THERMOXIDATIVE AGING EFFECTS ON MECHANICAL PERFORMANCES OF POLYCHLOROPRENE

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ABSTRACT

The effect of thermoxidative aging on fracture performance of polychloroprene (CR) is investigated using tensile, tearing and cutting tests. The results obtained from the Mooney-Rivlin equation show that crosslinking is dominant during aging of CR. In the early stage of aging, the tensile strength and tearing energy increase, thanks to an optimized balance between the strength enhancement from the crosslink network and the network capability in dissipating energy. Prolonged aging results in gradual decreases in strength, tearing and cutting energy and these decreases are more pronounced with higher aging temperatures. It is found that the decrease in tearing energy is due to a decrease of the strain energy density of fracture, rather than to a change in the crack tip radius. The cutting energies of unaged and aged CR are about ten times smaller than those obtained from tearing tests due to the smaller crack tip diameter imposed by the razor blade in cutting. The variation of cutting energy with thermoxidative aging confirms that fracture performance of elastomers strongly depends on the viscoelastic energy dissipation at the crack tip.

Key Words: polychloroprene, thermal aging, strength energy density, tearing, cutting.

I. INTRODUCTION

Under certain environmental conditions, polymers lose their useful properties because of chain degradations. In oxygen-containing environments, the strength of rubbers can be seriously affected by thermoxidative degradation and this effect strongly increases with temperature. Accelerated aging tests performed in a circulating air oven are commonly used to determine the resistance of a vulcanizate to oxidation. The resistance to oxidation is quantified by measuring the changes in tensile properties such as tensile strength, ultimate elongation, hardness, and stress at selected levels of elongation (Gillen *et al.*, 1996; Budrugeac, 1997; Huy and Evrard, 1998; Hamed and Zhao, 1999). Although tearing and cutting resistances of elastomers are important in many applications, there are currently no reported works on the effects of thermal aging on tearing and cutting

behaviors of elastomers. The crack growths in tearing and cutting of elastomers have been successfully described by fracture mechanics (Rivlin and Thomas, 1953; Lake and Yeoh, 1978; Bhowmick *et al.*, 1983; Gent *et al.*, 1994; Gent and Wang, 1996; Cho and Lee, 1998; Tsunoda *et al.*, 2000). In general, the fracture energy per unit surface required to propagate a crack, G, appears to be the sum of the threshold energy, G_o, expended in rupture of chemical bonds, and a dissipation energy that is approximately proportional to G_o but many times larger. This dissipation energy is therefore an important parameter for elastomer strength after aging. During thermal aging, main chain scission, crosslink formation and crosslink breakage can take place (Morand, 1977). If chain scission dominates during aging, the elastomer softens and eventually may become sticky, resulting in decreases in tensile stress at a given elongation, decreases in hardness, and either increases or decreases in ultimate elongation depending on the extent of degradation. This is the usual behavior of unfilled natural and Butyl rubbers (Gent, 1992). If crosslinking dominates during aging, the elastomer hardens and embrittles resulting in increases in the

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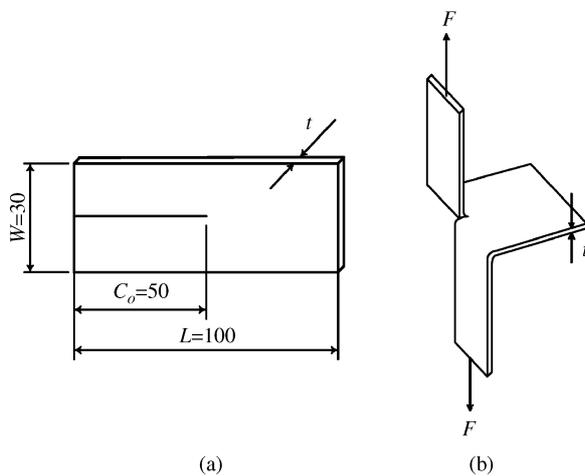
Fig. 1   Trouser test specimen: (a) undeformed state; (b) extended state

Fig. 2   Schematic representation of the cutting apparatus

Fig. 3   Pre-strained sample on the sample holder after a cut test

tensile stress at a given elongation and the hardness, but a decrease in the ultimate elongation. This is the general behavior of butadiene-based material such as polybutadiene, styrene-butadiene rubber, and acrylonitrile-butadiene rubber. After aging, the chain structure of elastomers changes (e.g. main chain scission, crosslinking, etc.), leading to variation in their ability to dissipate energy, and consequently, in the fracture energies of both tearing and cutting processes. It has also been noted that thermo-oxidative aging of elastomers typically results in the formation of a brittle surface layer (Clough and Gillen, 1992; Malek and Stevenson, 1992; Wise *et al.*, 1995; Celina *et al.*, 1998; Celina *et al.*, 2000). This hard surface skin can be considered as a fracture initiation zone, which also affects the measurements of tearing and cutting resistances of elastomer samples. The aim of this study is to investigate the effects of thermal aging on tearing and cutting behaviors of polychloroprene rubber (CR). The major limitation of CR is its relatively poor aging resistance. These materials show reasonably good resistance to oxidative aging up to about 80°C but degradation becomes significant for temperatures above 100°C (Fletcher, 1982) with a high probability of brittle fracture.

II. EXPERIMENTAL

The polychloroprene (neoprene) sheets, with a thickness of 1.6 mm, were provided by Fairprene Industrial Products Co. USA. Thermal aging experiments were performed in a convection oven, Model B45 C40 (Gruenberg Electric Company Inc.) under various combinations of aging time and aging temperature.

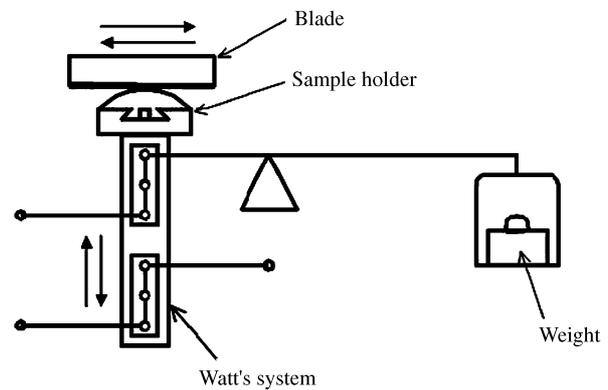The tensile test was prepared according to the ASTM Standard D 412, using the Die C test method for tensile properties of elastomers. The tests were performed on an Instron Automatic Material Testing System, Model 1137, at a loading rate of 10 mm/min. The elongation was measured using a Laser Extensometer, Model MTS LX 500.
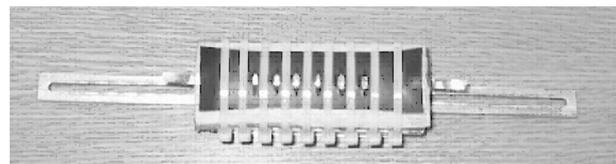
The trouser test was used to measure the tearing energy. The sample dimensions are shown in Fig. 1, in both the undeformed and the extended states. The arms were formed by an initial cut of 50 mm using a razor blade. For test pieces of these dimensions, the tearing energy during the tear propagation may generally be derived with sufficient accuracy using Eq. (1).

$$T = \frac{2F}{t} \tag{1}$$

The cutting test method consists of sliding a blade at a given constant speed on a thin sample, which is mounted on the sample holder by the double phase tape and determining the blade displacement at which the blade cuts through the material under a given applied normal load. Cutting tests were performed in the cut-test apparatus (Fig. 2), which is similar to the TDM 100 apparatus used in the International Standard ISO 13997 (Vu Thi *et al.*, in press (a)). During the test, the normal load, the horizontal force applied on the blade and the blade displacement were recorded. To exclude the friction contribution the material sample was extended to a given elongation on the Instron machine and mounted on the sample holder in the extension state. The cable ties as presented in Fig. 3 were used to prevent the retraction of the sample during cutting. Cut resistance of rubbers is nearly constant over a range of sliding speeds from 100 to 900 mm/min (Vu Thi *et al.*, in press (b)) so in
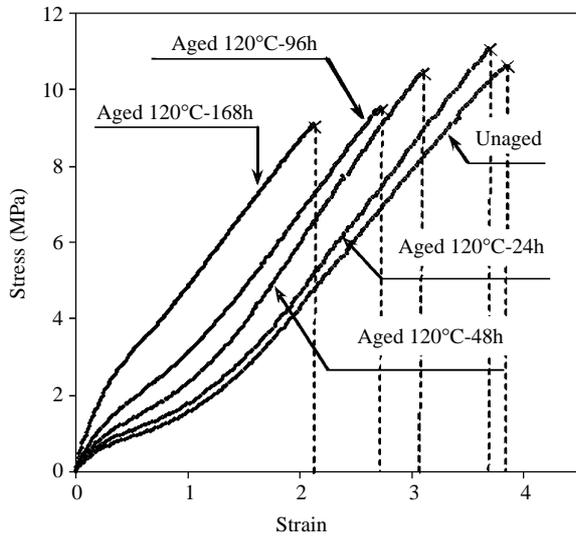
Fig. 4 Stress-strain curves of CR after various times of aging at 120°C

Fig. 5 Stress-strain curves of CR after various aging temperatures during 48 h

this study all the cutting tests were performed with sliding speed of 150 mm/min.

III. RESULTS AND DISCUSSION

1. Effects of Thermal Aging on Tensile Behaviors

Stress-strain curves for CR after aging at 120°C are given in Fig. 4. It can be seen that thermal aging of CR generally resulted in increases in modulus and decreases in both tensile strength and tensile ultimate elongation. However, influences of aging on these properties are not similar. As opposed to the steady variations of the modulus and the ultimate elongation with aging time, the tensile strength initially increases to a maximum value after about 1 day of aging at this temperature and decreases afterwards. With further aging, the elastomer stiffens and the extensibility and strength continue to decrease. After 7 days of aging, there is a substantial decrease of about 50% in ultimate strain, but only about 15% in tensile strength. This behavior is also observed for CR aged thermally at different temperatures, as shown in Fig. 5. For instance, during the same aging period of 48 hours, specimens aged at 160°C have about one-half the strength, but only one-twentieth the ultimate elongation of specimens aged at 120°C.

It is clear from the reduction in tensile strength and ultimate elongation that substantial network alteration takes place after a relatively brief aging at these temperatures. Although the exact mechanism of each process is unknown, the steady increase in stiffness indicates that crosslinking is dominant during aging of CR. The degree of crosslinking of
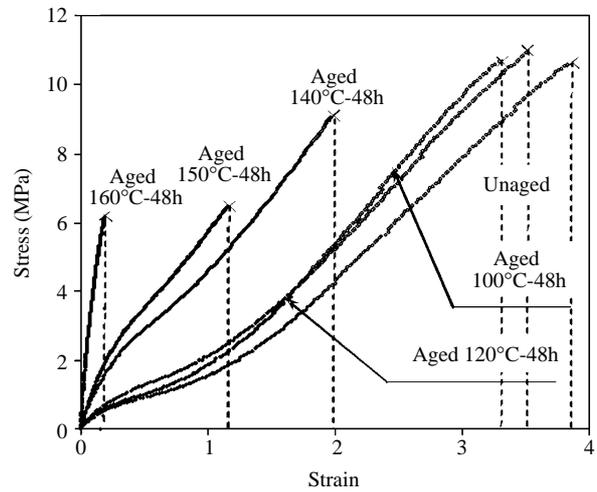
rubbers is usually related to the tensile stress-strain relationship, which may be represented by the two-constant Mooney-Rivlin equation:

$$\sigma = 2(\lambda - \frac{1}{\lambda^2})(C_1 + \frac{C_2}{\lambda}) \qquad (2)$$

where σ is the stress applied, λ is the extension ratio, and C_1 and C_2 are material's constants. According to Eq. (2), a plot of $\frac{\sigma}{2(\lambda - \frac{1}{\lambda^2})}$ as a function of $\frac{1}{\lambda}$ should yield a straight line, from which the values of C_1 and C_2 can be obtained. Eq. (2) has been used to characterize the effects of various environments on the tensile behavior of elastomers such as swelling (Allen *et al.*, 1971), the presence of diluents during crosslinking (Gee, 1966), etc. Fig. 6 shows an example of the plots of $\frac{\sigma}{2(\lambda - \frac{1}{\lambda^2})}$ versus $\frac{1}{\lambda}$ for CR samples aged at 120°C for various aging times. From these plots, C_1 can be obtained by extrapolating linearly the curve to $\lambda^{-1}=0$, and C_2 can be derived from the slope of these linear plots. The values of C_1 and C_2 for CR aged at various combinations of aging time and temperature are given in Table 1. It can be seen that as the aging time and aging temperature increase, both C_1 and C_2 increase.

In molecular terms, the constant C_1 depends primarily on the crosslink density and is independent of the network swelling (Allen *et al.*, 1971). According to the kinetic and the statistical theory of rubber elasticity (Treloar, 1975), the degree of crosslinking N can be determined as:
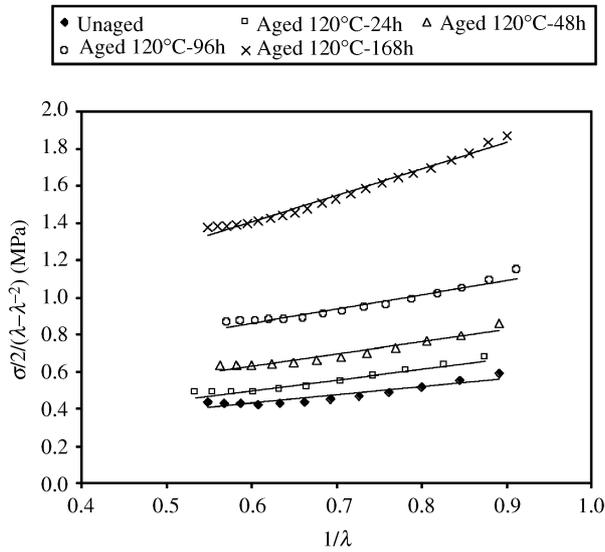
$$N = \frac{2C_1}{kT} \qquad (3)$$

Fig. 6 Plots of $\dfrac{\sigma}{2(\lambda - \dfrac{1}{\lambda^2})}$ versus $\dfrac{1}{\lambda}$ for CR after different times of aging at 120°C

From the variation of the crosslink density N shown in Table 1, it can be seen that thermal aging of CR results in an increase in the crosslink density and this effect is more pronounced with increasing aging time and aging temperature. For instance, at 100°C, there is an increase in crosslink density of about 80% after an aging period of 7 days. Up to about 1 day of aging at 160°C, CR exhibits a four-fold increase in the degree of crosslinking compared to the unaged state. Thus, the constant C_1 is related to crosslink formation, which is more important at higher temperatures.

2. Effects of Aging on Tearing Behaviors

The dependence of tearing performance upon aging can be seen in Fig. 7, showing an example of the tearing force versus displacement curves of CR samples aged at 120°C for different aging times. As the aging time increases, the tearing force initially goes up to a maximum value and decreases afterwards. For samples aged at 120°C, the tearing force reached a maximum value after about 24 hours (Fig. 7). This behavior is similar to the variation of tensile strength with aging time as shown in Fig. 4. Furthermore, the peaks of tensile strength and tearing force seem to occur after a similar aging time, suggesting that they are due to a similar degree of crosslinking. Using Eq. (3), the tearing energy was calculated from the force-displacement tearing curves and is presented in Fig. 8 as a function of logarithm of aging time, at various temperatures between 100°C and 160°C. In general, the fracture energy G of an elastomer consists of two terms (Gent and Kinloch, 1971):

$$G = G_0 + G_0 f(Ra_T) \tag{4}$$

where G_0 is a threshold fracture energy expended in the rupture of chemical bonds, and the second term involves other dissipation energies that are often approximately proportional to the threshold energy but many times larger. These dissipation energies reflect the variation of tear strength of elastomers with crack speed and temperature. At high aging temperatures, crosslinking becomes important and restricts the chain motions. This "tight" network is incapable of dissipating energy, and the elastomer fails in a relatively easy, brittle manner, with low tearing energy.

A more fundamental approach based on the strain energy density function has also been proposed to predict fracture performance by Sih and co-workers (Sih and MacDonald, 1974; Kipp and Sih, 1975; Sih and Madenci, 1983). In this theory, the strain energy density function, dW/dV, in front of the crack tip has been expressed in the form:

$$\frac{dW}{dV} = \frac{S}{r} \tag{5}$$

where S is the strain energy density factor and r is the distance from the crack tip. The location of fracture initiation is assumed to coincide with the maximum or minimum of (dW/dV) or $(dW/dV)_{min}^{max}$. Failure by crack initiation and growth is assumed to occur when $(dW/V)_{min}^{max}$ reaches a critical value $(dW/dV)_c$ being characteristics of the material. Stable crack growth increments r_1, r_2, etc., are assumed to be governed by:

$$\left(\frac{dW}{dV}\right)_c = \frac{S_1}{r_1} = \frac{S_2}{r_2} = \cdots \frac{S_j}{r_j} = \cdots = \frac{S_c}{r_c} \tag{6}$$

Unstable fracture is assumed to take place when:

$$\left(\frac{dW}{dV}\right)_c = \frac{S_c}{r_c} \tag{7}$$

where r_c is the critical ligament ahead of a crack. Eventual crack arrest occurs if:

$$r_1 > r_2 > \cdots > r_j > \cdots > r_a \text{ and } S_1 > S_2 > \cdots > S_j > \cdots > S_a \tag{8}$$

Leading to unstable rapid crack propagation if all of the inequalities in Eq. (8) are reversed and r_a and S_a become r_c and S_c, respectively. Note that $S_c = (1+v)(1-2v)K_{IC}^2/2\pi E$ while $(dW/dV)_c$ is the area under the true stress and strain curve. Once S_c and $(dW/dV)_c$ are known, r_c is determined from Eq. (7). A combination of crack arrest and instability can occur where the crack could grow with increasing and then decreasing segments or vice versa.

It is well known that the tearing energy G is related to the viscoelastic work done at the crack tip.

Table 1 Mooney-Rivlin coefficients, crosslinking degree, and Young modulus of CR after different thermal aging conditions

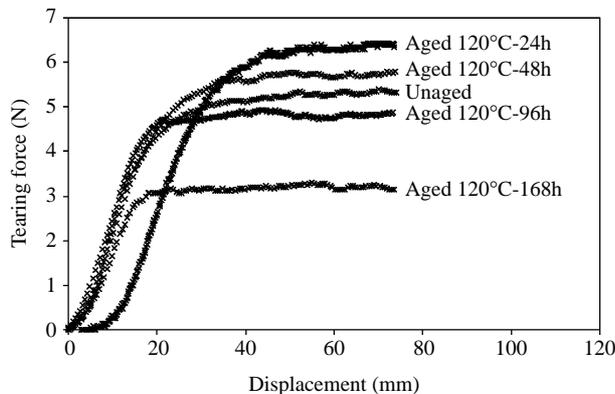| Aging temperature (°C)	Aging time (h)	C_1 (kPa)	C_2 (kPa)	Crosslink density $N \times 10^{-26}$ (m^{-3})	$6(C_1+C_2)$ (MPa)	E (MPa)
UNAGED	0	169	443	0.82	3.67	3.41
100	12	192	407	0.93	3.59	3.51
	24	195	408	0.95	3.62	3.60
	48	199	413	0.97	3.67	3.69
	96	214	454	1.04	4.01	3.68
	168	299	541	1.45	5.04	4.84
120	24	204	504	0.99	4.25	4.05
	48	243	619	1.18	5.17	4.74
	96	343	834	1.67	7.06	6.96
	168	588	1329	2.86	11.50	10.93
130	16	212	459	1.03	4.03	4.25
	24	220	483	1.07	4.22	4.00
	48	293	607	1.42	5.40	5.14
	72	463	778	2.25	7.45	6.75
	112	680	1412	3.31	12.55	9.35
	144	1125	2177	5.47	19.81	17.31
	168	1186	3189	5.77	26.25	24.58
140	24	345	786	1.68	6.78	6.53
	48	523	1221	2.54	10.46	10.43
	96	1129	2920	5.49	24.29	27.20
150	7	222	456	1.08	4.07	3.84
	17	379	543	1.84	5.54	4.96
	24	429	631	2.08	6.36	5.92
	40	615	1214	2.99	10.97	8.34
	48	740	1435	3.60	13.05	11.81
	72	–	–	–	–	31.26
160	16.5	425	835	2.07	7.56	7.28
	20	486	1104	2.36	9.54	8.83
	28	931	1482	4.52	14.48	12.36
	39.5	–	–	–	–	20.03
	44	–	–	–	–	32.45
	48	–	–	–	–	43.91

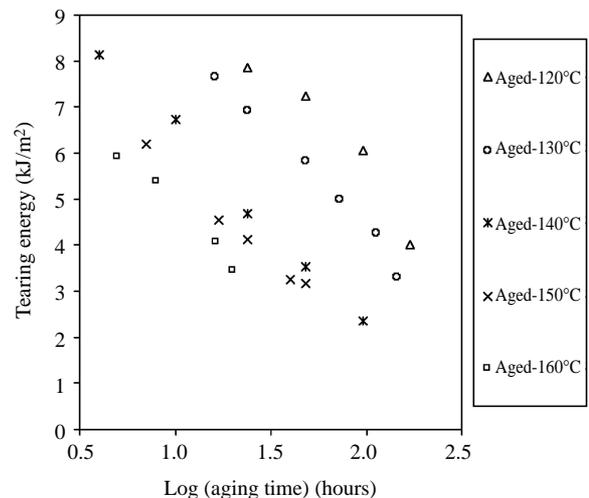Fig. 7 Tearing force versus displacement of CR after various times of aging at 120°C

Fig. 8 Variation of tearing energy of CR with logarithm of aging time at various aging temperatures

This energy is a function of the crack tip diameter and can be expressed by:

$$G = W_t d \tag{9}$$

where W_t is the strain energy density at break of a small amount of the material in front of the crack tip, and d is the crack tip diameter. The validity of Eq. (9) has been verified by direct photoelastic measurements (Thomas, 1955) of the strain energy distribution around a crack tip. A good agreement has been found between the tearing energy and that calculated from the stress-strain curve. Using the tearing energy G determined from the trouser tests, and the strain energy density at break, W_t, measured from the area under the tensile stress-strain curve up to rupture, the effective diameter of the tear tip can be determined from Eq. (9) and is given in Table 2. It can be seen that the diameter of the tear tip of CR remains relatively constant during thermal aging with a value of about 0.5mm. This is in agreement with the range between 0.1mm to 1mm in diameter, determined from observations of the roughness of the fracture surface of a propagating tear in rubbery solids. The results suggest that the decrease in tearing energy is due to a decrease of the strain energy density of fracture, rather than to a change in the crack tip radius.

3. Effects of Aging on Cutting Behaviors

In practical applications, cut resistance is also one of the most important properties of elastomers. It has been found that the cutting energy is generally much lower than that involved in tearing, due to the fact that the tip radius of the cutting bade is much smaller than the effective radius of the tear tip, resulting in a much smaller plastic yielding. The cutting energy is thus assumed to be directly related to the radius of the cutting blade. This approach allows measuring the intrinsic property of materials in terms of cut resistance. However, it reflects a very specific condition in which the sample is stretched in a specific range of deformations. It has been shown cutting usually involves a sliding movement of a sharp object under a normal load so that this condition is reproduced in both the International ISO 13997 and the ASTM F1790 standards (ASTM F1790-97; ISO 13997, 1998) test methods to characterize the cut resistance of protective materials. In these test methods, the measured cut resistance of a material is strongly controlled by its coefficient of friction. It has recently been found (Vu Thi *et al.*, in press (a)) that the total energy required to propagate a cut in these standard tests comprises two components: a lost energy dissipated by the gripping force exerted by the material on the blade sides; and an essential cutting energy dissipated in the cut, at the tip of the blade. These energies also have opposite effects on the cutting resistance as measured by these standards. These standard characterization methods can have, therefore, serious consequences in characterizing cut resistance of protective materials. The first consequence is the effect of lubricating substances in contact with the protective material in service. Since the cut resistance determined by these standards mostly reflects the friction coefficient between the blade and the material, the substance in contact with the material in service strongly alters the coefficient of friction and the cut resistance determined by these standards is no longer relevant. Furthermore, most protective materials undergo a certain level of deformation in realistic practical-conditions of use. This deformation strongly affects the friction of the material with the cutting edge and, consequently, alters the material's cut resistance. It has been found that when the sample is stretched in tension, the cut resistance measured by the above standard methods shows a reduction from five to ten times the value measured in an unstretched state. When the sample is in a tensile pre-stretched state, both the cutting horizontal force and energy are related to the cutting process, taking place at the blade tip. The friction coefficient does, therefore, not affect these parameters. The cut

Table 2 Values of crack tip diameter evaluated for various combinations of aging time and aging temperature

T (°C)	$t(h)$	G (kJ/m^2)	W_t (MJ/m^3)	d (mm)
Unaged	0	6.52	16.93	0.4
100	24	7.42	15.73	0.5
	48	7.57	15.59	0.5
	96	8.19	16.1	0.5
	168	7.13	16.06	0.4
120	24	7.86	18.63	0.4
	48	7.24	16.14	0.4
	96	6.07	12.39	0.5
	168	4	10.51	0.4
130	24	6.92	16.79	0.4
	48	5.84	14.93	0.4
	72	4.98	11.69	0.4
	144	3.32	5.27	0.6
140	24	4.69	14.12	0.3
	48	3.52	9.27	0.4
	96	2.34	3.12	0.8
150	24	4.13	8.82	0.5
	48	3.17	4.71	0.7
160	16	4.06	9.14	0.4
	20	3.44	6.77	0.5

(a)

(b)

(c)

(d)
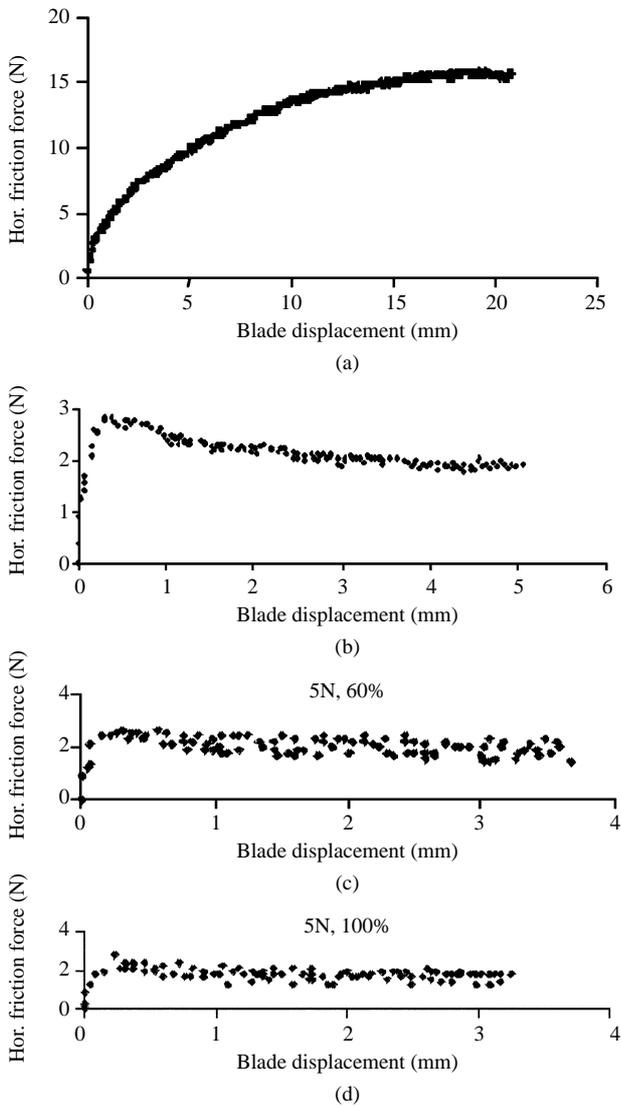
Fig. 9 Horizontal force versus blade displacement under pre-strained of 0% (9a), 35% (9b), 60% (9c) and 100% (9d)

Fig. 10 Cutting energy versus pre-strain with applied normal load of 5N

energy measured under this condition is also independent of the nature and geometry of the blade. The results demonstrate that the cut energy of the sample determined under a stretched state is in agreement with the cutting energy measured in the absence of friction, under a pure Mode I cutting experiment.

Figs. 9a, 9b, 9c and 9d present the typical relationship between the horizontal force and the blade displacement in cutting unaged CR samples with an applied normal load of 5 *N* under the pre-strain of 0%, 35%, 60% and 100% respectively. In the unstretched state (Fig. 9a), the horizontal force increases continuously with the blade displacement during cutting. The maximum value at the end of blade displacement corresponds to the moment when the material sample is cut through. However, when cutting the pre-stretched samples (Fig. 9b, 9c and 9d)
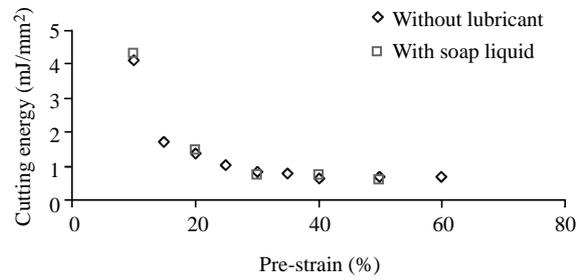
the horizontal force increases abruptly to a maximum value; and after overcoming static friction it falls down and becomes nearly constant. When the pre-strain level is sufficiently large, the plateau region is reached immediately without going through a maximum value. The presence of pre-strain gives the instant release of lateral pressure on the blade sides. This retraction immediately removes the friction between the material and the two blade sides. It has been shown that the horizontal force consists of two components. One is the friction force due to the lateral gripping exerted by the material on the blade sides and the other is the essential cutting force at the edge of the blade. The observed constant horizontal force in pre-strained samples suggests that the lateral friction is eliminated and the recorded horizontal force is due only to the friction at the blade tip. This force is thus directly related to the cutting process. In this case, by assuming that the elastically stored energy due to the pre-strain is used completely for the retraction of the sample, the cutting energy can be evaluated by:

$$G_c = (E_{load} + E_{hor})/A_{cut} \tag{10}$$

where E_{load} is the energy expended by the normal load after cutting: $E_{load} = N_n * t$, in which N_n is the normal force applied on the blade, and t is the thickness of the sample. E_{hor} is the energy expended in the horizontal force, calculated from the area under the plot of the horizontal force versus blade displacement. A_{cut} is the cutting area of the sample. Fig. 10 illustrates cutting energies calculated by Eq. (10) of unaged CR samples versus various pre-strains, under both dry and lubricated conditions. It can be seen that for pre-strains higher than 40%, the cutting energy of CR reaches a stable value of about 0.7 kJ/m². This value was almost unchanged even in cutting with soap liquid; this confirms again that in this case, the horizontal force, taking place at the blade tip, entirely contributes to cutting.

It is noteworthy that fracture energies of elastomers determined by cutting tests are much

Table 3 Fracture energy in cutting unaged and aged CR samples under pre-strain of 50%

Aging conditions	Unaged	Aged at 130°C during 48 h	Aged at 140°C during 48 h
Fracture energy (kJ/m^2)	0.7	0.51	0.39

smaller in comparison with the tearing energy measured by tear tests. This difference can be attributed to the difference in the effective diameter of the tear tip and the cut tip. In the cutting process, the crack tip diameter is determined by the razor blade tip radius, that is about 0,1 μm. However, the observed diameter of the tip of a propagating tear in rubbers is usually in the range of 0.1 mm to 1 mm. The strain energy density in the crack tip region for cutting process is the intrinsic strength of elastomers, which is known to be about 5 GJ/m^3 for C-C bond rupture (Lake and Yeoh, 1978) whereas one for the tearing process is approximately equal to the work to break measured in a normal tensile test. Putting these values in Eq. (9) gives the cutting energy about ten times smaller than those obtained from tearing tests in Table 2.

In order to investigate the effect of thermal aging on cutting performance, the ASTM F1790 cutting tests were also performed on the CR samples aged at 130°C and 140°C for 48 h. For these cutting tests, the specimens were pre-stretched to a pre-strain level of 50% to avoid the lateral friction of the blade with the sample. Table 3 shows the cutting energy of CR samples after aging. It can be seen that after aging at 130°C and 140oC for 48 h there is a reduction of about 27% and 44% respectively in the cutting energy. Since the tip of the razor blade controls the crack tip diameter, only the C-C bond rupture cannot explain the cutting behaviour, it includes other energy dissipation processes. Whereas the value of cutting energy is about ten times smaller than that of tearing energy, the ratio of reduction in cutting energy due to aging is similar to that of tearing energy, suggesting that cutting of elastomers also depends on viscoelastic dissipation energy.

IV. CONCLUSION

Crosslink formation dominates during aging of CR, leading to an increase in hardness, and a decrease in ultimate elongation. In terms of strength and fracture performance, thermal aging of CR seems to consist of two primary stages. In the early stage of aging, the tensile strength and the tearing energy increase

with aging to a maximum value corresponding to the moment at which the elastomer reaches an optimized balance between the strength enhancement from additional crosslink formation and the capability of the crosslinked network to dissipate deformation energy. Further aging results in a restriction of the chain motions and reduces both the strength and tearing energy of CR. During aging, the diameter of the tear tip of CR remained almost constant with a value of about 0.5 mm. The results suggest that the decrease in tearing energy is due to a decrease in the strain energy density of fracture rather than a change in the crack tip radius. Using pre-strained specimens, the cut test method described in both the International ISO 13997 and the ASTM F1790 standards allows measuring the intrinsic property of materials in terms of cut resistance. The fracture energies of elastomers determined by cutting tests are much smaller in comparison with those measured by tear tests. This discrepancy can be attributed to the difference in the effective diameter of the tear tip and the cut tip. Cutting performance of elastomers does not depend only on the rupture of C-C bonds but also on viscoelastic dissipation energy.

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