Effects of thermal aging on fracture performance of polychloroprene

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Measurements of tensile and tearing resistance have been conducted as a function of aging time and aging temperature for a polychloroprene (CR). The steady increase in stiffness indicates that crosslinking is dominant during the aging of CR. In the early stage of aging, 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 after a characteristic time results in a gradual decrease in strength and tearing energy and this change is more pronounced with higher aging temperatures. The superposition principle between aging time and aging temperature was used to determine the activation energy controlling the change of tearing energy in thermal aging. This value agrees with the activation energy $E_a = 91$ kJ/mol reported in current literature by monitoring the oxygen consumption rates during the aging of CR, suggesting that the change in tearing energy is controlled by chemical reactions much the same as the change in oxygen consumption dissolved in the material. It was also found that the variation in the strain energy density to break is also controlled by the same activation energy.
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1. Introduction

It is well known that for most rubbers in oxygen-containing environments, the strength can be greatly affected by oxidation and the effect becomes worse with higher temperatures [1]. The trend to higher service temperatures in many industrial applications in automobiles, electrical insulation, etc., has demanded the use of more thermally, oxidatively stable elastomers. In order to determine the resistance of a vulcanizate to oxidation, accelerated aging at higher temperatures are commonly used to predict the long-term behavior. Most investigations on aging of elastomers have been focused on the change in chemical nature of the elastomer during extended exposure to heat, oxygen, ozone, and various other environments. During thermal aging, main-chain scission, crosslink formation and crosslink breakage can occur, leading to severe changes in mechanical properties. Hamed *et al.* [2] found that networks of diene elastomers, such as SBR and NR, are readily altered by reaction with oxygen, which causes chain scission and crosslinking. Depending on whether chain scission or crosslinking is more extensive, an elastomer will soften or stiffen after oxidation. The effect of thermal aging on the dynamic mechanical properties of three different crosslink structures has also been recently reported [3]. According to this work, heat aging leads to an increase in the glass transition temperature, T_g, and in the loss factor, $\tan\delta$, through the whole range of temperatures, mainly due to changes in the total crosslink density and crosslink types. In the study by Deuri *et al.* [4], the critical cut length of natural rubber (NR) above which there is a drastic fall in tensile properties has been observed to increase with aging time. Other works have dealt mainly with the changes in ultimate tensile properties, i.e., strength and elongation at break, due to aging [2, 5–7].

There are however currently no works dealing with the effects of thermal aging on the tearing behaviors of elastomers. The fracture mechanics approach based on the tearing energy G proposed by Rivlin and Thomas [8] has proven to be successful in characterizing fracture behaviors of rubber. The applicability of the energetic approach developed by Rivlin and Thomas has been verified by a number of researchers [9–11]. The approach has been applied successfully in a range of phenomena involving the growth of cracks or the separation of bonds, such as tear behavior [12–14], crack growth and fatigue [15–17], cutting by a sharp object [18–20], and abrasion [21]. Because of the possibility of heterogeneous oxidation during aging at high temperatures, oxidative hardening is more significant at the sample surface than in the interior regions regions, thus leading to the formation of a brittle surface layer [22–25]. This hard surface skin can be considered as a fracture initiation zone, which may markedly affect the tearing behaviors of elastomers. Moreover, since

elastomers fail by slow crack growth in many applications, the change in fracture behavior with time is of great practical significance. This study aims to foster the understanding of the variations in tearing behaviors of polychloroprene rubber (CR) caused by thermoxidative aging. CR is widely used in wire and cables sheathing applications due to its good resistance to weathering, ozone, abrasion, flame and oil [26]. The major limitation with using CR is its poor aging resistance. CR rubbers show reasonably good oxidative aging resistance at up to 80°C, but degradation becomes more pronounced when they are aged above 100°C [27], leading to a higher probability of brittle fracture.

2. Experimental

The polychloroprene (neoprene) sheets, Style NS-5550 with a thickness of 1.6 mm, were provided by Fairprene Industrial Products Co. USA. This material is the calibration material recommended in Standard ISO 13997 and the ASTM F1790 to control the cutting-edge sharpness of the blade. 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 torn states. When a tearing force F is applied to the arms to produce tearing along the central axis, if the length of the cut is sufficiently large compared with the half-width of the specimen, there will be a region of each arm which is substantially in simple extension, with an extension ratio λ determined by the force F. The tearing energy in this case has been proved to be as [8, 10]:

$$G = \frac{2F\lambda}{t} - W_o W \qquad (1)$$

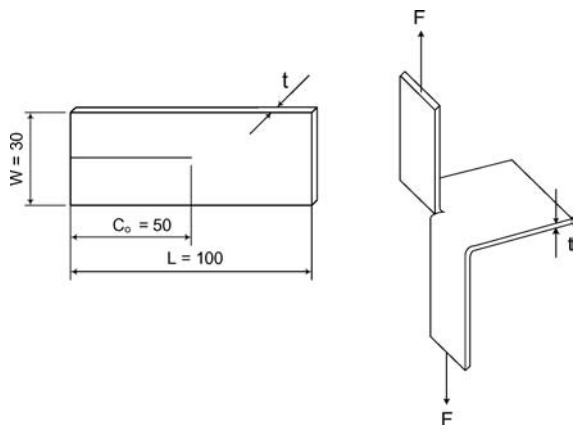where λ is the extension ratio, t and W are respectively the thickness and the width of the specimen, and W_o is the strain energy density of deformation of the rubber in simple extension to the extension ratio λ. It has been shown that if the width W of the test-piece is sufficiently large ($\lambda \approx 1$ and $2F \gg W_o Wt$), Equation 1 reduces to:

$$G = \frac{2F}{t} \qquad (2)$$

In this work, trouser samples with $W = 30$ mm and $L = 100$ mm were used. 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 tear propagation may generally be derived with sufficient accuracy using Equation 2.

3. Results and discussions
3.1. Effects of aging on tear behavior

The dependence of the tearing performance on thermal aging can be seen in Fig. 2 for CR samples aged at various temperatures from 100 to 160°C.

For temperatures below 150°C, the tearing energy first increases to a maximum value at a given aging time before decreasing with aging time. For 150 and 160°C, the time to obtain the maximum was too short so that the peak was not detected by the experiments. The drop in tearing energy is more pronounced at higher aging temperatures. It has been suggested that in general, the fracture energy is the sum of the threshold energy expended in the rupture of the chemical bonds and a dissipation term which is many times larger [28]. At high aging temperatures, the crosslinking degree increases, causing restriction in chain motions, and the "tight" network is incapable of dissipating much energy. As a result, the elastomer fails in a relatively brittle manner, with low elongation and tearing energy.

In general, the degradation reactions underlying oxidation of polymers involve complex combinations of chemical reactions that yield an effective reaction rate
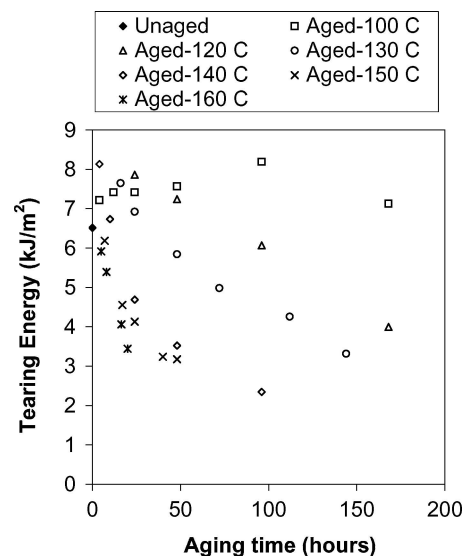

Figure 1 Trouser test specimen: (a) undeformed state; (b) torn state (Dimensions given in mm).

Figure 2 Variation of tearing energy of CR with aging time at various aging temperatures.
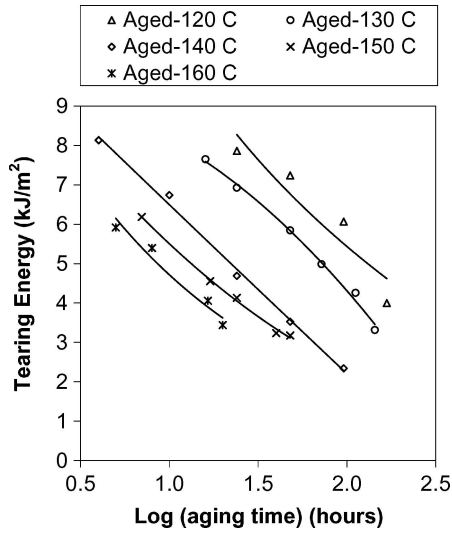
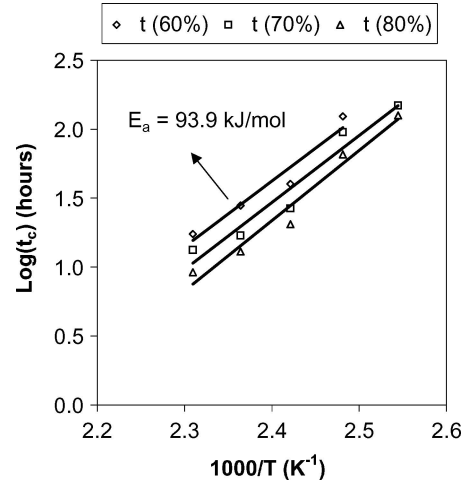Figure 3 Variation of tearing energy of CR with logarithm of aging time at various aging temperatures.

Figure 4 Arrhenius plots of the logarithm of the aging time to reach 60, 70 and 80% of the initial value of tearing energy of unaged CR samples.

constant with an effective activation energy. The parallel decrease of the tearing energy of CR with the logarithm of aging time at various aging temperatures, shown in Fig. 3, suggests that the effective activation energy may remain unchanged throughout the experimental temperature range. According to the Arrhenius' equation [29], the temperature dependence of the rate of a chemical reaction is proportional to $\exp(-E_a/RT)$, where E_a is the activation energy, R is the ideal gas constant, and T is the absolute temperature. If the effective activation energy is constant within the temperature range, raising the temperature increases the rate by the Arrhenius factor. Consequently, the time to reach a certain amount of damage, t_c, can be given by [30]:

$$t_c = \text{const.} \, e^{\frac{E_a}{RT}} \qquad (3)$$

or in the logarithmic form:

$$\log\,(t_c) = \frac{E_a}{RT}\,\log(e) + \text{const.} \qquad (4)$$

The time, t_c, has then become known as the "life" of the material corresponding to the given criterion. Choosing 60, 70 and 80 % of the original value of tearing energy of unaged CR samples as failure criteria, the corresponding "life" time to reach these limits are presented in the Table I

Using the same procedure suggested in [6], Fig. 4 shows plots of the logarithm of the aging times to reach

several limits of tearing energy versus $1000/T$. These plots appear relatively linear and parallel, suggesting that the change in tearing energy during aging be controlled by an Arrhenius behavior, which has a constant activation energy in the range of experimental tests. From the average slope of these straight lines, a global activation energy of 93.9 kJ/mol can be obtained using Equation 4. Recently, Wise *et al.* [23] have found that the degradation of the CR is dominated by oxidation rather than by dehydrochlorination and can be described by an activation energies of 91 ± 8 kJ/mol, which were obtained by measuring the dependence of O_2 consumption rate, CO_2 formation rate and CO formation rate, on the degree of thermal degradation. Thus, the result suggests that the change in tearing energy is controlled by chemical reactions in the same way as the change in oxygen consumption or carbonyl formation in the material and can be predicted with aging time and aging temperature.

For a specified value of tearing energy, Equation 4 indicates that the raw data in Fig. 3 can be shifted to a selected reference temperature T_{ref} by multiplying the times appropriate to experiments at temperature T by a shift factor a_T:

$$a_T = \ln\left(\frac{t_{T_{\text{ref}}}}{t_T}\right) = \exp\left[\frac{E_a}{R}\left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)\right] \qquad (5)$$

Normally, T_{ref} is chosen as the lowest one in the range of experimental temperatures. In this study, however, T_{ref} of 120°C was chosen due to the insufficient data at the aging temperature of 100°C. The shift factors a_T were chosen empirically to obtain the best superposition of the data for each temperature. The plot of $\log(a_T)$ versus $1000/T$ using a reference temperature of 120°C is relatively linear as shown in Fig. 5, confirming therefore the Arrhenius behavior, and the best superposition of the tearing energy for neoprene is shown in Fig. 6 using $E_a = 93.4$ kJ/mol calculated from the slope of the Arrhenius plot in Fig. 5. It should be noted that this value is almost the same as the activation energy of 93.9 kJ/mol determined using Equation 4, shown in Fig. 4 above, suggesting that both approaches are valid.
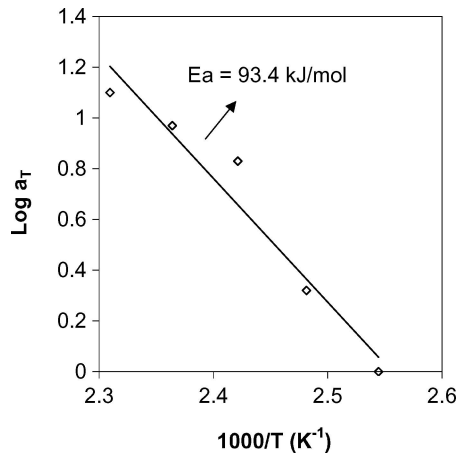
TABLE I Aging times necessary for the aged CR samples to reach the 60%, 70% and 80% of the original value of tearing energy of unaged CR

Aging temperature (°C)	$1000/T\ (K^{-1})$	$t_{60\%}$(h)	$t_{70\%}$(h)	$t_{80\%}$(h)
120	2.54		148	126
130	2.48	124	95	66
140	2.42	40	27	20
150	2.36	28	17	13
160	2.31	17	13	9

Figure 5 Arrhenius plot of horizontal shift factors a_T used to superpose aging tearing energy data at a reference temperature of 120°C.
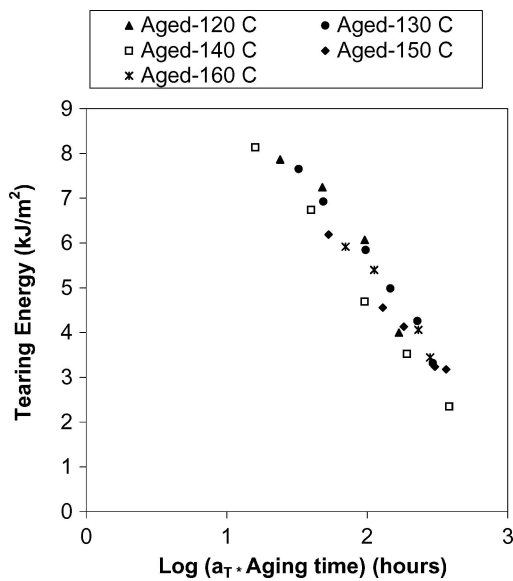

Figure 6 Empirical aging time/aging temperature superposition of the tearing energy data from Fig. 3 at a reference temperature of 120°C.

3.2. Effects of aging on tensile behavior

Fig. 7 presents the stress-strain curves for CR after aging at 120°C for various times. The thermal aging of CR results in an increase in the modulus indicat-
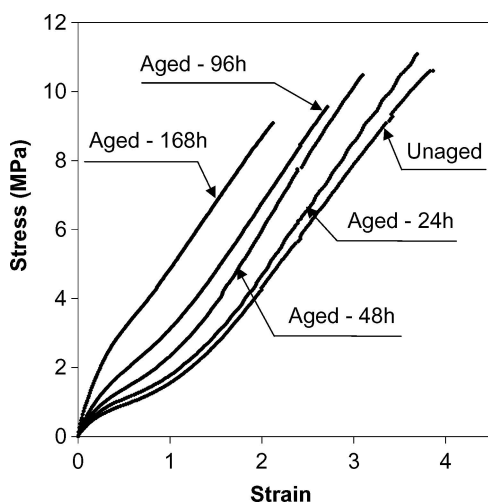

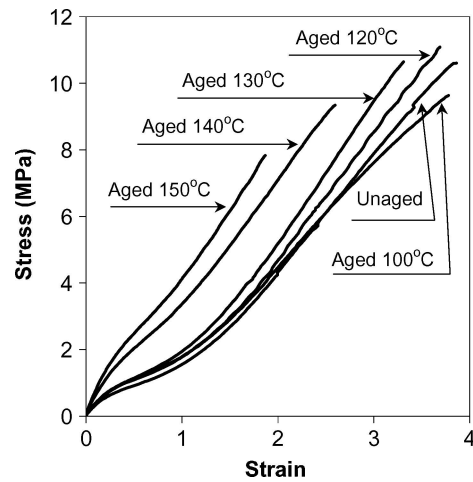*Figure 7* Stress-strain curves of CR after various times of aging at 120°C.

Figure 8 Stress-strain curves of CR after aging for 24 h at various temperatures.

ing that crosslinking dominates during aging. However, whereas the modulus and the failure strain change steadily with increasing aging time, the tensile strength initially increases to a maximum value after about 1 day of aging, and then decreases. This observation was also found for CR thermally aged at different temperatures, as shown in Fig. 8.

It is worthy of note that the existence of a peak in variation of tensile strength is similar to that observed in tearing behaviors of CR samples during thermo-oxidative aging (Fig. 2). The result appears to suggest that the fracture properties of CR alter through two different stages. In the early stage of aging, the tensile strength and tearing energy increase rapidly to a maximum value, resulting probably from an optimized balance between the strength enhancement from additional crosslinked network and the network capability of dissipating strain energy. Moreover, the peaks of tensile strength and tearing force seem to occur after a similar aging time as that of the tearing energy, (i.e., with similar degree of crosslinking). The time when an elastomer reaches its maximum mechanical value might therefore be defined as a characteristic time t_a, that decreases with increasing aging temperature. For instance, at 100 and 140°C, the characteristic times t_a are 96 and 4 h respectively. Although the values t_a obtained are not very accurate, due to the limited experimental data, a plot of $\log(t_a)$ versus the reverse of absolute temperature (Fig. 9) seems to be relatively linear, giving an activation energy of about 95.2 kJ/mol from its slope. Since this energy is almost the same as that found for the aging time-aging temperature superposition of tearing energy calculated above, the increase in fracture energy of CR would be controlled by the same chemical reactions of oxidation, which can also be monitored by the change in oxygen consumption dissolved in the material.

In terms of local deformation at the crack tip, fracture has been successfully described by the strain energy density. The strain energy released rate G is related to the visco-elastic work at the crack tip, as the crack propagates [8, 11, 31–34], by:
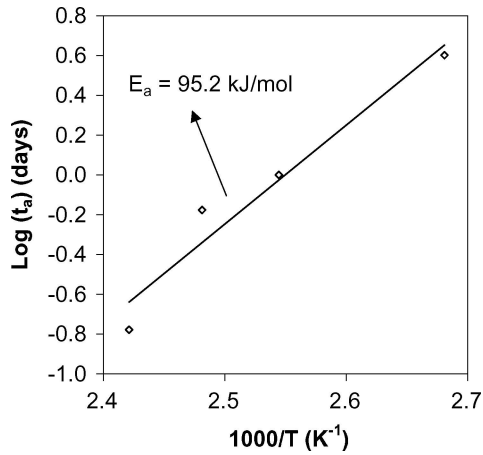
$$G = W_t d \qquad (6)$$

Figure 9 Arrhenius plot of the logarithm of the time t_a against reciprocal temperature.

where W_t is the strain energy density at break of a small amount of material in the crack tip region, and d is the crack tip diameter. W_t can be estimated from the work to break per unit volume in tensile test. Using tearing energy G obtained from the trouser tests, and the strain energy density at break W_t (measured from the area under tensile stress-strain curves up to rupture), the effective diameter of the tip of the tear were calculated according to Equation 6 and given in Table II. The results show that the diameter of the tear tip of CR remains almost constant during thermal aging with a value about 0.5 mm. This agrees well with the range between 0.1 to 1 mm in diameter of a propagating tear in rubbery solids, determined from observations of the roughness of fracture surfaces [10, 35]. During aging, the decrease in the magnitude of G is therefore governed by the reduction in the strain energy density. Consequently, it can be expected that G and W_t vary in a similar manner with aging temperature and aging time.

Fig. 10 shows the variation of the strain energy density at fracture of CR as a function of the logarithm of
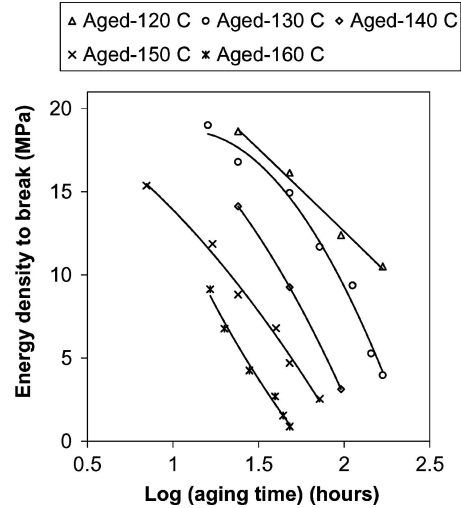

Figure 10 Variation of energy density to break (obtained from tensile tests) of CR with logarithm of aging time at various aging temperatures.

aging time at various aging temperatures. It can be seen that the variations of the strain energy density with aging time and aging temperature are similar to the tearing energy (see Fig. 3). Using the method of superposition
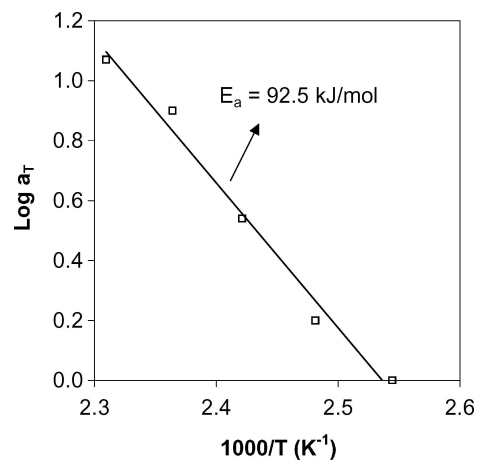

Figure 11 Arrhenius plot of horizontal shift factors a_T used to superpose tensile fracture energy data at a reference temperature of 120°C.

TABLE II Values of crack tip diameter evaluated for various combinations of aging time and aging temperature

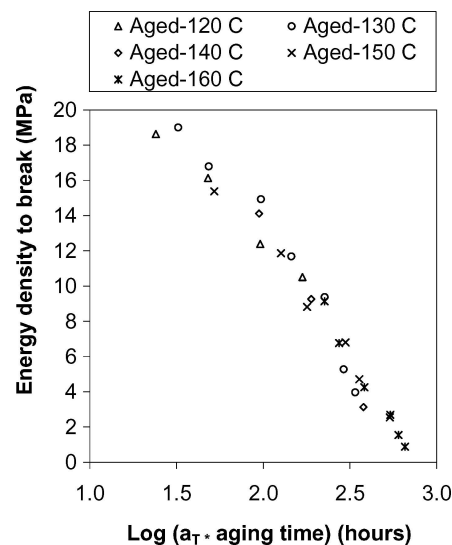| T (°C)	t (h)	G (kJ/m^2)	W_t (MJ/m^3)	d (mm)
Unaged	0	6.52	16.93	0.4
100	24	7.42	15.73	0.5
	48	7.57	15.59	0.5
	96	8.19	16.1	0.5
	168	7.13	16.06	0.4
120	24	7.86	18.63	0.4
	48	7.24	16.14	0.4
	96	6.07	12.39	0.5
	168	4	10.51	0.4
130	24	6.92	16.79	0.4
	48	5.84	14.93	0.4
	72	4.98	11.69	0.4
	144	3.32	5.27	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

Figure 12 Empirical aging time/aging temperature superposition of the tensile fracture energy data from Fig. 10 at a reference temperature of 120°C using E_a = 92.5 kJ/mol.

between aging time-aging temperature as above, the master curve of the strain energy density of fracture can be determined for CR (Fig. 12) utilizing an activation energy $E_a = 92.5$ kJ/mol, evaluated from the slope of the plot shown in Fig. 11. This value of activation energy is also nearly the same as that obtained from tearing tests indicating an implicit relationship between tearing and strain energy density theory.

4. Conclusion

Tensile and tearing tests have been carried out in this work to study the effects of thermal aging of CR samples above 100°C. The results show that crosslink formation is dominant during aging of CR, leading to an increase in the hardness, and a decrease in the ultimate elongation. In terms of fracture performance, thermal aging of CR seems to consist of two primary stages that might be separated by a characteristic aging time t_a. In the early stage of aging below t_a, the tensile strength and the tearing energy increase with thermal aging. 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 after the characteristic time results in a restriction of the chain motions and reduces both the strength and tearing energy of CR. The aging time-aging temperature dependence of tearing energy is controlled by an energy activation process and can be predicted in the same manner as the oxygen consumption or carbonyl formation rate. By using the activation energy of 90–95 kJ/mol determined from the experimental data, a master curve of tearing energy as a function of aging time and aging temperature can be obtained. This activation energy is the same as measured by the strain energy density at fracture in tensile tests. The results also suggest that the decrease in tearing energy is due to a decrease in the strain energy density, rather than by a change in the crack tip radius. During aging, the diameter of the tear tip of CR maintained almost constant with a value of about 0.5 mm.

Acknowledgment

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