The Effect of Water Immersion on Fatigue Crack Growth of Two Engineering Rubbers

R. SELDÉN

Swedish Institute for Fibre and Polymer Reasearch, P.O. Box 104, S-431 22 Mölndal, Sweden

Received 12 August 1997; accepted 8 December 1997

ABSTRACT: Fatigue properties of two engineering rubbers have been measured in air and water. The fatigue crack growth rate, dc/dN, where c is the crack length and N the number of cycles, was measured as a function of tear energy for chloroprene rubber (CR) and natural rubber (NR). In general, the effect of water immersion on crack growth rates was relatively small. For NR, little effect of water immersion was seen and the fatigue threshold, which is the limit below which no mechano-oxidative fatigue growth will occur, was measured as 25 J/m^2 in both environments. For CR, a factor of two to three times lower crack growth rates was obtained in water compared to air, probably due to less influence of oxygen in water. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 941–946, 1998

Key words: rubber; fatigue; crack growth; threshold; water

INTRODUCTION

Fatigue properties in engineering rubbers are often evaluated by fracture mechanics testing. Cracks are introduced into test specimens of various geometries, and the crack growth rate is measured as a function of the rate of strain energy release at the crack tip (tearing energy). Environmental influences are obtained in many rubbers at low crack rates by ozone, and below the so-called fatigue threshold the crack growth rate is proportional to the ozone concentration in the surrounding medium (usually air). At higher crack growth rates a mechano-oxidative region is reached where atmospheric oxygen strongly influences the crack rate. Removing oxygen or adding antioxidants to the rubber will decrease the crack growth rate, for example, for natural rubber (NR) by a factor of 2–3.[1,2]

The effect of water is important in some applications, for exmaple, for rubber products used in offshore engineering. Water is absorbed by a diffusion mechanism, and the amount of absorbed water is dependent on both polymer type and the hygroscopic properties of the added compounding ingredients.[3–6] In strips of NR, an equilibrium level of 4–5% of absorbed salt water is reached after 1–2 weeks. In polychloroprene rubber (CR), the rate of water absorption is higher and the equilibrium in water content is not reached even after more than 125 days. The effect of absorbed water on properties of NR is not significant, including the effect on fatigue properties. For CR tensile strength and strain to failure decreases 20 and 10%, respectively, after more than 100 days in salt water.[5] It was shown in a quasistatic tensile test for CR compounds that the rate of tearing was similar in air and water at a certain tear energy.[6]

In this article fatigue crack growth rates in two engineering rubbers, NR and CR, have been studied both in air and water, with special emphasis on the fatigue threshold.

Contract grant sponsors: The Swedish Rubber Industry, Svedala-SKEGA AB, and Trelleborg AB.

Journal of Applied Polymer Science, Vol. 69, 941–946 (1998)
 CCC 0021-8995/98/050941-06

THEORETICAL BACKGROUND

In fatigue crack growth measurements of rubber, the crack growth rate, dc/dN, where c is the crack length and N the number of cycles, is related to the tearing energy, T, defined as:[7,8]

$$T = -(\partial W/\partial A)_l \quad (1)$$

where W is the total elastic strain energy, A the crack area of one crack surface, and index "l" indicating that the specimen is held under constant deformation so that the applied forces do no work. Rivlin and Thomas[7] have shown that the tearing energy is a true material property independent of specimen geometry.

For a tensile strip provided with an edge notch (single edge notched, SEN, specimen) the tearing energy is obtained approximately as[8,9]:

$$T = 2 \cdot k \cdot W_o \cdot c \quad (2)$$

where W_o is the strain energy density (strain energy divided by volume), c the crack length, and k a constant, slowly decreasing with increasing elongation, λ, according to $k \approx \pi \cdot \lambda^{-1/2}$.[8,9]

Depending on the applied tearing energy, different relations between crack growth rate and tearing energy have been suggested. These are summarized below, from low to high tearing energy[2,8]:

$$dc/dN = \alpha q = \text{constant} \quad T < T_o \quad (3)$$

$$dc/dN = A(T - T_o) \quad T_o < T < T_t \quad (4)$$

$$dc/dN = BT^{\beta} \quad T_t < T < T_c \quad (5)$$

$$dc/dN = \infty \quad T = T_c \quad (6)$$

In eq. (3) at low tearing energies, q is the ozone concentration in the surrounding medium (air) and α a material constant. In this region the crack growth is entirely due to ozone. Removing ozone or adding antiozonants can make the growth rate decrease to zero. The quantity T_o is an important parameter; it denotes the fatigue threshold and is the limit below which no mechano-oxidative fatigue growth will occur.

In eq. (4), just above the threshold, A is constant, and if dc/dN is plotted vs. T, a straight line will result with a slope equal to A, which will cut the T-axis at the fatigue threshold, T_o.

Equation (5) describes the so-called power law region and applies at high tearing energies. B and β are constants, depending on the material. If dc/dN is plotted vs. T on double logarithmic scales in this region, a straight line will result with a slope equal to β. For filled NR, a value of 2, and for CR a value of 3.4 is given for β.[9–11] In eq. (6), unstable crack growth is initiated after only a few cycles. T_c is the critical tearing energy and can be measured, for example, in a short-time tensile test.

Table I Formulations for Investigated Rubber Compounds

Ingredients in phr	NR	CR
Natural rubber	100	—
Chloroprene rubber	—	95
BR	—	5
TMTD	—	0.6
Vulkacit	—	1.1
MgO, ZnO	5	9
Sun protection wax	—	2
Paraffin wax	—	2
6 PPD	1	1
TMQ	1	—
Polyethylene	—	4
Sulphur	2	—
TMTM	0.2	—
CBS	0.8	—
CB N550/N774	70	55
Oil	15	34

EXPERIMENTAL

Materials

Two engineering rubbers were chosen for this study—a natural rubber (NR), and a chloroprene rubber (CR). Mix formulations for the two materials are given in Table I. Fatigue crack growth specimens were cut from compression-molded quadratic plates, 150 × 250 mm, thickness 2.0 mm for NR and 2.5 mm for CR. The specimens were straight coupons, 25 mm wide and 150 mm long.

Procedure

Fatigue testing was done in strain control using MTS servohydraulic testing machines. Frequency of testing was 100 cpm. All testing in air was made at +22°C. Prior to testing, specimen thickness was measured at several locations. Distance between clamps was 100 mm. Conditioning at the

maximum strain used during the fatigue test was made first to reduce the Mullins effect. The conditioning cycle, i.e., loading/unloading cycle, was repeated two thousand times. The area under the retraction curve was then measured up to the maximum strain. Strain energy density, W_o, was calculated dividing this area by the specimen volume.

A sharp edge notch was made with a razor blade, $\approx$ 1.0 mm in depth, forming a single edge-notched specimen. A fatigue load was initiated to make the sharp notch grow slightly ($\approx$ 0.1 mm) before the actual fatigue testing was started. By this procedure a "natural" crack instead of the artificially made notch was obtained. After a suitable number of cycles, ΔN, the test was interrupted and the crack length, c_n, was measured with an accuracy of two significant figures using a traveling microscope. The increase in crack length, Δc, between two consecutive measurements was usually larger than 10% but smaller than 20% of the previously measured length.[8] During crack length measurements a slight load was applied to make the crack become open and visible. Crack growth rate $\Delta c/\Delta N$ and the corresponding tearing energy, T, was calculated. The test was interrupted when the crack had grown to approx. 20% of the specimen width.[8]

Testing in water was performed in a specially built cylindrical container, length 400 mm, 60 mm diameter, made of transparent PMMA. It contained one flat observation window that was used for observing crack lengths. An aluminium clamp was fitted to the lower end of the cylinder, which could grip the lower part of the specimen. The container could be attached to the frame of the MTS, and was filled with cold tap water. Specimens for testing were conditioned in the same manner as described above, while remaining in the water. To make the initial notch the specimen had to be released from the lower clamp and notching was made in air. The fatigue testing was made in water. Due to some thermal conduction from the frame of the MTS to the container, the temperature of the water was slightly higher than ambient. Measurements showed that the temperature reached an equilibrium level approx. 5–7°C above room temperature.

RESULTS AND DISCUSSION

Crack Growth in Air

Results where crack growth rate in air have been plotted vs. tearing energy on logarithmic scales

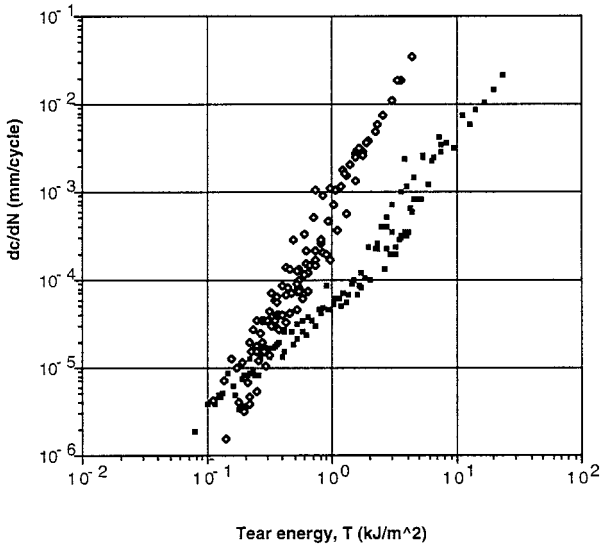

Figure 1 Fatigue crack growth rate vs. tear energy for CR (◇) and NR (■).

for both materials are shown in Figure 1. For CR, the majority of the data fall on one single straight line, corresponding to a power law relation in accordance with eq. (5). The slope of the line is approximately 2.9, similar to what has been found elsewhere[10,11] for CR in this region. For NR, the data seem to fall on two separate lines having slightly different slopes, corresponding to eqs. (4) and (5), respectively. The transition occurs approximately at 2 kJ/m^2. The slope of the line above the transition is approximately 2.0, in accordance with previous results for β for natural rubber[8,9] in the power law region.

Crack Growth in Water

The effect of water immersion on crack growth rates for CR and NR is shown in Figures 2 and 4, respectively. The data for CR in water looks very similar to the data in air. An almost straight line is obtained with a slope that is only slightly lower than in air. Most of the data, however, seem to fall below the data in air, corresponding to a decreasing crack growth rate by approximately a factor of two to three times, for a given tearing energy.

There are two possible explanations for the decreased crack growth rate in water, as shown in Figure 2. One explanation comes from the fact that the fatigue crack growth process is a mechano-oxidative process.[1,2] Oxygen in the air contributes to the fatigue crack growth by a chemical

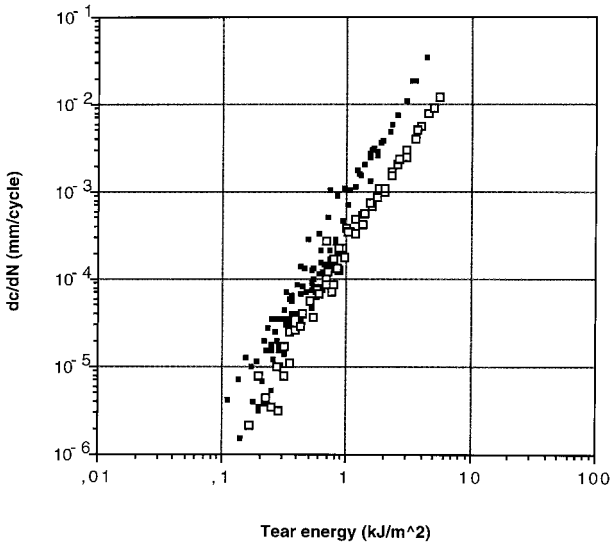

Figure 2 Fatigue crack growth rates vs. tear energy for CR in air (■) and water (□).

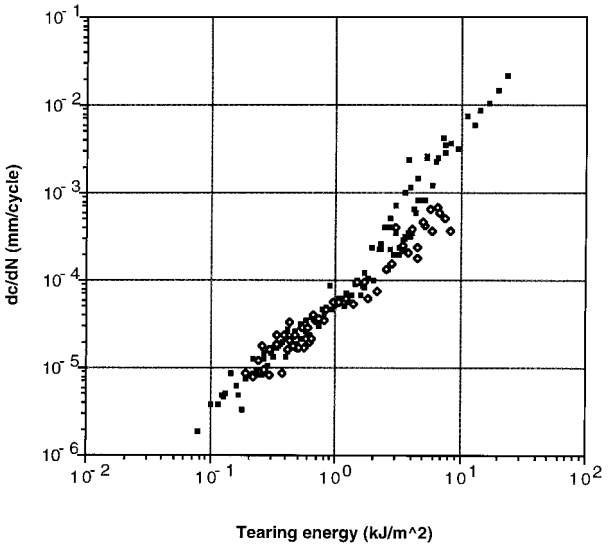

Figure 4 Fatigue crack growth rates vs. tear energy for NR in air (■) and water (◇).

reaction at the crack tip. In water, the concentration of oxygen is lower,[4] and the oxidative contribution to fatigue crack growth rate therefore becomes less. In contrast, tensile and tear strengths are normally not affected by oxygen, except at high temperatures or slow extension rates.[12–14]

It is also possible that absorbed water can have a plasticizing effect on the rubber and cause crack tip blunting.[3] Crack tip blunting will lead to a higher energy dissipation at the crack tip and lower crack growth rate.

Scanning electron micrographs were taken from fatigue fracture surfaces of the CR samples. Some results at a lower magnification are shown in Figure 3. Comparing fracture surfaces for samples tested in air and water, there is little evidence of increased ductility in the samples tested in water. Photographs taken at higher magnification supports this conclusion. Thus there is little visual evidence of any crack blunting.

For NR, the crack growth data in air and water are almost indistinguishable (see Fig. 4), espe-

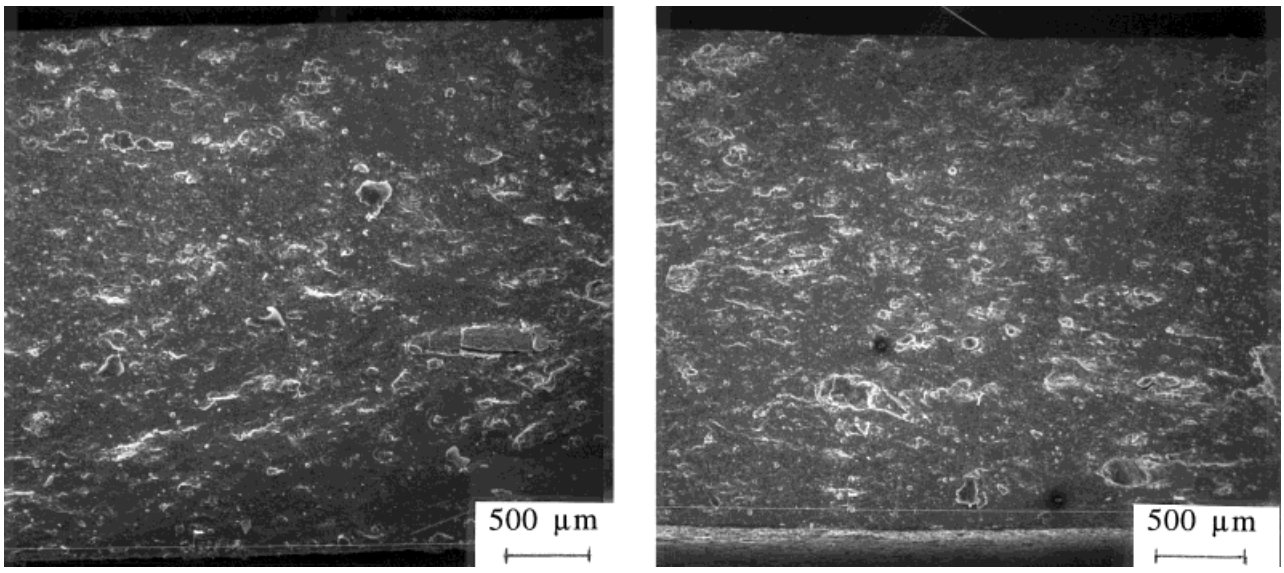

Figure 3 Fatigue fracture surfaces for CR in air (left) and water (right). Crack growth from left to right. Magnification 24.25×.

cially at low crack growth rates. This is in accordance with what has been reported elsewhere[3,4] for the effect of water on fatigue properties of NR.

The Fatigue Threshold, T_o

The fatigue threshold is an important property, for example, when calculating fatigue lifetimes for rubber parts, and therefore, attempts were made to measure this quantity. It was assumed that the crack growth rates for both materials follow eq. (4) close to the threshold. Then plotting dc/dN vs. T on linear scales in this region gives straight lines that will cut the T-axis at the threshold value, T_o.[8]

Experimental results for both materials showed that the scatter of the data was quite large. Scatter could be reduced by making nonlinear regression analysis of the curves showing crack length as a function of the number of cycles. Examples are shown for NR in Figure 5.[8] The continuous lines are the fitted five degree polynomials. Having established crack length as a continuous function of number of cycles, then both dc/dN and T can easily be calculated for any value of N and dc/dN plotted vs. T.

Results for NR from three individual measurements in air are shown in Figure 6, together with one measurement in water. Both set of data are close to each other, in accordance with the results of Figure 4. The value of the fatigue threshold, ≈ 25 J/m^2, is similar to what has been reported elsewhere for NR in air, 17–40 J/m^2.[1,8]

The results for CR still displayed a significant amount of scatter, and the application of eq. (4) could not be verified from these data. This is in accordance with the results in Figure 2, which showed that most of the data followed eq. (5).

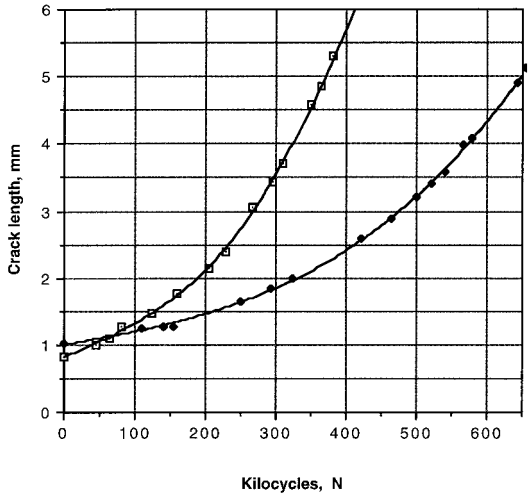

Figure 5 Crack length vs. number of kilocycles for NR. Continuous lines are the regression lines.

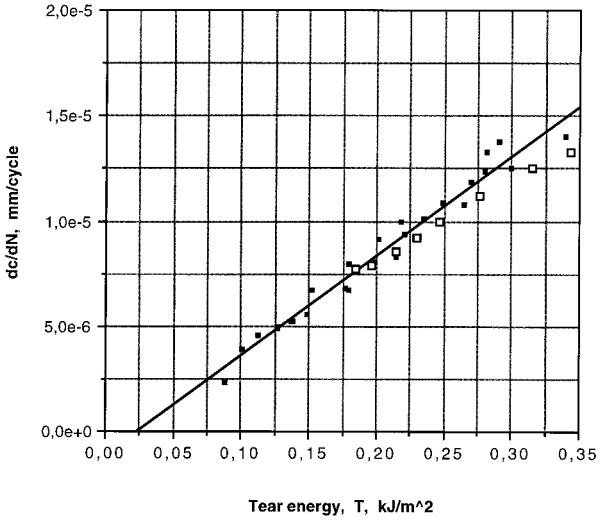

Figure 6 Fatigue crack growth rate vs. tear energy for NR at low crack growth rates, in air (■) and water (□).

CONCLUSIONS

Fatigue crack growth measurements have been performed in air and water on two engineering rubbers. For NR the crack growth rate vs. T relation could be described by a relation according to eq. (4), and a power law relation according to eq. (5). The transition occurs approximately at $T = 2$ kJ/m^2. For CR, the majority of the data could be fitted to the power law, eq (5).

In general, the effect of water immersion on fatigue crack growth rates was quite small. For NR, at low crack growth rates, almost identical growth rates were obtained and the fatigue threshold becomes close to 25 J/m^2 in both environments. For CR, the crack growth rates in water becomes two to three times lower than in air, probably due to less influence of oxygen in water.

Thanks are due to the Swedish rubber industry, Svedala-SKEGA AB and Trelleborg AB for support and providing materials for this investigation.

REFERENCES

1. G. J. Lake and P. B. Lindley, *Rubber J.,* **146,** 30 (1964).

2. G. J. Lake and A. G. Thomas, in *Engineering with Rubber—How to Design Rubber Components,* A. N. Gent, Ed., Hanser Verlag, Munich, 1992, p. 96.
3. A. Stevenson, *Int. J. Adhesion Adhesives,* **5,** 81 (1985).
4. A. Stevenson, *Rubber in Offshore Engineering,* PRI, London, 1983.
5. F. Sedillot, *Rubber in Offshore Engineering,* PRI, London, 1983.
6. A. K. Bhowmick and A. N. Gent, *Rubber Chem. Technol.,* **56,** 8 (1983).
7. R. S. Rivlin and A. G. Thomas, *J. Polym. Sci.,* **18,** 177 (1955).
8. R. Seldén, *Prog. Rubber Plast. Technol.,* **11,** 56 (1995).
9. G. J. Lake, *Prog. Rubber Technol.,* **45,** 89 (1983).
10. J. Royo, *Polym. Testing,* **11,** 325 (1992).
11. D. G. Young, *Rubber Chem. Technol.,* **63,** 567 (1990).
12. G. J. Lake, *Rubber Chem. Technol.,* **68,** 435 (1995).
13. F. Bueche, *J. Appl. Polym. Sci.,* **7,** 1165 (1963).
14. G. J. Lake, *8th International Conference on Deformation, Yield and Fracture of Polymers,* PRI, Cambridge, 1991.