the weight loss per revolution was obtained from the slope of the plot for cumulative loss in weight against revolution and then the abrasion rate was calculated using Eq. (2).

The abrasion rate, i.e. the loss in thickness per revolution as a function of molecular weight between cross-links, is given for NBR in Fig. 2. These abrasion experiments were carried out at room temperature. The abrasion rate was almost constant irrespective of molecular weight between cross-links at low frictional input work, say, 234 J m^{-2}. However, the abrasion rate increased with frictional input work, and the trend of increase in the abrasion rate with frictional input work was different in each NBR. It was found that the abrasion rate was minimal at a molecular weight between cross-links of 5810 g mol^{-1}. These results imply that the abrasion rate and the abrasion mechanism are dependent on molecular weight between cross-links. The abrasion mechanism under conditions of different frictional input work will be discussed in detail in the following section.

3.2. Rubbers with critical frictional input work

The abrasion rate of NBR cross-linked with 3.0 phr dicumylperoxide ($M_C = 2310$ g mol^{-1}) as a function of frictional input work is shown in Fig. 3. The abrasion rate increased slowly as the frictional input work increased; however, the abrasion rate increased abruptly above the critical value of the frictional input work. This phenomenon was also observed in the abrasion rate of NBR cross-linked with 1.0 phr dicumylperoxide($M_C = 4060$ g mol^{-1}), as shown in Fig. 4. The same phenomenon was also observed in the abrasion of SBR cross-linked with 1.0 phr dicumylperoxide ($M_C = 4650$ g mol^{-1}), and the result is shown in Fig. 5. Below the critical frictional input work, the slope was unusually flat as in Fig. 5, unlike Figs. 3 and 4. This flatness is attributed to difficulty in the measurement of loss in weight due to the formation of a sticky layer on the rubber surface that resulted from the smearing of SBR. The smearing is the formation of a sticky layer on the surface of the rubber specimen due to chemical degradation [2]. In the case of NBR cross-linked with 0.5 phr dicumylperoxide, the critical frictional input work was not observed at room temperature(Fig. 6), and this phenomenon will be described in detail later. However, the critical frictional input work was observed at a test temperature of 65°C. From the above mentioned results showing the change in the abrasion rate at the critical frictional input work (Fig. 3–6), it is supposed

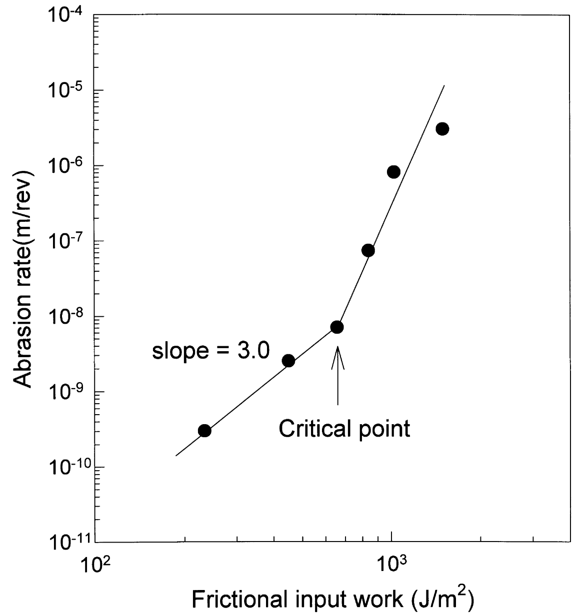

Fig. 3. Abrasion rate of NBR cross-linked with 3.0 phr dicumylperoxide ($M_C = 2310$ g mol^{-1}) as a function of frictional input work at room temperature.

that the abrasion mechanism changes at the critical frictional input work.

According to previous works [2–4], the abrasion of rubber by a razor blade occurs through the mechanical fatigue. This means that abrasion occurs as a result of repeated crack propagation on a small scale. In order to correlate the abrasion with fatigue, a fatigue test was performed using NBR cross-linked with 1.0 phr dicumylperoxide, and the

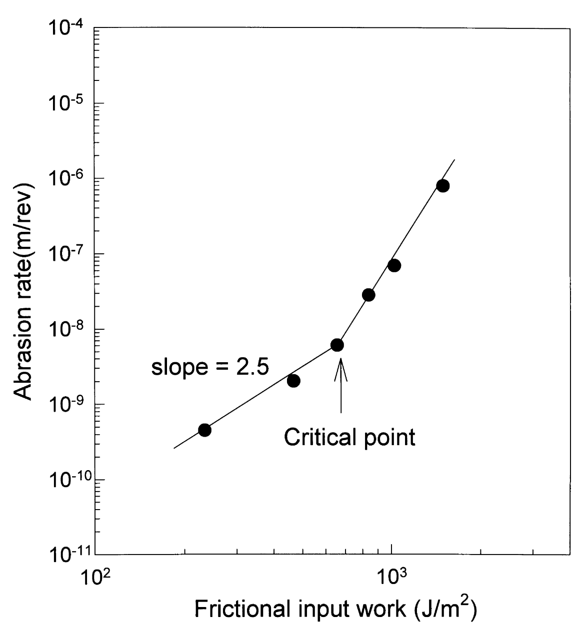

Fig. 4. Abrasion rate of NBR cross-linked with 1.0 phr dicumylperoxide ($M_C = 4060$ g mol^{-1}) as a function of frictional input work at room temperature.

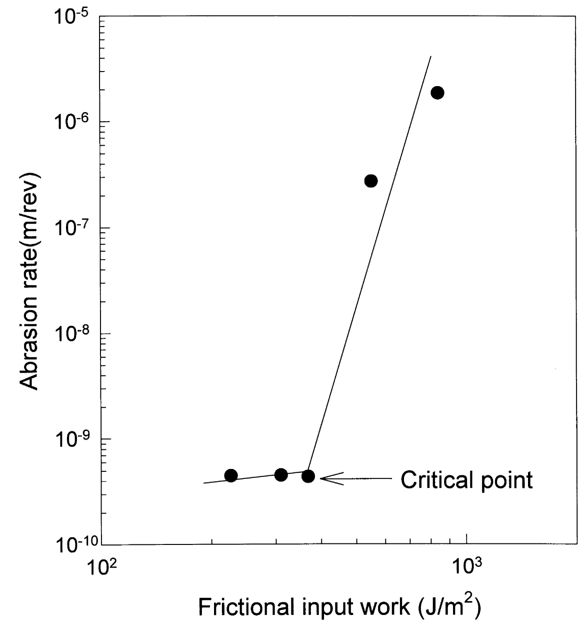

Fig. 5. Abrasion rate of SBR cross-linked with 1.0 phr dicumylperoxide ($M_C = 4650$ g mol^{-1}) as a function of frictional input work at room temperature.

result is shown in Fig. 7. The crack growth rate increased slowly below the critical tearing energy and increased abruptly above the critical tearing energy. The shape of the graph is similar to that of abrasion (Fig. 4). It is well known that the crack growth rate in fatigue is dependent on tearing energy, as expressed in Eq. (4) [11]:

$$dc/dn = BT^{\beta} \quad (4)$$

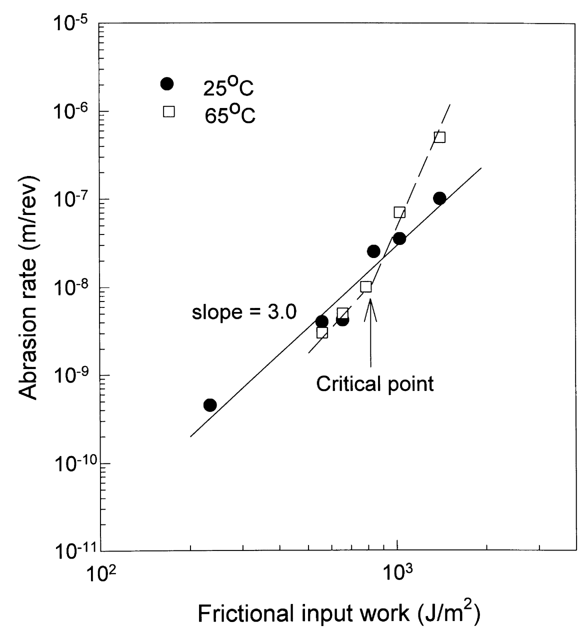

Fig. 6. Abrasion rate of NBR cross-linked with 0.5 phr dicumylperoxide ($M_C = 5810$ g mol^{-1}) as a function of frictional input work at room temperature and 65°C.

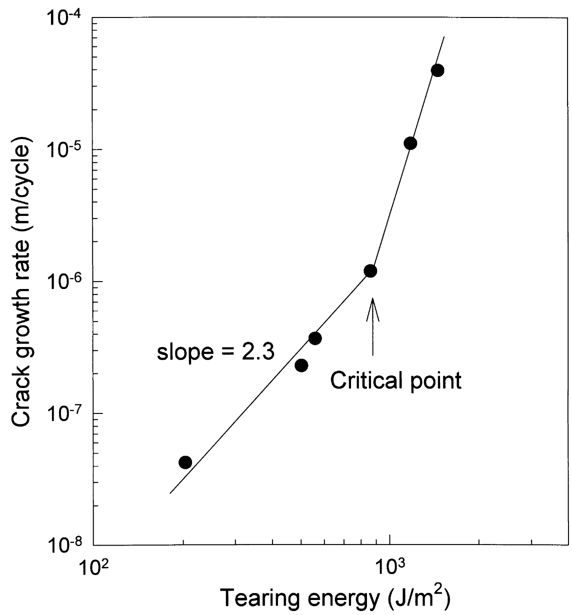

Fig. 7. Crack growth rate of NBR cross-linked with 1.0 phr dicumylperoxide as a function of tearing energy in fatigue at room temperature.

where c is the crack growth length, n is the number of cycle, and B and β are constants. The constant β of NBR is known to be about 2.7 [12], and this value agrees with the slope below the critical tearing energy in the fatigue test (Fig. 7). It was also found that the value of the slope, 2.3 in Fig. 7, is very close to that of the slope below the critical frictional input work in abrasion, as shown in Fig. 4. Therefore, the abrasion below the critical frictional input work appears to occur through mechanical fatigue in NBR cross-linked with 1.0 or 3.0 phr dicumylperoxide and SBR cross-linked with 1.0 phr dicumylperoxide.

The critical frictional input work in abrasion(Fig. 4) was similar to the critical tearing energy in fatigue (Fig. 7). It was also found that the critical frictional input work in NBR cross-linked with 0.5 phr dicumylperoxide was observed only at a high test temperature as mentioned before. The tensile strength and tearing strength of rubber decrease with increasing test temperature. Therefore, the fact that the observation of critical frictional input work occurred only at a high temperature (Fig. 6) may be attributed to the lowering in fracture energy of rubber at high temperature. And it was supposed that these critical values in abrasion and fatigue were related to the fracture energy of rubber. So, the fracture energy of rubber was measured by trouser tear test and the result was compared with the critical frictional input work and the critical tearing energy in Table 2. The critical frictional input work in abrasion and the critical tearing energy in fatigue were in good agreement with the fracture energy in each rubber. Therefore, the critical energies in abrasion and fatigue are the fracture energy of rubber. And it is suggested that the abrasion mechanism is mechanical fatigue below the critical frictional input work, i.e. the fracture energy of rubber and the abrasion mechanism changes from mechanical fatigue to direct tearing above the critical frictional input work.

3.3. Rubbers without critical frictional input work

In the case of NBR cross-linked with 0.5 phr dicumylperoxide, the fracture energy measured by trouser tear test at room temperature was 4606 J m^{-2}, and this value was much higher than the highest value of frictional input work of abrasion employed in this study. Consequently, the critical frictional input work was not observed in the abrasion test at room temperature (Fig. 6), and the abrasion mechanism was only mechanical fatigue. In order to prove the proposed mechanism, a fatigue test was performed. For NBR cross-linked with 0.5 phr dicumylperoxide the crack growth rate as a function of tearing energy in the fatigue test is given in Fig. 8. The slope at room temperature in the fatigue test was similar to that in the abrasion test and the critical tearing energy was not observed in the fatigue test performed at room temperature as expected. Therefore, for rubbers with low cross-link density abrasion occurs only through the mechanical fatigue, and the abrasion rate increases with frictional input work because direct tearing has not occurred. At a high test temperature, critical tearing energy was observed (Fig. 8) and this phenomenon was also observed in abrasion (Fig. 6). These results are attributed

Table 2
Critical frictional input work in abrasion, critical tearing energy in fatigue, and fracture energy of various rubbers at room temperature

Rubber	Content of dicumylperoxide(phr)	Critical energy (J m^{-2})	Fracture energy (J m^{-2})
NBR	3.0	658	593 ± 106
	1.0	841	897 ± 261
		865[a]	
	0.5	791[b]	953 ± 124[c]
		839[d]	
SBR	1.0	466	477 ± 88

[a] Critical tearing energy in fatigue at room temperature.
[b] Critical frictional input work in abrasion at 65°C.
[c] Fracture energy at 65°C.
[d] Critical tearing energy in fatigue at 65°C.

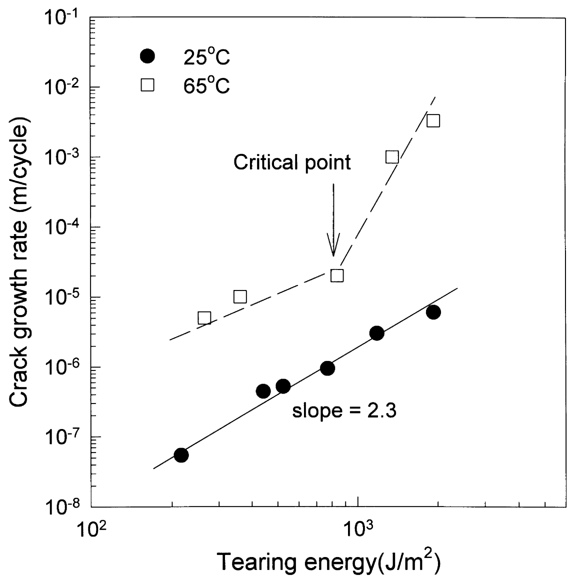

Fig. 8. Crack growth rate of NBR cross-linked with 0.5 phr dicumylperoxide as a function of tearing energy in fatigue at room temperature and 65°C.

to the lowering of fracture energy at a high test temperature as mentioned before.

For NBR cross-linked with 0.25 phr dicumylperoxide ($M_C = 7580$ g mol^{-1}) and NR cross-linked with 1.0 phr dicumylperoxide ($M_C = 7370$ g mol^{-1}) the abrasion rate as a function of frictional input work is shown in Fig. 9. The fracture energy of these rubbers were higher than the frictional input work employed in this study. Thus, critical frictional input work was not observed for both of the rubbers. The value of the slope in Fig. 9 was higher than that in the fatigue test, which was known to be 2.7. And it was not possible to measure the crack growth rate of NBR cross-linked with 0.25 phr dicumylperoxide due to the buckling of the specimen during the fatigue test.

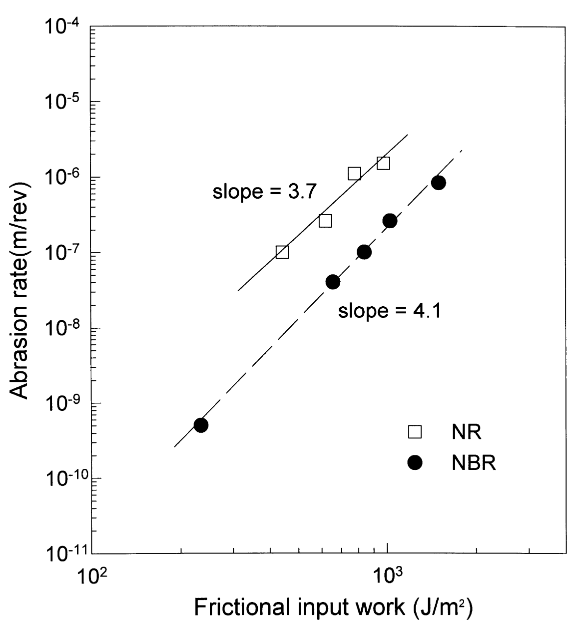

Fig. 9. Abrasion rate of NBR cross-linked with 0.25 phr dicumylperoxide and NR cross-linked with 1.0 phr dicumylperoxide as a function of frictional input work at room temperature.

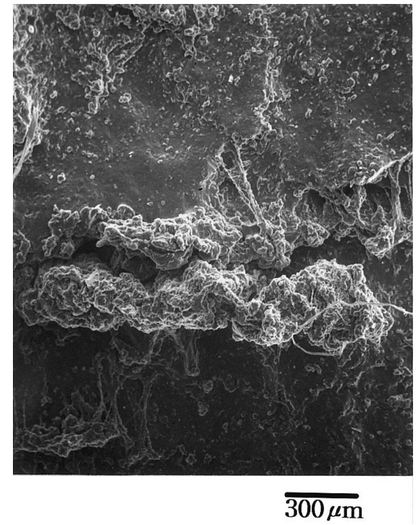

Fig. 10. Abraded surface of NBR cross-linked with 0.25 phr dicumylperoxide after 5400 revolutions at the frictional input work, 1028 J m^{-2} at room temperature. The direction of abrasion is upward.

It is well known that the slope in a fatigue test is lowered as the hysteresis increases [13]. Therefore, the hysteresis, W_d, was determined by evaluating the area between the extension and the retraction curves, and the hysteresis ratio, h_r, was determined by Eq. (5)

$$h_r = (W_0 - W_r)/W_0 = W_d/W_0 \quad (5)$$

where W_0 and W_r are the input and the retraction strain energy densities, respectively. The hysteresis ratio of NBR cross-linked with 0.5 phr and 0.25 phr dicumylperoxide were 0.12 and 0.28, respectively.

According to the previous work [13], the slope of NBR cross-linked with 0.25 phr dicumylperoxide should be lower than that of NBR cross-linked with 0.5 phr dicumylperoxide in a fatigue test, because the hysteresis of the former is higher than that of the latter. And the slope of NBR cross-linked with 0.25 phr should also be lower than that of NBR cross-linked with 0.5 phr dicumylperoxide in abrasion if the abrasion occurs via only mechanical fatigue. However, the slope of NBR cross-linked with 0.25 phr dicumylperoxide (Fig. 9) was higher than that of NBR cross-linked with 0.5 phr dicumylperoxide (Fig. 5) in abrasion. This finding implies that the abrasion of NBR cross-linked with 0.25 phr dicumylperoxide and NR cross-linked with 1.0 phr dicumylperoxide occurs via another abrasion mechanism besides mechanical fatigue.

In order to investigate the abrasion mechanism of NBR cross-linked with 0.25 phr dicumylperoxide, the abraded surface was observed after 5400 revolutions at the frictional input work of 1048 J m^{-2}, using a scanning electron

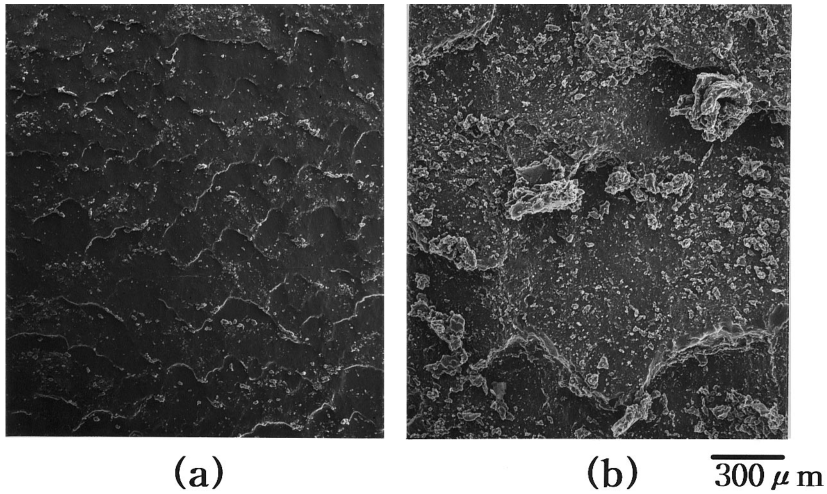

Fig. 11. Abraded surface of NBR cross-linked with 0.5 phr dicumylperoxide after 5400 revolutions at the frictional input work: (a) 658 J m^{-2}; (b) 1501 J m^{-2}. The test was performed at 25°C and the direction of abrasion is upward.

microscope, and the result is shown in Fig. 10. The rolling type surface and elongated fibrils could be observed in the abraded surface.

This phenomenon can be explained as follows. As the blade moves, the tongue of cut rubber is bent backward as proposed by Thomas et. al. [3]. However, the bent rubber tongue can not be released due to self-adhesion and set behavior. This set behavior was confirmed by the buckling which occurred in the fatigue test and high hystersis ratio. As a result of the repeated action of the blade, a thin surface layer was peeled away, and the abraded surface of the rolling type was formed. The morphology of the abraded surface is in good agreement with the result of the previous work [14] on the abrasion of rubber with high self-adhesion. Therefore, in the case of NBR cross-linked with 0.25 phr

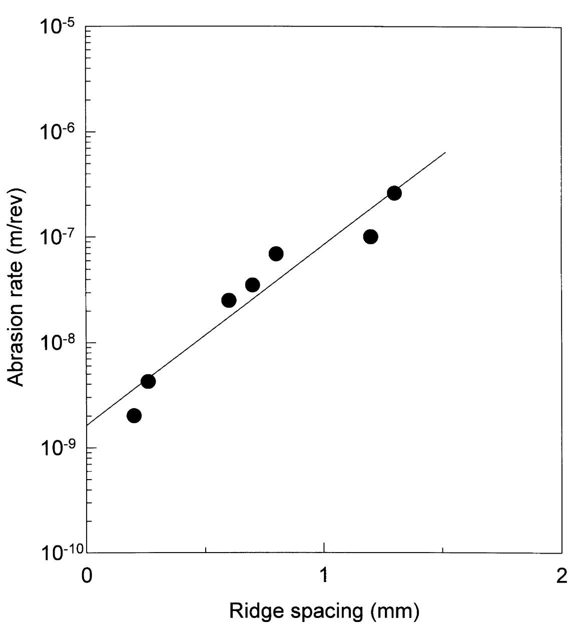

Fig. 12. Abrasion rate of NBR as a function of ridge spacing.

dicumylperoxide and NR cross-linked with 1.0 phr dicumylperoxide, i.e rubbers with molecular weight between cross-links of about 7500 g mol^{-1} and above, abrasion occurs by peeling away a thin surface layer.

3.4. Morphology of abraded surface

The abraded surface of NBR cross-linked with 0.5 phr dicumylperoxide was observed using a scanning electron microscope and the result is shown in Fig. 11. The abraded surface shows the typical abrasion pattern, i.e. ridge formation. The abraded surface at low frictional input work (658 J m^{-2}) was smooth and ridge spacing was small (Fig. 11(a)). However, the abraded surface at high frictional input work (1501 J m^{-2}) was rough and ridge spacing was large (Fig. 11(b)). It was also found that debris was formed on abraded surface and the debris size increased with frictional input work. This result implies that crack growth rate at high frictional input work is high. Consequently, the bent rubber tongue at high frictional input work is longer than that at low frictional input work. The result also implies that the rubber surface under the bent tongue is not abraded by a blade. The ridge spacings are compared with the abrasion rate, and the abrasion rate as a function of ridge spacing is given in Fig. 12. Fig. 12 was obtained using all NBR specimens with a ridge pattern. It was found that the abrasion rate increased linearly with the ridge spacing. This result is consistent with previous work [15]. From the above results, it is inferred that ridge formation accelerates the abrasion of rubber.

4. Conclusions

The effect of molecular weight between cross-links on the abrasion behavior of rubber was investigated using a blade type abrader. It was found that the abrasion rate changed abruptly at the critical frictional input work for rubbers with high cross-link density. The critical tearing energy at which crack growth rate increased abruptly was also observed in a fatigue test. The critical frictional input work in abrasion and the critical tearing energy in fatigue coincided with the fracture energy of rubber. Therefore, abrasion occurred because of mechanical fatigue below the critical frictional work, i.e. the fracture energy of rubber. And the abrasion mechanism above the critical frictional input work was direct tearing.

As the cross-link density decreased, the critical frictional input work was not observed due to the high fracture energy of rubber, and the abrasion mechanism was only mechanical fatigue. Therefore, the abrasion rate was relatively low. However, the critical frictional input work was observed at a high test temperature, which was attributed to the lowering of the fracture energy at a high test temperature.

In the case of rubbers with very low cross-link density, the abraded surface showed the rolling type and elongated fibrils. These rubbers showed self-adhesion and set behavior. Thus, the abrasion might occur by peeling away a thin surface layer.

Acknowledgements

This work was supported in part by a research grant from the Pohang Steel Company. A research grant from the School of Environmental Engineering of Pohang University of Science and Technology and the Center for Advanced Functional Polymers is also gratefully acknowledged. The authors wish to thank Dr. C. Nah for the assistance in the construction of abrasion apparatus.

References

[1] Schallamach A. Trans Inst Rubber Indust 1952;28:256.
[2] Gent AN, Pulford CTR. J Appl Polym Sci 1983;28:943.
[3] Champ DH, Southern E, Thomas AG. Am Chem Soc: Coatings Plast Div Preprints 1974;34:237.
[4] Thomas AG. J Polym Sci Symp 1974;48:145.
[5] Schallamach A. J Appl Polym Sci 1968;12:281.
[6] Williams RL, Cadle SH. Rubber Chem, Technol 1978;51:7.
[7] Brisco BJ. In: Mittal KL, editor. Physicochemical Aspects of Polymer Surface, New York: Plenum Press, 1982. pp. 387.
[8] Cho K, Lee D. J Polym Sci, Polym Phys Ed 1998;36:1283.
[9] Gent AN, Nah C. Rubber Chem, Technol 1996;69:819.
[10] Flory PJ. Principles of Polymer Chemistry, New York: Cornell University Press, 1953. Ch. 11.
[11] Hertzberg RW, Manson JA. Fatigue of Engineering Plastics. New York: Academic Press, 1979.
[12] Clamroth R, Eisele V. Kautsch Gummi Kunst 1975;28:433.
[13] Lake GJ, Thomas AG. Proc R Soc London A 1967;300:108.
[14] Reznikovskii MM, Brodskii GI. Sov Rubber Technol 1961;20:13.
[15] Thavamani P, Bhowmick AK. J Mater Sci 1993;28:1351.