ELSEVIER

Polymer 41 (2000) 179–183

polymer

Fatigue crack growth of elastomers in the swollen state

Kilwon Cho[a,*], Wook Jin Jang[a], Daeho Lee[a], Hyunaee Chun[a], Young-Wook Chang[b]

[a]*Department of Chemical Engineering/Polymer Research Institute, Pohang University of Science and Technology, Pohang, 790-784 South Korea*
[b]*Department of Chemical Engineering, Hanyang University, Ansan 425-791, South Korea*

Received 14 October 1998; received in revised form 4 January 1999; accepted 15 February 1999

Abstract

The values of crack growth rate for styrene–butadiene copolymer (SBR) and acrylonitrile–butadiene copolymer (NBR) under dynamic tearing condition were measured in both dry and swollen conditions. For swollen samples, tearing energy was adjusted by a simple geometrical factor λ_s^2 (where λ_s is the linear swelling ratio), in order to take into account the reduction in number of molecular chains per unit fracture plane. The crack growth rate of a swollen elastomer was observed to be significantly increased over the measured range of tearing energy compared to that of an unswollen elastomer. The effects of the type of elastomer, degree of swelling, and crosslinking structure on fatigue crack behaviour of swollen elastomers are discussed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Elastomer; Swelling; Fatigue

1. Introduction

When an elastomer is subjected to the repeated deformation, small-scale crack growth can occur in elastomers at energies below those required for tearing or catastrophic failure. Since the amount of cyclic crack growth is mainly determined by the maximum tearing energy attained during a cycle G, the fatigue crack growth can be represented as [1–3]

$$\mathrm{d}c/\mathrm{d}n = BG^{\alpha} \tag{1}$$

where c is the crack length, n is the number of load applications, and B and α are constants. For most rubber vulcanizates, values of exponent α range from 2 to 6, depending strongly on the type of elastomers and to a lesser extent on other factors such as the degree of crosslinking and the type of crosslink [4,5]. It tends to be lower if the material exhibits the higher mechanical hysteresis, since the fatigue crack growth is mainly governed by dissipative processes, particularly those arising from internal molecular motions and from stress-induced crystallization [6].

There are many evidences that the strength of elastomer is significantly influenced by the test conditions, such as temperature and environment [3,7–12]. For example, in the presence of low-viscosity fluid, tear and adhesive strength of elastomers are observed to be remarkably decreased. In some case, however, the swollen material has been usefully employed to determine the threshold strength of elastomers, since the viscoelastic energy dissipation during deformation may be minimized in the presence of solvent [11,12].

Even though the presence of low-viscosity fluid is also expected to give the significant influence on fatigue behaviour of elastomers, there is little published reference. Therefore, in this study, an experimental study of swollen vulcanizates was carried out in an attempt to clarify effects of swelling on fatigue crack growth of elastomers.

2. Experimental

2.1. Materials and sample preparation

The elastomers used were a standard styrene–butadiene copolymer (SBR, Kumho Petrochemical Co., SBR-1502, styrene content:23.5 wt.%) and acrylonitrile–butadiene copolymer (NBR, Kumho Petrochemical Co., KNB230H, Acrylonitrile content: 35 wt.%). For SBR, crosslink density and degree of swelling were varied, whereas only degree of swelling was varied for NBR. Mix formulation and vulcanization conditions are given in Table 1.

SBR vulcanizates were swollen in mineral oil at room temperature till equilibrium swelling had been reached. NBR vulcanizates were swollen to various extents in decahydronaphthalene. The degree of swelling of NBR vulcanizate was controlled by varying the swelling temperature and

---

[*] Corresponding author. Tel: +82-562-279-2270; fax: +82-562-279-2699.

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

PII: S0032-3861(99)00142-1

Table 1
Mix formulations (phr), vulcanization and swelling conditions

	SBR-L	SBR-H	NBR
Ingredients			
SBR	100	100	
NBR	–	–	100
Zinc oxide	5	5	3
Stearic acid	2	2	1
Sulfur	1.5	2.5	1.5
Delac NS[a]	1.2	1.2	0.7
Vulcanization			
Temperature/time	150°C/30 min	150°C/30 min	150°C/40 min
Crosslinking density			
(10^5 mol/cm^3)	9.2	10.8	–
Swelling			
Solvent	mineral oil	mineral oil	decahydronaphthalene
λ_s (temperature/time)	1.26 (25°C/40days)	1.21 (25°C/40days)	1.07 (25°C/ 4 days), 1.10 (25°C/50 days), 1.13 (60°C/3 days)

[a] *N-t*-butylbenzothiazole-2-sulfenamide (TBBS).

time. In the case of partially swollen sample, elastomer was placed in an oven at 60°C for three days in order to achieve the homogenous distribution of solvent prior to the test.

2.2. Fatigue test

Pure-shear specimens with a length of 100 mm, a width of 25 mm and a thickness of 1.8 mm were used for crack growth measurements. A specimen with sharp precrack was subjected to an intermittently applied strain at a frequency of 150 rpm at room temperature. The magnitude of applied deformations was varied from 10 to 35%. The tearing energy of pure-shear specimen is determined at the deformation rate of 10 mm/min at room temperature using universal testing machine (Instron 4206). For this geometry tearing energy of elastomer (G) is given by [3,13]

$$G = Wh_0 \tag{2}$$

where h_0 is the unstrained width of the specimen and W is the strain energy density. The values of W were determined from tensile stress–strain relation for uncut specimen. For swollen samples, tearing energy G was adjusted by a simple geometrical factor λ_S^2 (where λ_S is linear swelling ratio), in order to take into account the reduction in number of molecular chains per unit fracture plane.

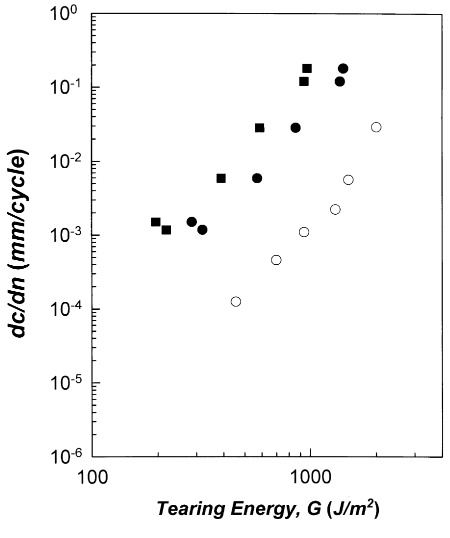

Fig. 1. Crack growth rate versus tearing energy G for SBR-H vulcanizates: (○) in dry condition; (■) in swollen condition without correction of G; (●) in swollen condition after correction of G.

2.3. Equilibrium swelling test

The crosslinking density (N), network molecular strand per unit volume, was determined by equilibrium swelling method using the Flory–Rehner equation [14]

$$[\ln(1 - \upsilon_2) + \upsilon_2 + \chi_1\upsilon_2^2] = -V_1N\{\upsilon_2^{1/3} - \upsilon_2/2\} \tag{3}$$

where υ_2 is the volume fraction of polymer in the swollen mass, V_1 is the molar volume of the solvent, and χ_1 is the Flory–Huggins interaction parameter, taken as 0.391 in SBR/toluene system [15].

3. Results and discussion

The rates of fatigue crack growth of SBR vulcanizates with high sulfur content (SBR-H) were determined as a function of tearing energy and the results are given in Fig. 1. By swelling, the rate of crack growth of SBR is increased remarkably, becoming as much as 100 times dc/dn of unswollen vulcanizate. However, in the case of swollen elastomer, it should be taken into account that the number of molecular chains crossing a unit fracture plane is reduced and thereby contributes to the fracture energy [11,16]. Thus, the values of G for the swollen elastomer are multiplied by geometrical factor λ_S^2, where λ_S is the linear swelling ratio (λ_S is unity for unswollen elastomer). The values of dc/dn

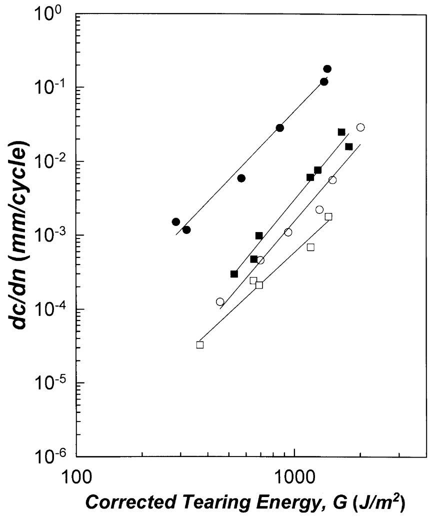

Fig. 2. Crack growth rate versus corrected tearing energy G for vulcanizates: (○) SBR-H in dry condition; (●) SBR-H in swollen condition; (□) NBR in dry condition; and (■) NBR in swollen condition.

are replotted against the corrected G and results are also given in Fig. 1. After adjustment for tearing energy G, the effect of swelling on fatigue behaviour becomes less significant. In this study, thereafter, reduced concentration of molecular strands crossing unit fracture area is considered in determining G of the swollen sample.

Rates of fatigue crack growth of SBR-H and NBR are plotted against corrected tearing energy G on logarithmic scale in Fig. 2. Over measured range of tearing energy G, the rates of crack growth of SBR-H and NBR are in good agreement with power law Eq. (1). The values of α of SBR-H and NBR in unswollen state are ca. 3.0 and 2.7, respectively. At a given value of G, the rates of crack growth of elastomers in swollen state are observed to be much higher than in dry state. However, the fatigue resistance of the swollen elastomer is not lowered by the constant factor, depending on the magnitude of tearing energy and the type of elastomer. That is, the increase of fatigue crack growth (FCG) of swollen NBR is most prominent in the high values of G, whereas the effect of swelling on FCG of SBR-H seems to be slightly larger in the low tearing energy region over the measured region of G, and the effect of swelling on fatigue behaviour seems to be more significant in highly swollen SBR-H ($\lambda_S = 1.21$) than NBR ($\lambda_S = 1.10$). Fig. 3 manifests the influence of the degree of swelling more clearly. The fatigue crack resistance of NBR vulcanizates is lowered in proportion to the degree of swelling as the linear swelling ratio λ_S is increased gradually from 1.00 to 1.13.

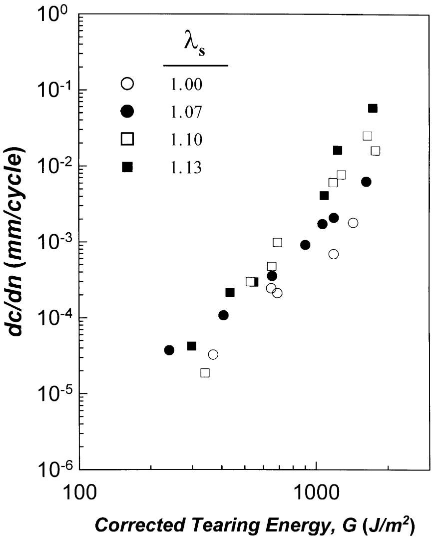

Fig. 3. Crack growth rate versus corrected tearing energy G for NBR vulcanizates with different swelling ratio, λ_S.

The increase of crack growth rate of the swollen elastomer is considered to arise mainly from the reduced internal friction between network strands during deformation due to swelling, since the internal energy dissipation such as mechanical hysteresis is a major factor governing the mechanical strength of elastomers [11,12,17]. In addition, it is speculated that the variation of torn surface roughness in swollen state may also contribute to the fatigue behaviour of elastomers. Fig. 4 presents SEM micrographs of the fractured surface for SBR-H. The tearing energies imposed repeatedly on specimens during fatigue test are 454 J/m^2 in dry state (Fig. 4(a)) and 400 J/m^2 in swollen state (Fig. 4(b)). As shown in Fig. 4, torn surface of swollen specimen looks much smoother, compared with that of unswollen elastomer, i.e. the steps are more widely spaced on the fracture surface of the swollen elastomer. It has been reported that the smooth surface indicates sharp tear while the rough surface results from blunt tear [18]. Thus it is suggested that the propensity for crack tip sharpening in swollen state also contributes to the lowering of fatigue resistance of elastomers, since the strength of elastomers is strongly dependent on the radius of the crack tip [19,20].

It can be suggested that pre-strain may be imposed on molecular strands by the penetration of solvent into network structure, which may lead to the poor fatigue resistance. However, the effect of pre-strain on fatigue resistance of elastomers is conjectured to be small in this study, since the relatively long flexible molecular chains between junction points may have sufficient time to relax during the period of swelling.

The crack growth rates for SBR-L and SBR-H are plotted against corrected tearing energy G in Fig. 5, using logarithmic scales for both axes. The crosslinking density of SBR-H vulcanizate is higher than that of SBR-L vulcanizate (see Table 1) and SBR-H is likely to consist of a higher proportion of polysulfidic crosslinks than SBR-L, based on the ratio of sulfur to accelerator in mix formulations [21]. Fig. 5 shows that, unlike the SBR-H, SBR-L shows the change of slope at $G =$ ca.700 J/m^2, probably due to the variation of fatigue crack growth pattern from the mechano-oxidative to power law regions [4,20,22]. In spite of different values of slope α, however, the rates of crack growth of both systems

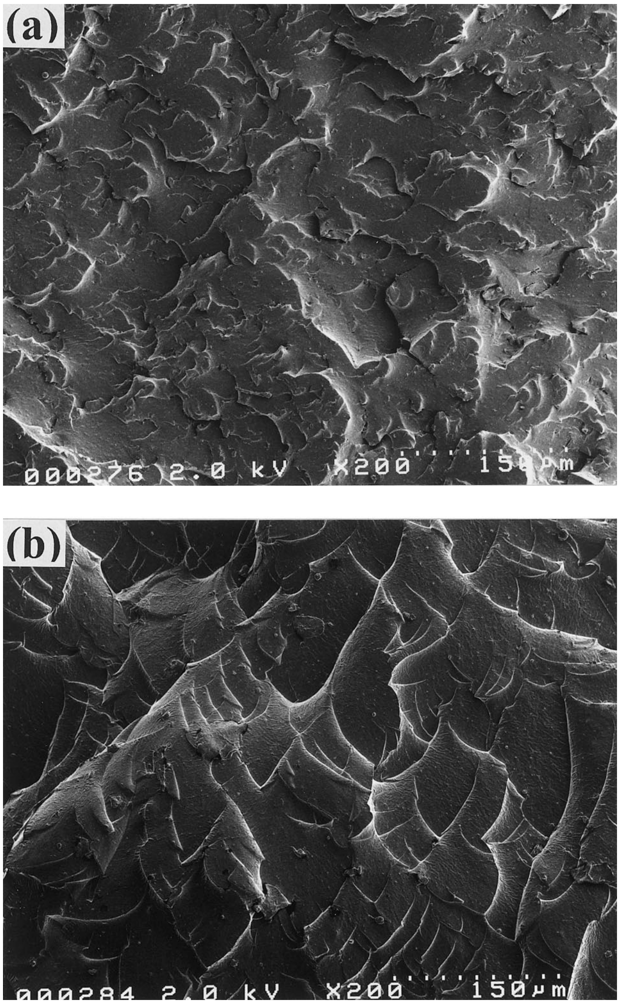

Fig. 4. Scanning electron micrographs of torn surface for SBR-H vulcanizates: (a) in dry condition; (b) in swollen condition.

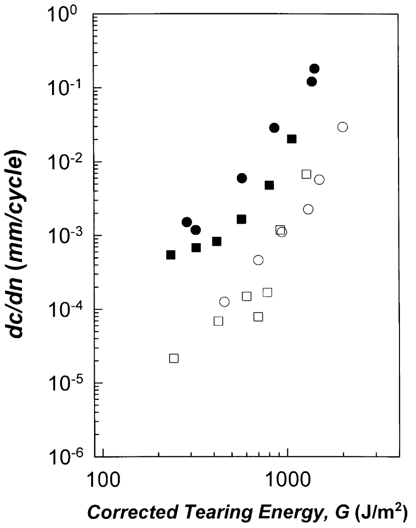

Fig. 5. Crack growth rate versus corrected tearing energy G for SBR-H and SBR-L vulcanizates: (○) SBR-H in dry condition; (●) SBR-H in swollen condition; (□) SBR-L in dry condition; and (■) SBR-L in swollen condition.

are more or less in the similar order of values. It arises from the fact that at a given strain the higher crosslinking density of elastomer gives rise to a higher tearing energy G, which simultaneously increases the rate of fatigue crack growth.

Similarly for elastomers in dry states, the swollen SBR-H holds for Eq. (1) over the measured range of G, whereas the swollen SBR-L shows the change in slope at $G =$ ca. 700 J/m^2. In contrast, the reduction in fatigue resistance in the swollen state seems to be greater in SBR-H than SBR-L, especially in the high tearing energy region. If the crosslink density determines the fatigue properties in the swollen state, the reduction in fatigue resistance will be less significant in SBR-H vulcanizate with a higher crosslinking density (more elasticity), since (a) the degree of swelling is lower and (b) the loss of internal friction in the presence of solvent will be less significant compared with SBR-L vulcanizate. Thus the observation in Fig. 5 may leads to a conclusion that the crosslink type contributes to the fatigue of swollen SBR systems more than the crosslinking density. That is, in the unswollen state, polysulfidic crosslinks easily break and reform during deformation, which is an important strengthening mechanism of the vulcanizates [17]. However, in the swollen state sulfide radicals formed from the breakage of polysulfidic crosslinks are exposed to a solvent, which may suppress the recombination of sulfide radicals and thereby contributes to the lowering of the strength. Therefore, the effect of swelling will be more significant in SBR-H, which is expected to contain the higher concentration of polysulfidic linkage, compared with SBR-L.

4. Conclusions

The fatigue resistance of elastomer is remarkably decreased in the presence of low-viscosity fluid, in proportion to the degree of swelling. However, the rates of crack growth of swollen elastomers are not increased by a constant factor, depending on the magnitude of tearing energy and the type of elastomer. It is considered that the variation of fatigue resistance of elastomer in the swollen state is due to a reduction in viscoelastic energy loss and sharpening of crack tip in the swollen state.

In the presence of the swelling solvent, the reduction in fatigue resistance for SBR-H is greater than SBR-L. This may be due to the loss in the strengthening mechanism in the swollen state, since the recombination of sulfide radicals formed from the breakage of polysulfidic crosslinks may be hindered due to the solvation of sulfide radicals with the solvent.

Acknowledgements

This work was supported in part by a research grant from the center for Advanced Functional Polymers and School of Environmental Engineering of Pohang University of

Science and Technology. H. Chun thanks the Korea Science and Engineering Foundation for support.

References

[1] Gent AN, Lindley PB, Thomas AG. J Appl Polym Sci 1964;8:455.
[2] Lake GL, Lindley PB. J Appl Polym Sci 1964;8:707.
[3] Gent AN, Liu GL, Sueyasu T. Rubb Chem Technol 1991;64:96.
[4] Lake GJ. Progress of rubber technology. England: Applied Science Publisher, 1983. p. 89–143.
[5] Young DG, Danik JA. Rubb Chem Technol 1994;67:137.
[6] Greensmith HW, Mullins L, Thomas AG. In: Bateman L, editor. The chemistry and physics of rubberlike substances. London: Maclaren and Sons, 1963. ch. 10.
[7] Gent AN. J Appl Polym Sci 1962;6:497.
[8] Young DG. Rubber Chem Technol 1986;59:809.
[9] Bueche F. J Appl Polym Sci 1963;7:1165.
[10] Gent AN, Hindi M. Rubb Chem Technol 1990;63:123.
[11] Ahagon A, Gent AN. J Polym Sci: Polym Phys Ed 1975;13:1903.
[12] Chun H, Gent AN. J Polym Sci: Part B: Polym Phys 1996;34:2223.
[13] Rivlin RS, Thomas AG. J Polym Sci 1953;10:291.
[14] Treloar LRG. The physics of rubber elasticity. 3rd ed. Oxford: Clarendon Press, 1975.
[15] Bristow GM, Watson WF. Trans Faraday Soc 1958;54:1731.
[16] Mueller HK, Knauss WG. Trans Soc Rheol 1971;15:217.
[17] Hamed GR. Rubb Chem Technol 1994;67:529.
[18] Gent AN, Pulford CTR. J Mater Sci 1984;19:3612.
[19] Lake GJ, Thomas AG. Proceedings Royal Soc (Lon) 1967;A300:108.
[20] Lake G. J. Rubber Chem Technol 1995;68:435.
[21] Brown PS, Porter M, Thomas AG. Kautcsh Gummi Kunstst 1987;40:17.
[22] Ellul MD. In: Gent AN, editor. Engineering with rubber. New York: Hanser, 1992. ch. 6.