Some Physical Characteristics of Double-Networked Natural Rubber

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ABSTRACT: A double-networked natural rubber (DNNR) was prepared by a "two-step crosslinking" method, in which the crosslinking was achieved while the natural rubber was in a stretched condition. The swelling behavior, tensile properties, creep, recovery, and permanent set were investigated. Generally, the observed mechanical properties of DNNR, such as the Young's modulus, tensile strength, toughness, creep, recovery, and permanent set, were considerably improved as the residual extension was increased. They were, however, rather inferior to those of a single-networked natural rubber and showed a minimum at a lower residual extension of about 1.55. The degree of crosslinking and elongation at break were not greatly affected by the residual extension. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 917–924, 1997

Key words: natural rubber; double networks; swelling; tensile property; creep and recovery

INTRODUCTION

When a rubbery material is crosslinked in a state of macroscopically zero strain, i.e., in the typical manner of the rubber industries,[1] the resulting networks are composed of an equilibrium set of chain configurations.[2] However, when the crosslinking reaction takes place in a deformed state, especially in the extended state, an anisotropic crosslink network can be produced.[2–4] This anisotropy of the network may affect various properties of the final rubber products.[2,5,6] The concept of a dual network was theoretically treated by Tobolsky et al.[3] to describe the mechanical behavior, especially the permanent set of the dual networks having different strain conditions. Based on the theory, the degree of permanent set can be described quantitatively by using only two factors: (1) the relative ratio of the number of the two types of chains, i.e., one unstrained at the original length and the other at the stretched length and (2) the elongation at which the sample is held. The theory of Tobolsky et al. was successfully applied for the case of two networks of crosslinks and trapped entanglements,[7] even though some limitations were reported for the interpretation of stress-relaxation behavior.[8] Since the double network was introduced, several experimental investigations have been made of stress relaxation,[9] orientation and crystallization effects,[2] electrical conductivity,[10] and failure property.[2,4] However, little attention has been given to the creep-recovery behaviors of the double networks, despite of their significance in view of the engineering applications, such as automotive suspensions, engine

mounts, building mounts, and elastomeric tensioners for oil platforms.[11]

In this study, a double-networked natural rubber (DNNR) was made using a "two-step" crosslinking technique and the degree of crosslinking was determined. Creep, recovery, and permanent set behaviors of various double-networked rubbers were investigated, and they were compared in terms of residual extension with a single-networked rubber at the similar level of crosslinking. Tensile properties were also investigated in an attempt to examine any anisotropic feature of the double network.

EXPERIMENTAL

Preparation of Rubber Specimens

Natural rubber (SMR-CV60, Standard Malaysian Rubber, Mooney viscosity, ML_{1+4}: 60) was mixed with 2 phr of dicumyl peroxide using a two-roll mill (C. W. Brabender Instruments, Inc., U.S.A.) at about 70°C for about 10 min. Then, the optimum cure times of the mixed compounds were determined with an oscillatory disc rheometer (Benz, Model 674, U.S.A.). To obtain a double-network structure, curing was done in two steps: In the first step, the rubber sheet was cured partially for 10 min at 150°C under a pressure of about 17 MPa using a cure press (Dake, Model

Figure 1   A sketch of formation of the double-network structure.

Table I   Stretching Ratio, λ_e, and Residual Extension Ratio, λ_r, of Various Double-Networked Natural Rubbers

Sample	λ_e[a]	λ_r[b]
A	1.0	1.00
B	2.0	1.32
C	2.5	1.55
D	3.5	2.20
E	4.0	2.45
F	4.5	2.55
G	5.5	3.05
H	7.5	3.85

[a] Ratio of stretched length (l_i) to that of the first cured unstretched sheet (l_0).
[b] Ratio of the final length (l_f) of the double-networked rubber at the state of ease to that of the first cured unstretched sheet (l_0).

44-251, U.S.A.). In the second step, the partially crosslinked rubber sheet was uniaxially stretched to various desired lengths using a metal holder. Then, the stretched sheet was inserted between two steel plates (top and bottom), and the assembly was placed in a vacuum oven (Fisher, Model 13-261-50, U.S.A.) at 150°C for about 95 min. The fully cured rubber sheet was then placed in air at room temperature for 24 h. Finally, the double-networked natural rubber vulcanizate was obtained by releasing the strain.

Shown in Figure 1 is a schematic diagram of a possible change in the network structure during the curing process. The amount of stretching is expressed as λ_e, defined as the ratio of uniaxially stretched length (l_i) to that of the first cured unstretched sheet (l_0). Similarly, the residual strain, λ_r, is defined as the ratio of the final length (l_f) of the double-networked rubber at the state of ease to that of the first cured unstretched sheet (l_0). All the rubber samples in this study are given in Table I, together with λ_e and λ_r.

Determination of Crosslinking Density

To determine the degree of crosslinking, the volumetric swelling ratio, Q, of the rubber sheets in a solvent (decane) was measured as a function of time until an equilibrium was reached at room temperature. From the equilibrium swelling ratio, Q_e, the molecular weight between crosslinks, M_c, was calculated using the Flory–Huggins relation.[12–14] The detailed procedure is well described elsewhere.[15]
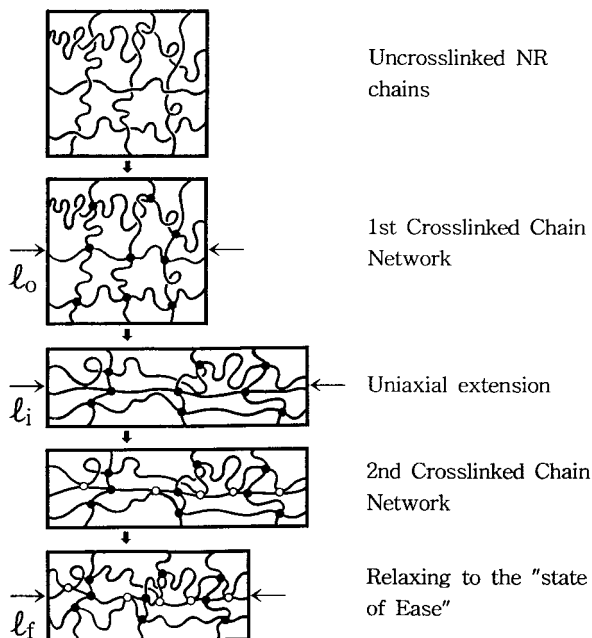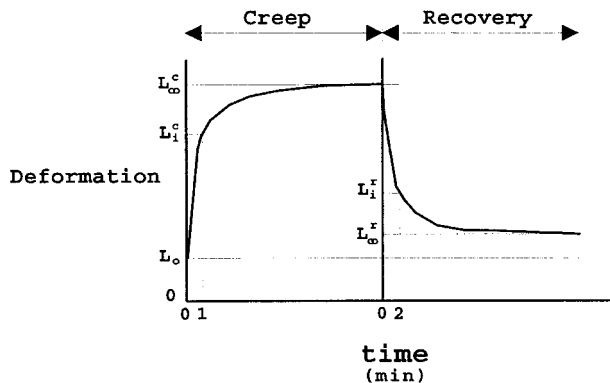
Figure 2   A schematic diagram of a typical deformation procedure in the creep-recovery experiment.

Measurement of Physical Properties

The tensile properties of various double-networked rubber vulcanizates were determined using a universal tensile tester (Shimadzu Autograph AGS-500D, Japan) at a constant crosshead speed of 50 mm/min at room temperature. In an attempt to see any anisotropy of a double network, the tensile modulus was determined for both the parallel and transverse directions.

For the creep-recovery test, a rectangular rubber strip having the dimensions of $15 \times 40 \times 0.7 - 1.5$ mm was bonded to steel clamps using an instant adhesive (Loctite 401, Korea Loctite Co.). A fiducial mark of 20 mm was drawn in the center of rubber strip. A constant stress of 1 MPa was then applied to the bottom of the rubber strip. Typical deformation characteristics of the creep-recovery experiment are given in Figure 2. In the creep experiment, the initial deflection, ΔL_i^c ($= L_i^c - L_0$), was measured at 1 min after the load was hung, and the continuous change in length due to creep, ΔL^c [$= L_t^c(t > 1 \text{ min}) - L_0$], was measured with time. Then, after about 10,000 min, the load was removed and the initial recovery, ΔL_i^r ($= L_\infty^c - L_i^r$), was determined 2 min after the load removal. Also, the continuous recovery, ΔL^r [$= L_\infty^c - L_t^r(t > 2 \text{ min})$], was measured. Finally, the permanent set, ΔL_{ps} ($= L_\infty^r - L_0$), defined as the unrecoverable length, was deter-

mined. All the creep and recovery experiments were performed in air at room temperature.

RESULTS

Swelling Behavior

To know the degree of crosslinking in each curing stage, the volumetric swelling ratios, Q, calculated from the weight gain of a rubber specimen during swelling,[12–15] were obtained for both first crosslinked rubber and second crosslinked rubber with no stretching. The results obtained as a function of swelling time are given in Figure 3. The initial swelling rate of the second crosslinked rubber was found to be much greater than the first crosslinked one and thus reached equilibrium faster. This is probably due to a swifter motion of the shorter molecular strands in the highly crosslinked networks.[16,17] The swelling ratio at equilibrium, Q_e, of the first crosslinked rubber was found to be about 6.8, while that of the second crosslinked rubber was 3.6. The corresponding molecular weights between crosslinks, M_c, was about 35,200 and 7400 g/mol, respectively, based on the Flory–Huggins relation.[12–14] From these results,
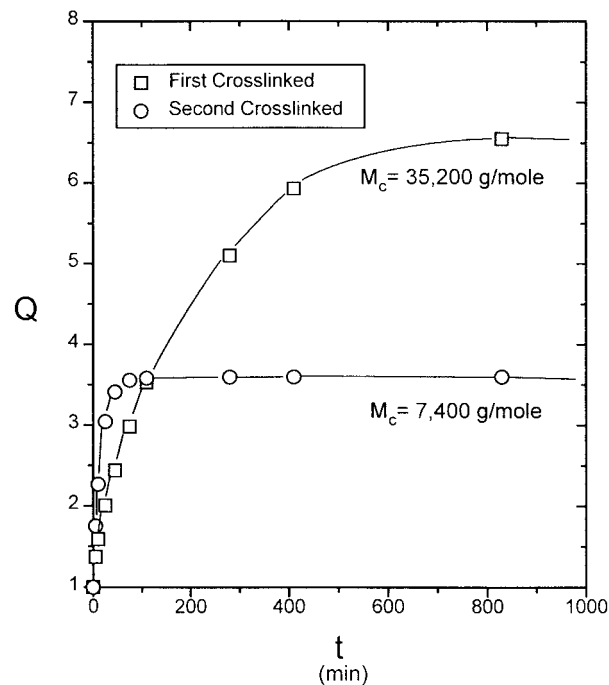

Figure 3   Volumetric swelling ratio, Q, of first crosslinked natural rubber and second crosslinked one as a function of swelling time, t.
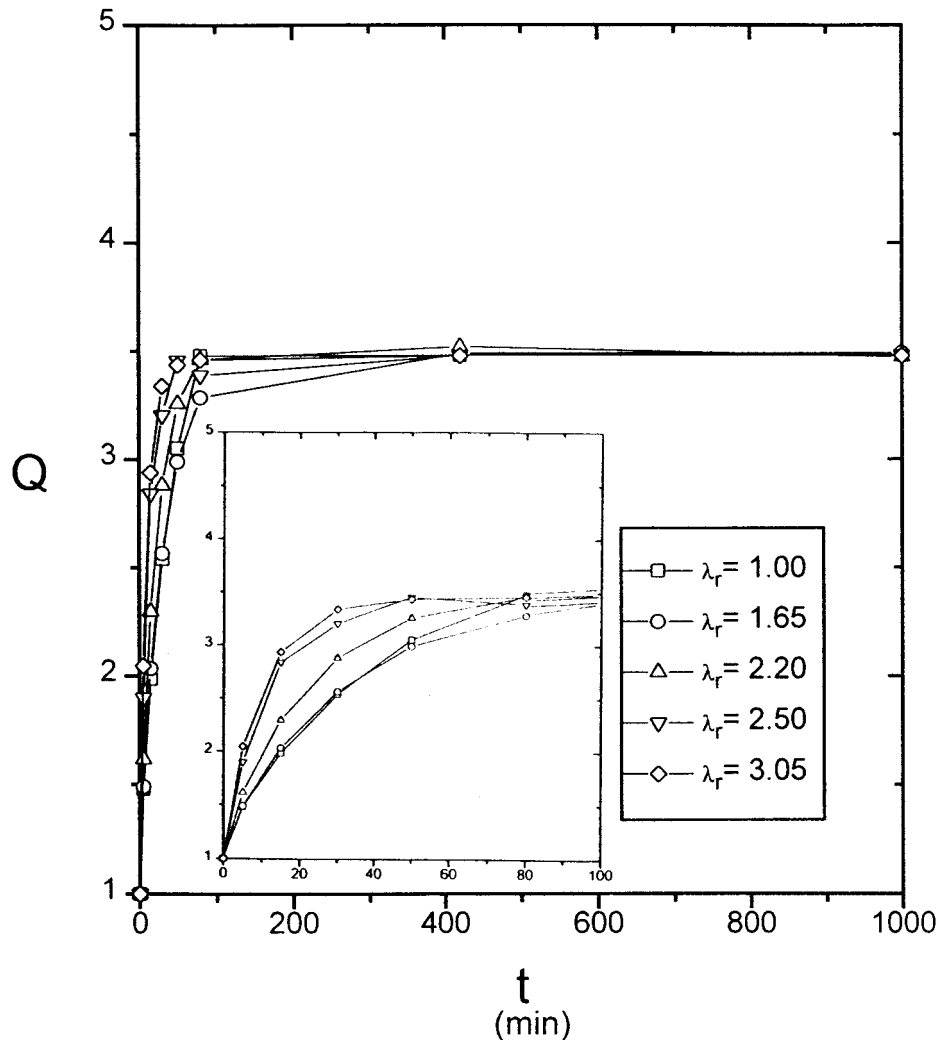
Figure 4   Volumetric swelling ratio, Q, of the various double-networked natural rubbers against swelling time, t.

it is inferred that the crosslinking density during the first step is about 20% of that of the second crosslinked rubber.

Further swelling measurements were made for various double networks to determine the effect of stretching during the second curing stage on swelling behaviors. These results are also plotted against swelling time in Figure 4. The swelling rate, based on the slope of the swelling curve, became faster with increased residual extension ratio, from 1 to 3.05. This is thought to be attributed to a restraint of sluggish motion in the chain network by the residual extension which is already in existence in the double-network structure. The equilibrium swelling ratios, Q_e, are found to be approximately the same for all cases, including

the zero residual extension case (single-network structure). Based on this result, it can be conjectured that the degree of crosslinking of the various DNNRs in this study is about the same. This is a very desirable condition, especially when there is a need to compare mechanical properties, since the degree of crosslinking strongly affects them.[1]

Tensile Properties

In an attempt to see any orientation effect, the Young's moduli (both parallel and perpendicular to the direction of stretching) were measured based on the initial slope of the stress–strain curves. They are compared in Figure 5. The trans-
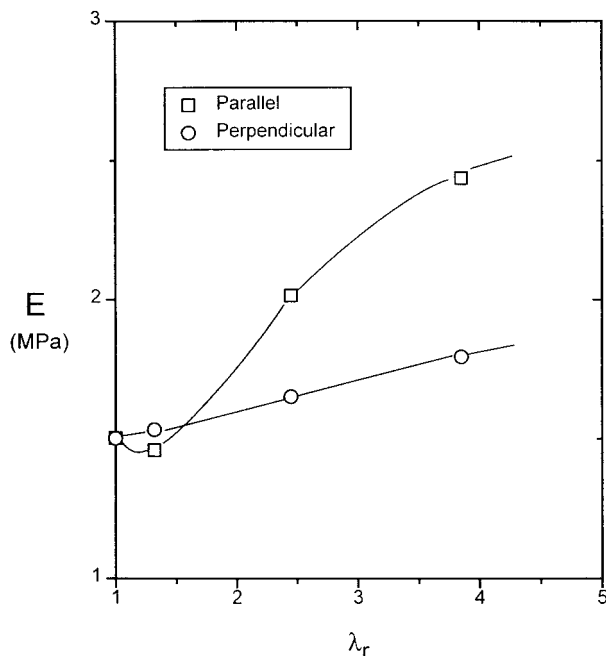
Figure 5 Young's modulus, E (both in parallel and perpendicular directions) vs. residual extension ratio, λ_r, for a double-networked natural rubber.

verse modulus was not affected much by the degree of stretching, i.e., it increased only slightly with increased residual extension. However, the modulus in the parallel direction was found to be considerably increased, from 1.5 to 2.4 MPa, as the residual extension was varied from 1 to 3.9, even though the overall degree of crosslinking was about the same for all the specimens investigated. This large difference strongly indicates an anisotropic nature in the DNNRs. Thus, the results obtained are somewhat opposed to the previous prediction that a double-networked rubber is mechanically isotropic[3] and is also opposed to the isotropic nature of swollen networks.[18]

Another interesting phenomenon that should be noted here is that the parallel Young's modulus seems to decrease with increased residual extension in the lower residual extension range and reaches a minimum at about 1.32. It then increases again with the further increase of the residual extension. A similar behavior of the lower modulus at lower residual strains was predicted[4] and observed experimentally.[4,19] This was explained by the breaking of original networks[19] and by the minimization in the changes of the first crosslinked network during the second crosslinking.[4,20] However, it is not clearly verified why

the double networks show such behavior. One plausible mechanism is that there seems to be two opposing effects: the increasing effect of the modulus (due to the orientation of the network structure to the direction of stretching and a higher probability of strain-induced crystallization during the tensile measurements)[2,21,22] and the decreasing effect of the modulus (due to a disentanglement of some weak mechanical interlocks during the second crosslinking step). At relatively low residual extensions, the decreasing process dominates. However, this effect is canceled out by the increasing effect above a certain level of residual extension. In addition, there might be another effect on the tensile properties present in the double networks, especially in the lower residual extensions caused by network defects, such as intermolecular entanglements and intramolecular loops. However, this effect will be diminished at higher residual extensions since the chemical crosslinks are the main factor for the resistance to deformation.

To determine if this interesting behavior also appears in other properties, the tensile toughness based on the area under the stress−strain curve and the stress and strain at break were also determined as a function of residual extension. The toughness and the stress at break were also found to first decrease and then increase with increased residual extension (Figs. 6 and 7). On the other hand, the strain at break was not affected greatly by the residual extension (Fig. 7).

It is interesting to note that both the ultimate strength, such as tensile strength and toughness, and the Young's modulus are improved as the network is changed to an anisotropic structure over the slightly higher residual extension range. Generally, rubbery materials having a higher modulus with increased crosslinking density exhibit lower ultimate strength.[23] Therefore, the utilization of a double network can provide a useful way of increasing the modulus without the loss of the ultimate strength, especially when there is a need to use a higher dosage of curing agents.

Creep, Recovery, and Permanent Set

An initially deflected length, ΔL_i^c, was determined 1 min after a constant weight was applied. It was found to be generally lower for the double networks than for a single network, except in the case of very low residual extension, as was ex-
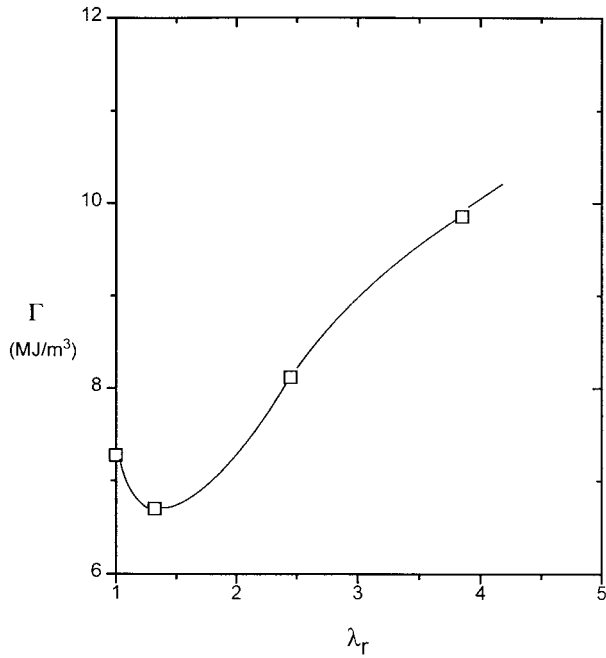
Figure 6 Toughness, Γ, vs. residual extension ratio, λ_r, for a double-networked natural rubber.

pected from the previous tensile modulus behaviors of the double networks. The obtained results can again be explained by the network defects mentioned previously in the discussion of tensile properties. The continuous creep, ΔL^c, was mea-
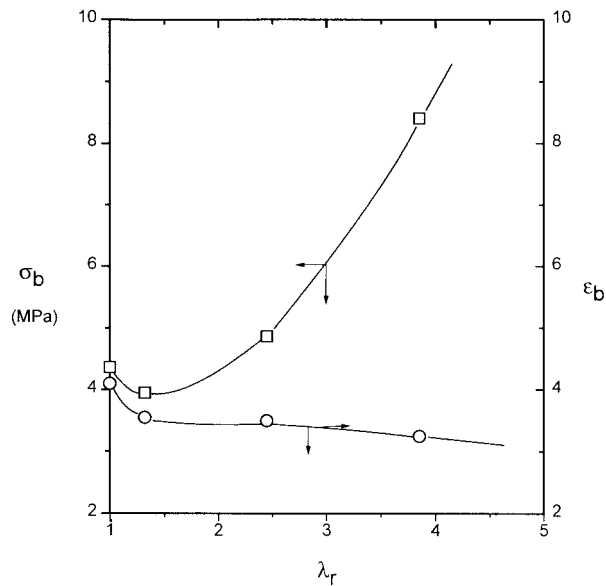

Figure 7 Tensile stress at break, σ_b, and strain at break, ε_b, vs. residual extension ratio, λ_r, for a double-networked natural rubber.
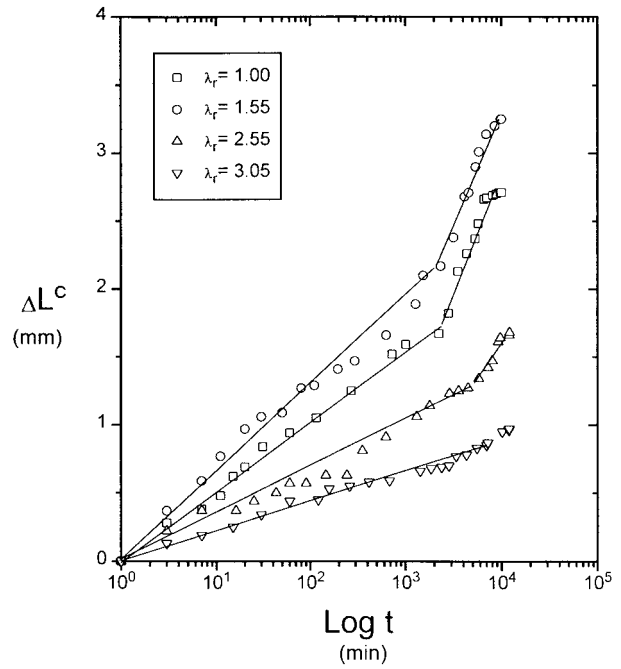

Figure 8 Creep, ΔL^c against creep time, t, for various double-networked natural rubbers.

sured at appropriate time intervals until a steady state was observed, in about 40,000 min (about 10 days). Generally, the creep of rubbery materials can be expressed as a summation of physical creep (due to molecular chain slippage) and chemical creep (due to molecular chain breaking).[11] Physical creep is usually expressed as a logarithmic function of time, and chemical creep at a constant temperature is approximately a linear relation with time. Thus, the total creep is given by

$$Creep = \alpha \log t + \beta t \qquad (1)$$

where α and β are constants. The first term of right-hand side of the above equation represents the physical creep and the second term represents the chemical one.

To examine whether the creep of double networks also follows the above relation or not, the observed creep, ΔL^c, of the various DNNRs in the present study are plotted against a logarithmic time scale and is displayed in Figure 8. As can be seen, linear lines can be drawn for all cases over the time range from 1 to 2000 min. The slope is generally lower for the higher residual extension, except for the case of residual extension of 1.55. This indicates that the physical creep process dominates under these conditions. However, in
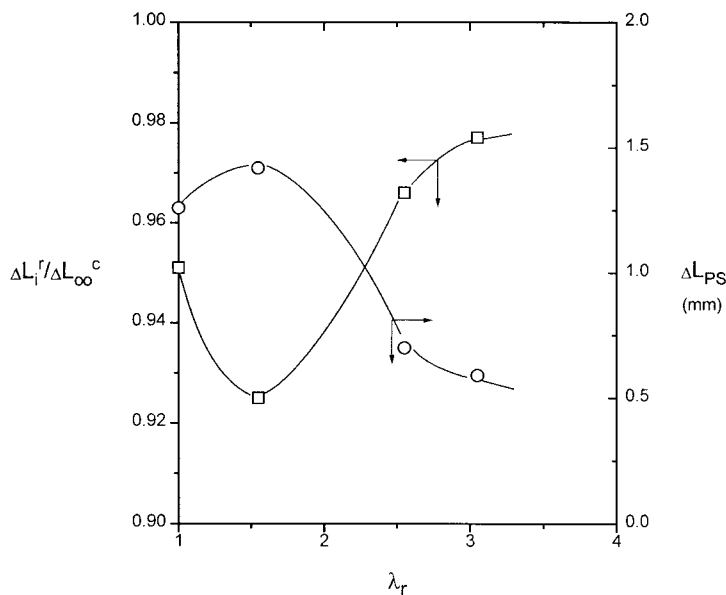
Figure 9 Instantaneous recovery, $\Delta L_i^r / \Delta L_\infty^c$, and permanent set, ΔL_{ps}, as a function of residual extension ratio, λ_r, for various double-networked natural rubbers.

the case of a single network and a double network of residual extension of 1.55, the double network shows an even greater creep than does the single one and there appears to be a transition at about 2000 min. The chemical creep (due mainly to the oxygen in air) is probably responsible for the observed transition, as can be surmised by the second term on the right-hand side of eq. (1). Thus, it should be noted here that the chemical creep is delayed or decreased by changing the network structure into the double network with relatively higher residual extensions. However, it is not clear that such a double-networked structure is more resistant to oxidation (or ozonation). Clearly, the effect of residual extension within the double-networked rubber upon the rate of oxidation requires further study.

Next, to understand the recovery of a double network, the instantaneously recovered length, ΔL_i^r, was determined 2 min after removing the applied load. Its ratio to infinite creep, ΔL_∞^c, was plotted against the residual extension ratio in Figure 9. As can be seen, the instant recovery decreases at a lower residual extension, 1.55, and then increases with a further increase of residual extension.

On the other hand, a completely opposite trend was observed for the permanent set, ΔL_{ps}. It increased slightly at lower residual extension and then considerably decreased as the residual ex-

tension was increased, as is also shown in Figure 9. Thus, it can be suggested that the natural rubber vulcanizates can be improved in dimensional stability for field service under tension by introducing the double-networked structure. However, it is not clear whether the observed results are also true for a double network formed in a compression mode. Thus, additional study is necessary for the elucidation of the characteristics of a double-networked rubber formed in a compression mode.

CONCLUSIONS

The following conclusions could be drawn from the experimental results of the double-networked natural rubber prepared by a "two-step crosslinking" method:

1. Based on the swelling experiments, the degree of the first step crosslinking was about 20% of that of the final double network after the second crosslinking step. The equilibrium swelling was, however, approximately the same for all double networks. The initial rate of volumetric swelling was found to increase and equilibrium was reached faster, as the residual exten-

sion ratio of the double-networked rubber was increased.

2. With increased residual extension, the tensile properties including the Young's modulus, tensile strength at break, and toughness were found to slightly decrease first, until they showed a minimum at a lower residual extension of about 1.55 and, thereafter, to increase considerably. On the other hand, the strain at break and the Young's modulus in the transverse direction were not greatly dependent on the residual extension.

3. Creep, recovery, and permanent set also showed a minimum or maximum at a lower residual extension of about 1.55 and then showed considerable improvement as the residual extension was further increased.

REFERENCES

1. A. Y. Coran, in *Science and Technology of Rubber,* J. E. Mark, B. Erman, and F. R. Eirich, Eds., Academic Press, New York, 1994, Chap. 7.

2. C. M. Roland and M. L. Warzel, *Rubb. Chem. Technol.,* **63,** 285 (1990).

3. R. D. Andrews, A. V. Tobolsky, and E. E. Hanson, *J. Appl. Phys.,* **17,** 352 (1946).

4. P. G. Santangelo and C. M. Roland, *Rubb. Chem. Technol.,* **67,** 359 (1994).

5. L. G. Baxandall and S. F. Edwards, *Macromolecules,* **21**(6), 1763 (1988).

6. R. A. M. Hikmet, J. Lub, and P. Maassen vd Brink, *Macromolecules,* **25**(16), 4194 (1992).

7. J. D. Ferry, *Polymer,* **20,** 1343 (1979).

8. D. K. Thomas, *Polymer,* **7,** 125 (1966); *Rubb. Chem. Technol.,* **40,** 621 (1967).

9. K. T. Gillen, *Macromolecules,* **21**(2), 442 (1988).

10. C. M. Roland and K. L. Peng, *Rubb. Chem. Technol.,* **64,** 790 (1991).

11. A. Stevenson and R. P. Campion, in *Engineering with Rubber: How to Design Rubber Components,* A. N. Gent, Ed., Hanser, New York, 1992, Chap. 7.

12. P. J. Flory, *J. Chem. Phys.,* **10,** 51 (1942).

13. M. L. Huggins, *J. Chem. Phys.,* **46,** 151 (1950).

14. P. J. Flory, *J. Chem. Phys.,* **18,** 108 (1950).

15. S. Kaang, PhD Dissertation, The University of Akron, May 1988.

16. A. N. Gent and R. H. Tobias, *J. Polym. Sci. Polym. Phys. Ed.,* **20,** 2317 (1982).

17. A. N. Gent and S. Y. Kaang, *J. Polym. Sci. Polym. Phys. Ed.,* **27,** 893 (1989).

18. C. M. Roland, *Rubb. Chem. Technol.,* **62,** 863 (1989).

19. J. P. Berry, J. Scanlan, and W. F. Watson, *Trans. Faraday Soc.,* **52,** 1137 (1956).

20. J. H. A. Grober and W. J. McGill, *J. Polym. Sci. Polym. Phys. Ed.,* **32,** 287 (1994).

21. A. N. Gent, *Trans. Faraday Soc.,* **50,** 521 (1954); *Rubb. Chem. Technol.,* **28,** 36 (1955).

22. A. N. Gent, *J. Polym. Sci. Part A-2,* **4,** 447 (1966).

23. H. W. Greesmith, L. Mullins, and A. G. Thomas, in *The Chemistry and Physics of Rubber-like Substances,* L. Bateman, Ed., Maclaren, London, 1963, Chap. 10.