Polymer Vol. 39 No. 11, pp. 2209–2214, 1998
© 1998 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/98/$19.00+0.00

PII: S0032-3861(97)00347-9

Fatigue crack growth of double-networked natural rubber

Shinyoung Kaang* and Changwoon Nah
Department of Fine Chemicals and Process Engineering, College of Engineering, Chonnam National University, Kwangju 500-757, Kwangju, South Korea
R and D Center, Kumho Tire Co., Ltd., Kwangju 506-040, Kwangju, South Korea
(Received 3 February 1997)

Tensile stress–strain behaviour, hysteresis and crack propagation resistance were investigated for various double-networked natural rubbers, prepared using a two-step crosslinking technique. Partially cured rubber is strained and then further crosslinked. They were compared with those of a conventional network (single network). The double-networked natural rubbers were found to show a significant improvement in tensile modulus, tensile strength at break, and strain energy density in the direction parallel to the cure stretching direction. The resistance to crack propagation across the residual strain direction was also greatly enhanced. Moreover, no significant deterioration in crack resistance was observed, even in the direction parallel to the residual strain direction. The morphology of the torn surfaces of the double networks generally resembled that of the single networks, except the cross-hatched pattern was somewhat developed and slanted to the residual strain direction. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: natural rubber; double network; fatigue-crack growth)

INTRODUCTION

A double network structure is formed when the partially crosslinked elastomer is further crosslinked in a state of straining[1–3]. Thus, two types of networks exist, having different states of strain in the relaxed state. Many investigators have extensively studied the mechanical behaviour of double networks[3–8]. It has been reported that the mechanical behaviours of the double-networked elastomers, notably the tensile modulus[3,5,7], the fatigue life[8,17] and the electrical conductivity[4] are much enhanced in the direction of residual strain, while the swelling behaviour[7,9] has been reported as not so much changed. This anisotropic phenomenon is apparently unique to the strain-crystallising elastomers, i.e. natural rubber.

Comparatively few studies have been published on the fracture behaviour of the double network rubbers, although this property is directly related to the service life of rubber products. Recently, it has been reported that the ultimate tensile strength of the double-networked natural rubber (DNNR) is somewhat invariant to residual strain[5], or even improved in the direction of residual strain[7], notwithstanding the higher tensile modulus. It has also been reported that the mechanical fatigue resistance of the double-networked natural rubber perpendicular to the cure stretching direction was greatly enhanced, about ten times, compared with that of a conventionally crosslinked one[8]. A similar anisotropic trend was observed in the tear strength for the stretched natural rubber vulcanisate during the measurement[10].

It is generally agreed that the fracture of rubber is initiated from defects, voids, inclusions and flaws, etc., inadvertently present in the body of the material. They may, then, propagate until their sizes are sufficiently large for macroscopic fracture to occur under the repeated or intermittent stress field. This crack growth characteristic is widely accepted to be the fundamental strength property of a rubber, and this is strongly affected by the strain-induced crystallisation. Thus, it is natural to study the characteristics of the crack propagation to see if the anisotropic feature is also present in the DNNR which may have a different ability to strain-crystallise in one direction to another due to the residual strain.

In this study, the rates of crack propagation in both parallel and transverse directions are measured for various DNNR using the pure shear specimens. They are compared in terms of the tear (or fracture) energy, G[11]. The fatigue-fractured surfaces are observed by a scanning electron microscopy (SEM) technique to assess any correspondence between the morphological features and the rate of crack growth. Tensile stress–strain behaviour and dynamic hysteresis are also discussed in terms of the residual strain.

EXPERIMENTAL

Preparation of double-networked rubber specimens

Natural rubber (SMR-CV60, Standard Malaysian Rubber) was mixed with 2 phr of dicumyl peroxide using a two-roll mill (C. W. Brabender Instruments, USA) at about 70°C for about 10 min. The cure characteristics of the mixed compounds were determined by an oscillatory disc rheometer (Benz, model 674, USA). A two-step curing process was applied to obtain a double network structure. In the first step, a partial crosslinking was made by curing the rubber sheet for 10 min at 150°C under a pressure of about 17 MPa in a cure press (Dake, model 44-251, USA). In the second step, the partially crosslinked rubber sheet was uniaxially stretched with various elongations, ranged from 0 to 650%, using a metal holder and was fully cured for about 95 min at 150°C in a vacuum oven. The detailed procedure is well described in previous work[7]. The characteristics of

---

* To whom correspondence should be addressed

Table 1 Residual strain, λ_r, of the rubber specimens investigated

Sample	λ_r^a	Remark
A	1.00	Single network
B	1.55	Double network
C	2.05	Double network
D	2.55	Double network
E	2.90	Double network
F	3.05	Double network
G	3.25	Double network
H	3.85	Double network

[a] Ratio of the final length of the DNNR at the relaxed state to that of the first cured unstretched sheet

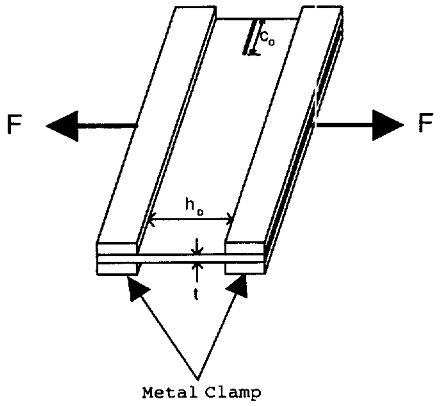

Figure 1 Crack growth test specimen (pure shear geometry)

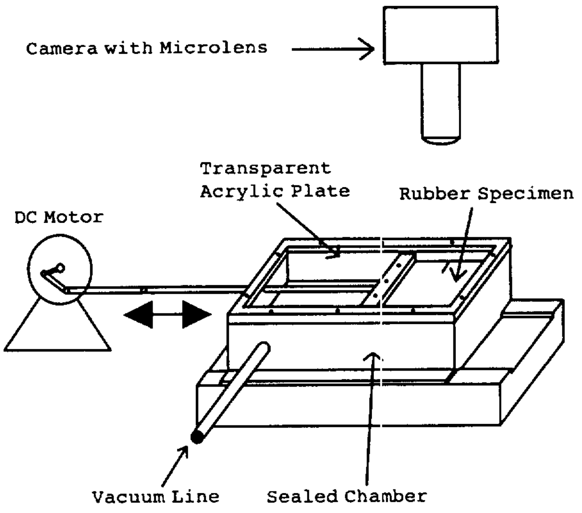

Figure 2 A sketch of the dynamic fatigue test apparatus

the obtained specimens are summarised in *Table 1*, where the residual strain, λ_r, is the ratio of the length of the finally cured relaxed sheet to that of the first cured unstretched one. The observed residual strain, λ_r, ranged from 1 to 3.85. Based on the previous swelling experiments[7], the crosslinking density during the first step is expected to be about 20% of that of the second crosslinked rubber and the crosslink density of the various DNNRs in this study to be independent of the residual strain.

Measurement of tensile property and hysteresis

A universal tensile tester (Shimadzu Autograph AGS-500 D, Japan) was used to determine the tensile properties of various DNNRs. The measurement was done at a constant crosshead speed of 50 mm min^{-1} at room temperature.

The dynamic loss tangent, tanδ, was measured at 20°C using a forced-vibration-type dynamic instrument (GABO 150 N, Germany) at a frequency of 30 Hz. The specimen was prestrained by 10%, and then a dynamic strain of 5% was applied to the sample. Tests were carried out parallel to the cure stretching direction.

Determination of crack growth property

A pure shear test geometry (*Figure 1*) in which the clamps effectively prevent the strip from decreasing in width[12] was selected to determine the rate of crack propagation. An initial cut, 10 mm long, was made in one end of the specimen, and the tip was sharpened using a lubricated razor blade. The pure shear specimen with the dimension of 40 mm × 60 mm × 0.7~1.5 mm, was then placed in the dynamic fatigue tester, which was designed in this study for the application of a series of dynamic fatigue strains, as shown in *Figure 2*. The dynamic fatigue strain, ranged from 0.18 to 1.2, was subjected at a speed of 1 Hz. All the fatigue experiments were performed under the fully relaxing condition, i.e. the minimum strain was zero, and in a vacuum state (~70 mmHg) in order to avoid any oxidation effects. The length of the crack propagated, c, was measured based on photographs taken at an appropriate time interval. Then, the rate of crack propagation, $\mathrm{d}c/\mathrm{d}n$, was obtained from the slope of the plot between the crack length, c, and the number of cycles, n. In an attempt to find any morphological change, the fatigue-failure surfaces were gold-coated in a vacuum evaporator and observed using a scanning electron microscopy (SEM).

For the purpose of comparison, the observed rate of crack, $\mathrm{d}c/\mathrm{d}n$, was analysed in terms of the tear (fracture) energy, G, described below. For the pure shear test geometry, tear energy can be calculated using the following relation[11]:

$$G = Uh_0 \tag{1}$$

where U is the strain energy density per unit volume at the instant of tearing and h_0 is the unstrained value of the test piece width h between clamps[11]. The strain energy density, U, was calculated from the observed relation between the tensile load and displacement using the uncut specimen at each strain level, which will be subjected to the real fatigue test[13]. It should be noted here that the calculation of the strain energy density, U, was based on the input stress–strain curve, i.e. input energy, rather than on the retraction stress–strain curve, since the unfilled natural rubber material showed little dissipation of energy during the loading–unloading cycle[10].

RESULTS AND DISCUSSION

Tensile property and hysteresis

Figure 3 shows a comparison of the stress–strain curves of the double network rubber with $\lambda_r = 3.85$ and the single network rubber of similar crosslink density. In the case of the double network, the extension was parallel to the residual strain direction. As found previously[5,7,8], the enhancement of modulus was significant, i.e. about three times higher for the double network at an elongation of 100%. This enhancement became much greater at higher elongations. Moreover, the upturn in the modulus of the double network was found at much lower elongations, about 200% than that of the conventional single network, about

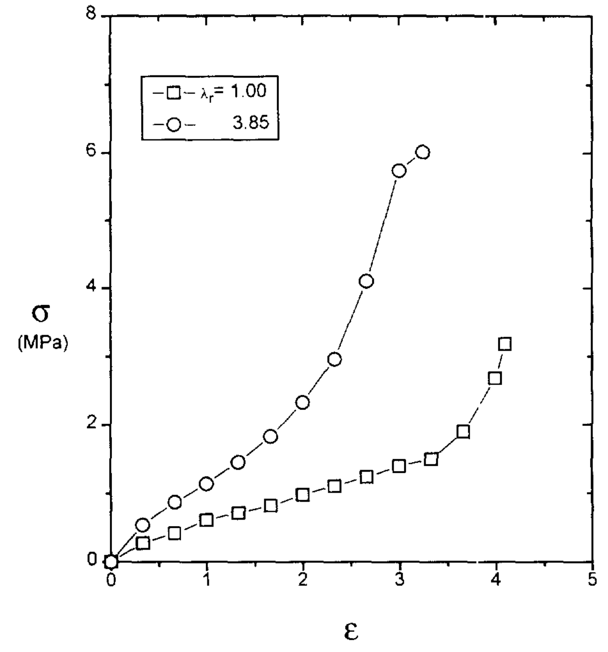

Figure 3 Stress-strain (σ-ε) curves of the single network (λ_r = 1.00) and the double network (λ_r = 3.85)

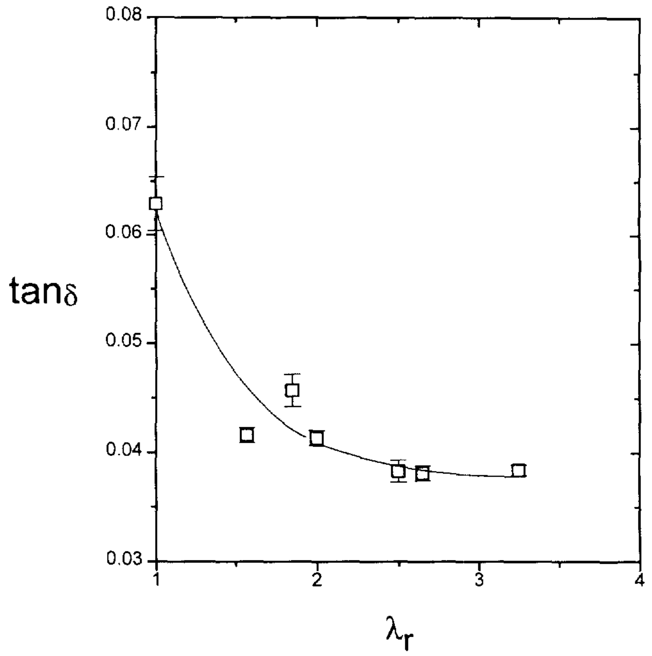

Figure 5 Tanδ *versus* residual strain, λ_r, for various DNNRs

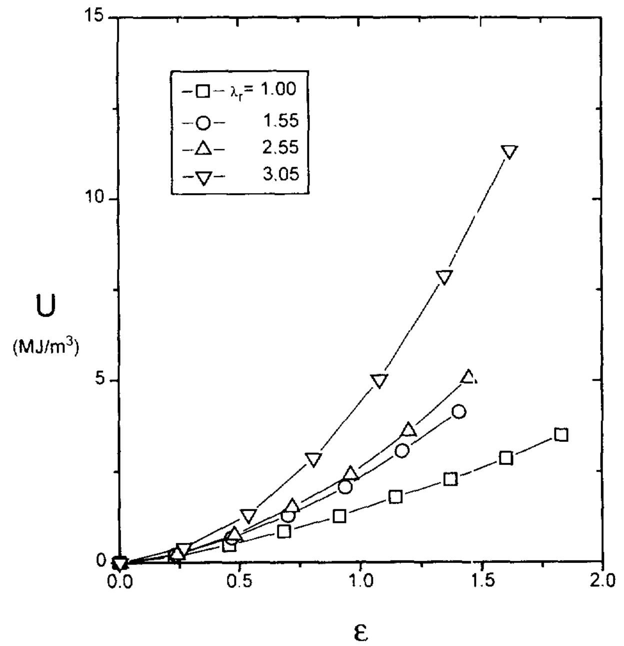

Figure 4 Strain energy density, U, *versus* strain, ε, for various DNNRs

350%. It was reported that the extent of the strain-crystallisation of the double networks was much higher than that of the single network based on the birefringence study by Roland and Warzel[3]. Thus, the difference in the upturn in modulus is responsible for the difference in the strain-crystallisability. Notwithstanding the higher modulus, the ultimate tensile strength of the double network was significantly improved by a factor of nearly 2. This finding is somewhat in contrast to the previous results with the ring-shaped specimens by Santangelo and Roland[5,8]. They found a negligible difference in the behaviour of the double networks in comparison with conventional rubber. In contrast to the tensile strength, the ultimate elongation of the double networks was slightly inferior to that of the single network.

For the calculation of tear energy, G, using equation (1), the strain energy density, U, was determined for the specimens used in this experiment. They are shown in *Figure 4* as a function of strain, ε. Over the range of the strain investigated, from 0 to 1.5, the strain energy density, U, increased with the increased residual strain, λ_r, mainly due to the increase in tensile modulus in the corresponding range of strain, ε.

Figure 5 shows a plot of hysteresis, tanδ, measured in the direction parallel to the residual strain direction. With increasing residual strain tanδ decreased dramatically, from 0.062 to 0.042, up to a residual strain of 2, and then it levelled off with further increase of the residual strain. This may be explained by the behaviour of disentanglement and orientation of long chain rubber molecules, an energy consuming process. For example, in the case of the single network such a loss process will arise during the dynamic testing, resulting in higher tanδ. These effects can, however, be reduced in the double networks, since such hysteresis may occur, at least to some degree, during deformation in the second curing stage.

Resistance to fatigue-crack growth

Figure 6 represents a typical plot of the propagated crack length, c, across the direction of the residual strain (transverse direction) *versus* number of cycles, n, for the double network of λ_r = 1.55 at the dynamic fatigue amplitude of 35%. A linear relation was observed over the period of experiment, about 250 min. A similar result was seen for all the specimens investigated. Thus, the rate of crack propagation, dc/dn, was obtained from the slope of each plot for all the cases encountered in this study.

In an attempt to elucidate the effects of the anisotropic structure of the double networks on resistance to crack propagation, cracks are propagated at right angles to the direction of the residual strain. The results obtained on the rates of crack propagation, dc/dn, of various DNNRs are plotted against the tear energy, G, using a log–log scale, and they are compared with that of the single network in *Figure 7*. It can be seen that linear lines can be drawn for all

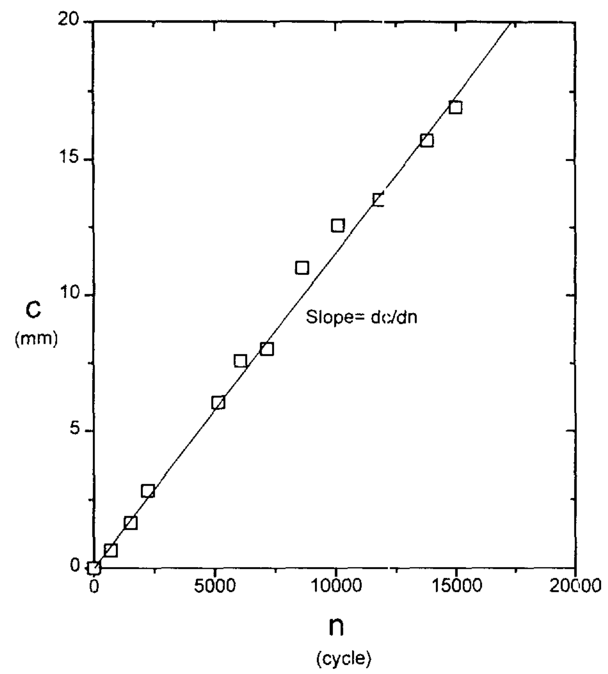

Figure 6 A typical plot of the propagated crack length, *c*, *versus* number of cycles, *n*, for the double network of residual strain of 1.55 under dynamic amplitude of 35%

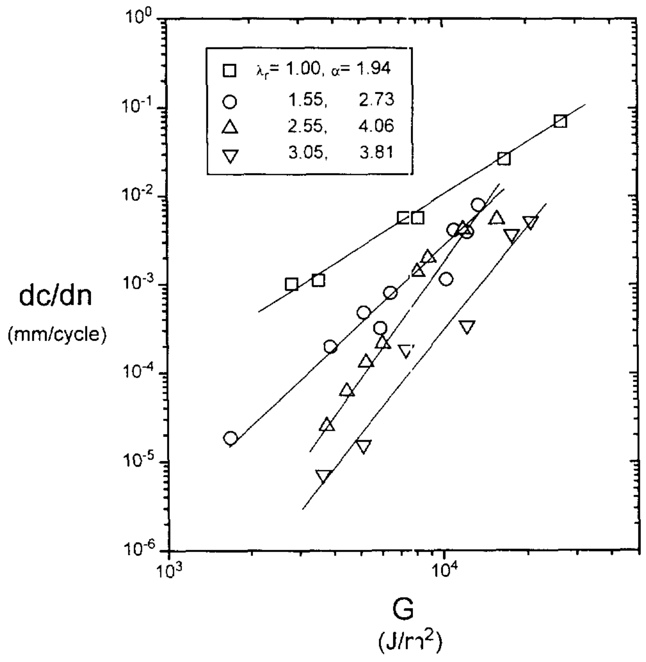

Figure 7 Rate of crack growth, d*c*/d*n*, *versus* tear energy, *G*, for various DNNRs

cases, indicating that the rate of crack growth, d*c*/d*n*, can be represented by the power-law relation with the tear energy, *G*, as found previously[14]:

$$\frac{dc}{dn} = KG^{\alpha} \tag{2}$$

where *K* is a constant and α is the exponent.

Over the range of tear energies employed, generally from 2 to 20 kJ m^{-2}, the rate of crack propagation at a constant fracture energy fell significantly as the residual strain was increased. For instance, the resistance to crack propagation of the double network of $\lambda_r = 3.05$ improved at least by a factor of 10 compared with that of the single network ($\lambda_r = 1$) and this improvement was much greater, more than 100 times, at relatively lower ranges of tear energy. The superior resistance to fracture of the double networks was also confirmed in the fatigue lifetime experiment (fatigue-to-failure test) with no precut, for relaxing deformation along with the direction of the stretching during curing[8].

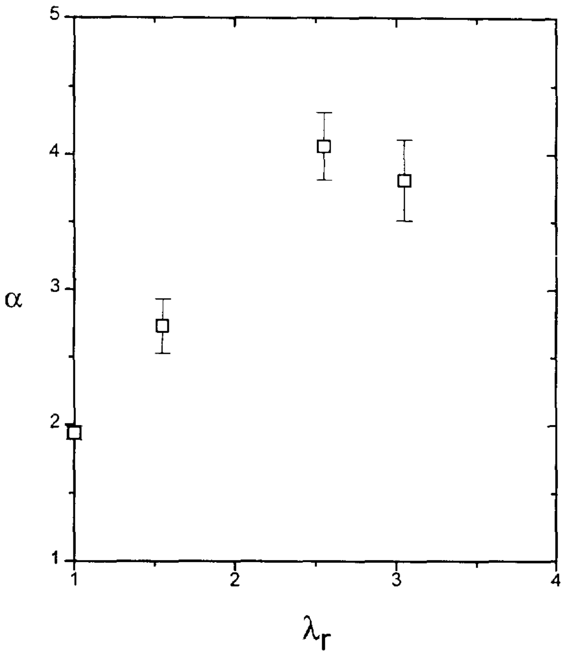

Figure 8 The exponent, α, *versus* residual strain, λ_r

The possible reason for the increase in resistance to crack propagation is the strain-induced crystallisation, which is a characteristic feature of natural rubber. It is known that the failure strength of natural rubber can be enhanced by the strain crystallisation[12,15]. This crystallisation effect is well supported by the fact that natural rubber exhibits much better resistance to fatigue failure under the non-relaxed than under the fully relaxed condition[16,17]. It is also known that the degree of strain-crystallisation of the DNNR is considerably higher than that of the single-networked one of equal crosslink density under the same elongation condition[3]. Thus, the rubber crystallites formed by the repeated stressing may act in the same way as reinforcing fillers, such as carbon blacks. For instance, the crystallites provide for an increased propensity to the blunting and branching of the crack tips. This mechanism seems to be responsible for the increased resistance to crack growth for the double networks perpendicular to the residual strain direction and it is more pronounced for the case of higher residual strains.

It is interesting to note that the power law exponent, α, in equation (2) is strongly affected by the residual strain, as shown in *Figure 8*. Based on previous results, α differs from one type of rubber to another, due mainly to mechanical hysteresis: 2 for natural rubber (NR), 4 for styrene–butadiene rubber (SBR), and 6 for polybutadiene rubber (BR)[13]. In the present study, it was found that the value of α for the single-networked NR was close to 2, as obtained by others[13]. However, it increased to about double this amount when the residual strain was increased from 1 to 3.05 (about three times). The increase in the value of α for the double networks may be responsible for the reduced hysteresis

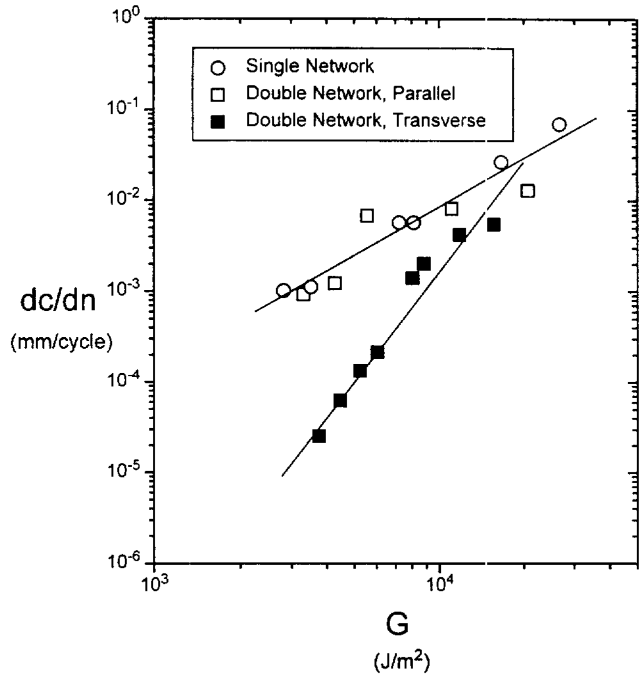

Figure 9 Rate of crack growth, d*c*/d*n*, *versus* tear energy, *G*, for the double network ($\lambda_r = 2.55$) together with that of the single network ($\lambda_r = 1$). In the case of the double network, the crack is propagated in parallel and transverse directions

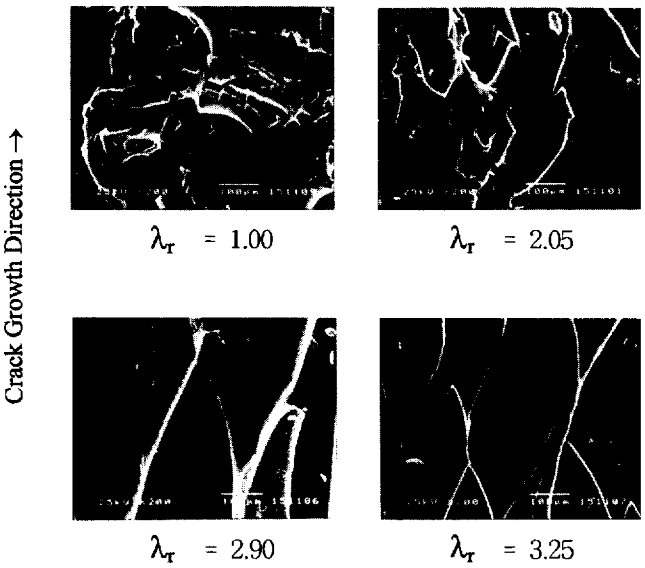

Figure 10 Fatigue-failure surfaces of various DNNRs. The direction of crack growth is shown as an arrow

Table 2 Change of the propagation angle, θ, formed between the step line and the direction of crack growth depending on the residual strain, λ_r

λ_r	θ (deg)
1.00	44 ± 15
2.05	31 ± 7
2.90	24 ± 5
3.25	20 ± 5

shown in *Figure 5*, i.e. the lower the hysteresis, the steeper the slope[13].

In a previous study, the strong anisotropic nature of the double networks was observed in the tensile modulus[7]. Thus, the anisotropic effect is expected to be present in the crack growth property.

Anisotropy in resistance to crack propagation

Another measurement of the rate of crack propagation was made for the double network of $\lambda_r = 2.55$ in both directions (parallel and transverse to the residual strain). In *Figure 9* the results are compared with that of the single network. A considerable difference is seen in the rate of crack growth of the double network depending on the applied stress direction, especially at the lower regions of tear energy. This suggests that a strong anisotropy is also present in the resistance to crack growth. Moreover, almost no difference in the rate of crack propagation is seen between the double network in the parallel direction and the single network.

Thus, it may be concluded that the use of a double network can provide a useful way to improve the tear strength of rubbery materials, notably strain-crystallisable rubber, in a desired direction without any deterioration of the strength in the remaining direction.

Morphology of fatigue-failure surfaces

The observation of the failure surfaces is very informative to understand the failure mechanisms. The fatigue-failure surfaces of various DNNRs at about 8 kJ m^{-2} of tear energy are shown in *Figure 10*, together with that of the single network. A characteristic morphology of the torn surfaces is the so called 'cross-hatched patterns'[18], which is composed of numerous webs and steps in different sizes, and this was seen for all cases. The mechanism of the formation of the webs and steps is well described by Gent and Pulford[18] by considering the linking of small cracks developed at the main tear tip, as they grow in size under the influence of the complex stress field. Nevertheless, in the case of the single network ($\lambda_r = 1$ in *Figure 10*) the morphology was found to closely resemble the typical cross-hatched pattern of unfilled rubber vulcanisates[18,19]. As the residual strain was increased, the surface between the steps became somewhat smoother and the steps were more closely spaced, indicating the higher resistance to crack propagation. Moreover, the step lines seemed to slant to the vertical (crack propagation direction in *Figure 10*). The slanting of the step lines is very interesting, because it has been reported that the tears propagated at an angle of about 45° to the direction of advance of main tear[18]. Thus, an attempt was made of measurement of the angle of the step lines, θ, with respect to the vertical line in *Figure 10* (overall crack propagation direction). These values are given in *Table 2*. Although a significant experimental error is encountered (notably for the single network of $\lambda_r = 1$, due probably to difficulty in the measurement for the small cross-hatched patterns of $\sim 10\ \mu$m), the angle represents a clear decreasing trend from 44 to 20°, as the residual strain is increased. It was also observed that the steps propagated at a somewhat smaller angle to the tear direction in stronger rubbery materials[18]. Based on this result, it may be concluded that the existing residual strain in the rubber network can change the tear path, resulting in a change in the tear property.

CONCLUSIONS

Some measurements were made of the tensile stress–strain behaviour, hysteresis, and crack growth resistance for DNNRs. The failure surfaces were also observed using scanning electron microscopy. The results obtained are summarised as follows:

(1) The DNNRs showed a great enhancement in tensile modulus, ultimate tensile strength, and strain energy density in a direction parallel to the residual strain direction. The ultimate tensile elongation showed a slight deterioration. Moreover, the natural rubber showed less hysteresis (lower tanδ value) when the single network was modified to the double network.

(2) In the range of tear energies from 2 to 20 kJ m^{-2}, a power-law relation was observed between the rate of crack propagation, dc/dn, determined by a pure shear test, and the tear energy, G, tested perpendicular to the cure stretching direction. The power-law exponent, α, was close to 2 for the single-networked natural rubber and it increased significantly with the increased residual strain. Moreover, the resistance to crack propagation of the double networks was greatly improved compared to that of the single network, when the crack was directed to growth at right angles (transverse) to the residual strain direction. In the parallel direction, however, no significant difference was found between them.

(3) The overall morphology of the failure surfaces of the double networks tested perpendicular to the cure stretching direction, resembled that of the typical torn surfaces of the single networks, 'cross-hatched patterns' composed of numerous webs and steps. As the residual strain was increased, the surface between steps became smoother and the step spacing became closer. Moreover, the step lines somewhat slanted to the tear direction.

ACKNOWLEDGEMENTS

This work was supported by a research grant (1994) from Chonnam National University, South Korea. The authors would like to thank Mr. Donghwa Gong for assistance with the experimental work.

REFERENCES

1. Andrews, R. D., Tobolsky, A. V. and Hanson, E. E., *Journal of Applied Physics*, 1946, **17**, 352.
2. Ferry, J. D., *Polymer*, 1979, **20**, 1343.
3. Roland, C. M. and Warzel, M. L., *Rubber Chemistry Technology*, 1990, **63**, 285.
4. Roland, C. M. and Peng, K. L., *Rubber Chemistry Technology*, 1991, **64**, 790.
5. Santangelo, P. G. and Roland, C. M., *Rubber Chemistry Technology*, 1994, **67**, 359.
6. Thomas, D. K., *Rubber Chemistry Technology*, 1967, **40**, 621.
7. Kaang, S., Gong, D. and Nah, C., *Journal of Applied Polymer Science*, 1997, **65**, 917.
8. Santangelo, P. G. and Roland, C. M., *Rubber Chemistry Technology*, 1995, **68**, 124.
9. Roland, C. M., *Rubber Chemistry Technology*, 1989, **62**, 863.
10. Gent, A. N. and Kim, H. J., *Rubber Chemistry Technology*, 1978, **51**, 35.
11. Rivlin, R. S. and Thomas, A. G., *Journal of Polymer Science*, 1953, **10**, 291.
12. Treloar, L. G. R., *The Physics of Rubber Elasticity*, 2nd edn. Oxford University Press, 1958.
13. Ellul, M. D., in *Engineering with Rubber; How to Design Rubber Components*, ed. A. N. Gent. Hanser Publishers, 1992, Chap. 6.
14. Lake, G. J. and Thomas, A. G., in *Engineering with Rubber; How to Design Rubber Components*, ed. A. N. Gent. Hanser Publishers, 1992, Chap. 5.
15. Greensmith, H. W., Mullins, L. and Thomas, A. G., in *The Chemistry and Physics of Rubber-like Substances*, ed. L. Bateman. John Wiley & Sons, New York, 1963, Chap. 10.
16. Lake, G. J. and Thomas, A. G., in *Natural Rubber Science and Technology*, ed. A. D. Roberts. Oxford University Press, New York, 1988, Chap. 15.
17. Roland, C. M. and Sobieski, J. W., *Rubber Chemistry Technology*, 1989, **62**, 683.
18. Gent, A. N. and Pulford, C. T. R., *Journal of Materials Science*, 1984, **19**, 3612.
19. Nah, C., Ph.D. dissertation, The University of Akron, 1995.