Effects of Thermal Aging on Fatigue of Carbon Black–Reinforced EPDM Rubber

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ABSTRACT: Deterioration of the parameters measuring the fatigue of rubber compounds as a result of thermal aging was investigated. The energy to break, tear strength, fatigue life, and fatigue crack propagation rate of EPDM rubber compounds reinforced with three different types of carbon black before and after different periods of thermal aging were measured and compared through a series of static and cyclic loading tests. The experimental results indicated that the fatigue resistance of EPDM rubber compounds with different types of carbon black was consistently reduced because of changes in the molecular structure and crosslink density as a result of thermal aging. Meanwhile, the intrinsic flaws of carbon black–reinforced EPDM rubber compounds after 6 months of thermal aging were smaller, regardless of the type of carbon black. Therefore, the effects of thermal aging on the fatigue of rubber compounds are significant and should be taken into account in designing rubber components. J Appl Polym Sci 103: 1244–1251, 2007

Key words: fatigue analysis; rubber; aging

INTRODUCTION

With the unique properties of large elastic deformation and excellent energy absorption, rubber is increasingly being used as load-bearing and earthquake-resistant components of many engineering structures such as buildings and bridges. The fatigue behavior of rubber in service becomes important and crucial when it is primarily subjected to cyclic mechanical or thermal loading. For example, neoprene rubber bearings with good aging resistance are typically employed as isolators in buildings and bridges but unfortunately fail after some cycles of mechanical or thermal loading as a result of propagation of a critical intrinsic flaw within them. To ensure the structural integrity of buildings and bridges that frequently suffer from the seismic loading of earthquakes and the cyclic loading of overloaded vehicles, the fatigue life and fatigue crack growth rate of rubber need to be exploited in detail.

Based on an energy approach, the energy release rate, G, of a rubber containing a crack under a uniaxial stretch of λ was found to be related to its strain energy density, W, and crack length, c:[1,2] $G = 2\pi\lambda^{-1/2}Wc$. Hence, the fatigue life and fatigue crack growth rate of rubber can be determined by conducting a series of cyclic loading tests under various energy release rates. The effects of energy release rate on the fatigue crack growth rate of rubber were reported by Lake and Lindley.[3–5] Under cyclic tensile loading with a zero stress ratio, the fatigue crack growth rate of rubber with respect to various energy release rates was divided into four regimes,[6] as schematically illustrated in Figure 1. The fatigue crack growth rate, dc/dn, in regime 1 was much slower and remained almost constant when G was below a threshold, G_0; however, the dc/dn in regime 4 became infinite when G was higher than a critical value, G_c, at which fast fracture of rubber occurred. There was also a transition value, G_t, between the threshold value, G_0, and the critical value, G_c.

In regime 2, the fatigue crack growth rate of rubber increased linearly with an increasing energy release rate:

$$\frac{dc}{dn} = A(G - G_0) \quad \text{for } G_0 \le G \le G_t \tag{1}$$

where A is a fatigue parameter and should be determined experimentally. The fatigue crack growth rate of rubber compounds in regime 3 increased dramatically with increasing energy release rate. A power-law relationship with the two fatigue parameters a and b is utilized to describe the fatigue crack growth rate of rubber:

$$\frac{dc}{dn} = aG^b \quad \text{for } G_t \le G \le G_c \tag{2}$$

It is clear that the fatigue crack growth rate of rubber was much lower in regime 2 than in regime 3. Presumably, the preexisting critical crack in rubber advanced at a slower rate when subjected to an energy release rate below G_t, leading to a larger fatigue life. But the

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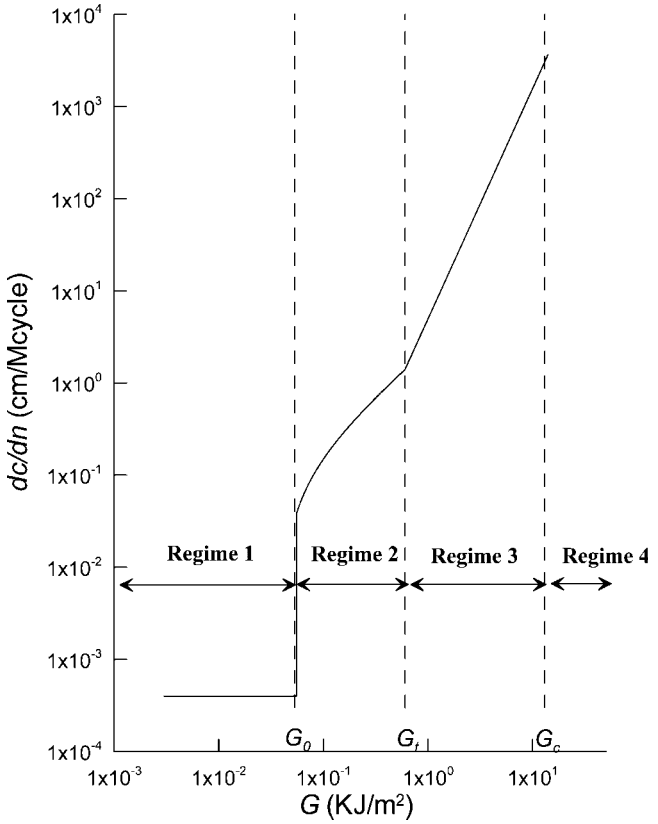

Figure 1 Four regimes of crack growth rates of rubber with respect to various energy release rates.

energy release rate could be suddenly increased and was thus higher than the G_t because of the crack propagation even of rubber under the same cyclic loading. As a result, the fatigue crack growth rate increased a lot, and catastrophic failure of the rubber might have occurred. Hence, the fatigue crack growth rate in regime 3 played an important role in predicting the fatigue life of rubber in service.

The size of intrinsic flaws in rubber is another essential material parameter that should be taken into account in estimating fatigue life. The intrinsic flaws resulting from the manufacturing process distribute randomly in rubber. For single-cut rubber under cyclic tensile loading with an energy release rate in regime 3, the fatigue crack growth rate can be expressed as:

$$\frac{dc}{dn} = a(2\pi\lambda^{-1/2}Wc)^b \tag{3}$$

By assuming that the intrinsic flaw size, c_0, is much smaller, the theoretical expression for describing the fatigue life of rubber can be simplified to:[6,7]

$$N = \frac{1}{a(b-1)\lambda^{-b/2}(2\pi W)^b c_0^{b-1}} \tag{4}$$

From the above equation, it is known that the fatigue life of rubber increases with decreasing intrinsic flaw size. The intrinsic flaw size in rubber compounds depends on carbon black type,[8] crosslink density,[9] and dispersion of compound ingredients.[10] Hence, rubber has increased resistance to fatigue if the intrinsic flaw size can be significantly reduced using appropriate methods of manufacturing.

In practice, rubber is normally subjected to various environmental attacks such as thermal aging, radiation exposure, and chemical erosion. Deterioration of the material properties of rubber is expected because of changes in molecular structure resulting from these environmental attacks. In Taiwan, the rubber in buildings and bridges fails mainly because of thermal aging in a high-temperature climate. Therefore, the effects of thermal aging on rubber fatigue are important and should be taken into account in designing rubber components. Rubber deteriorates faster at higher temperatures, which can be used to simulate the long-term deterioration of rubber at ambient temperature. Hence, in the present study a series of cyclic loading tests were conducted to investigate the effects of thermal aging on the fatigue of rubber after exposure to high temperatures for different durations.

Through a series of tests, Dizon et al.[8] investigated the effects of carbon black on the fatigue life of rubber compounds, comparing two types of carbon black used in rubber compounds with different particle sizes and material parameters. It was concluded that the fineness and structure of carbon black are two important factors in determining fatigue life, which decreased significantly with finer carbon black but increased with carbon black with a larger structure. Meanwhile, structure had a much more significant effect when finer carbon black was used, which could be regarded as reinforcing filler because of its uniform dispersion in rubber compounds. Fukahori[11] also proposed a double-layer model composed of carbon black particles surrounded by a new interface to explain the mechanism of carbon black reinforcement of rubber compounds under external loading. In the present study, three commonly used types of carbon black with different particle size distributions were first added separately during the manufacturing of ethylene–propylene–diene (EPDM) rubber compounds in order to reinforce their physical properties. Next, a series of static and cyclic loading tests were performed on the three EPDM rubber compounds, which had been subjected to different periods of thermal aging. Then the effects of thermal aging on the energy to break, tear strength, fatigue life, and fatigue crack growth rate of the EPDM rubber compounds were evaluated.

EXPERIMENTAL

Materials

The effects of reinforcement with various types of carbon black and of different durations of thermal aging

TABLE I
Material Properties of Carbon Blacks

	Particle size (nm)	Nitrogen absorption (m^2/g)	DBP absorption ($cm^3/100$ g)	CDBP absorption ($cm^3/100g$)
N220	20–25	115	114	100
N330	26–30	83	102	86
N990	201–500	8	43	42

on the energy to break, tear strength, fatigue life, and fatigue crack growth rate of ethylene–propylene–diene (EPDM) rubber compounds with better resistance to aging were evaluated. Three commercially available types of carbon black that differed in particle size—N220, N330, and N990—were introduced separately as reinforcement of the EPDM rubber compounds. Carbon black particle size of N220, N330, and N990 was in the range of 20–25, 26–30, and 201–500 nm, respectively; the material properties of the three carbon blacks are listed in Table I. The resulting rubber compounds with carbon blacks N220, N330, and N990 were designated EP220, EP330, and EP990, respectively.

Thermal aging tests

ASTM Standard D573[12] was followed to conduct a series of thermal aging tests on rubber compounds EP220, EP330, and EP990 at a temperature of 70°C in an air oven. According to ASTM Standard D573, the oxidation rate of rubber in an oven could be doubled with each 10°C increase in the inside temperature of the oven. Hence, how long the three rubber compounds would really last in service could be easily estimated from the results of the thermal aging tests. For instance, how much the material properties of rubber would deteriorate after 8 years of thermal aging at a temperature of 30°C could be estimated from the experimental results for the rubber compounds that had been subjected to the higher temperature of a 70°C oven for 6 months. A series of static and cyclic loading tests was conducted to examine the effects of different periods of thermal aging on the energy to break, tear strength, fatigue life, and fatigue crack growth rate of the three rubber compounds.

Static loading tests

Simple tension tests of the rubber compounds were performed according to ASTM Standard D412[13]; dumb-bell Die C specimens were prepared, and the speed of extension was set to 500 mm/min. At the same time, tests were performed according to ASTM Standard D624[14] with the same extension speed as that used in the simple tension tests, and Die C tear specimens were produced and tested to measure the tear strength of the rubber compounds. From the simple tension and tear resistance tests, the energy to break, W_B, and tear strength, G_c, of the three rubber compounds, EP220, EP330, and EP990, were determined before and after 2, 4, and 6 months of thermal aging, respectively.

Cyclic loading tests

The fatigue parameters of rubber compounds EP220, EP330, and EP990 before and after 6 months of thermal aging were determined by a series of cyclic extension tests. Dumb-bell Die C specimens with a thickness of 2.1 mm, as specified by ASTM D 412,[13] were produced for cyclic extension tests. A sinusoidal extension with a zero stress ratio and a frequency of 1 Hz was imposed on the rubber specimens in an Instron 8511 dynamic tester. Because the strain energy density in each cycle of sinusoidal extension imposed on the rubber specimens should be the same, displacement control of the dynamic tester was adopted for the cyclic extension tests. The stress–strain curves for EP220, EP330, and EP990 under sinusoidal extension were recorded and then used to compute the maximum strain energy densities that had been imposed on the rubber specimens. Furthermore, fatigue life, obtained from fatigue failure tests of the three rubber compounds subjected to higher energy release rates in regime 3, was used to determine intrinsic flaw size in the rubber specimens. Ten specimens were tested at each strain energy density, and their fatigue life values were averaged to determine the corresponding fatigue parameters in regime 3.

Other cyclic extension tests were performed to determine the fatigue crack growth rates and corresponding fatigue parameters of the three rubber compounds in regime 2 when subjected to lower strain energy densities. A razor blade was used to cut a through-thickness edge crack on each rubber specimen that had a width of 10 mm and a thickness of 2.1 mm, as shown in Figure 2. Because the strain energy densities in regime 2 were much lower than those in regime 3, the frequency of the sinusoidal extension imposed to measure the fatigue crack growth rate of the rubber compounds in regime 2 was raised from 1 to 3 Hz in order to reduce the time required to fail each rubber specimen. It has been confirmed that fatigue crack growth caused by cyclic loading is independent of frequency when the imposed frequency is above 1 Hz.[5,15] Therefore, a comparison could be done of the fatigue parameters and intrinsic flaw sizes of the three rubber compounds in regimes 2 and 3 before and after 6 months of thermal aging, which could be obtained from the experimental results of the cyclic extension tests.

RESULTS AND DISCUSSION

Energy to break and tear strength

The energy to break, W_B, and tear strength, G_c, of rubber compounds EP220, EP330, and EP990 before and

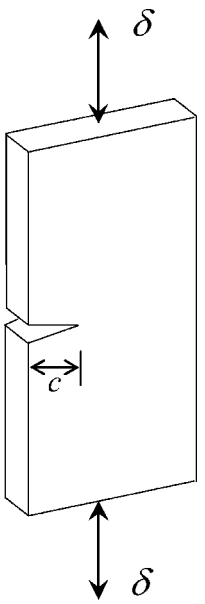

Figure 2 Rubber specimens with a through-thickness edge crack of length, *c*, subjected to a sinusoidal extension displacement, δ.

after 2, 4, and 6 months of thermal aging are shown in Figures 3 and 4, respectively, from which it can be seen that the W_B and G_c of the three rubber compounds deteriorated significantly as a result of thermal aging, a finding that cannot be neglected. In particular, the energy to break of rubber compound EP990 after 6 months of thermal aging dropped substantially, decreasing to only 10% of that before thermal aging, whereas its tear strength was reduced by as much as 25%. After 6 months of thermal aging, the energy to break and tear strength of rubber compounds EP220 and EP330 decreased at least 75% and 18%, respectively. The initial elastic moduli, *E*, of rubber compounds EP220, EP330, and EP990 before and after 6 months thermal aging were determined by simple tension tests and are listed in Table II. It was found that the moduli of the three rubber compounds were at least 41% higher after 6 months of thermal aging than they were before. These findings can be attributed to the increased crosslink density of the EPDM rubber compounds from thermal aging.

The change in crosslink density plays an important role in explaining the deterioration of the material properties of rubber compounds that results from thermal aging. The effect of thermal aging on the crosslink density of rubber vulcanizates was studied by Choi,[16] who found that crosslink density evidently increased with temperature in thermal-aging tests. Two mechanisms for the increased crosslink density of rubber compounds were proposed.[17] First, the curatives, especially sulfur, remaining in the vulcanizates reacted with rubber chains to produce additional crosslinks in the rubber compounds. Second, the pendent groups binding to rubber chains were combined in crosslinks when the rubber compounds were subjected to thermal aging, leading to increased crosslink density of the rubber vulcanizates. As a result, the rubber compounds became harder and more brittle because of the increased crosslink density after some periods of thermal aging. Hence, the modulus and hardness of the rubber compounds increased, but their energy to break and tear strength inevitably decreased.

Fatigue life

The fatigue failure of rubber compounds EP220, EP330, and EP990 was mainly caused by propagation of their intrinsic flaws after some cycles of loading. The size of the intrinsic flaws in rubber compounds represents the initial length of critical cracks, which gradually grew considerably larger. Thus, intrinsic flaw size is normally used to determine the fatigue life of rubber

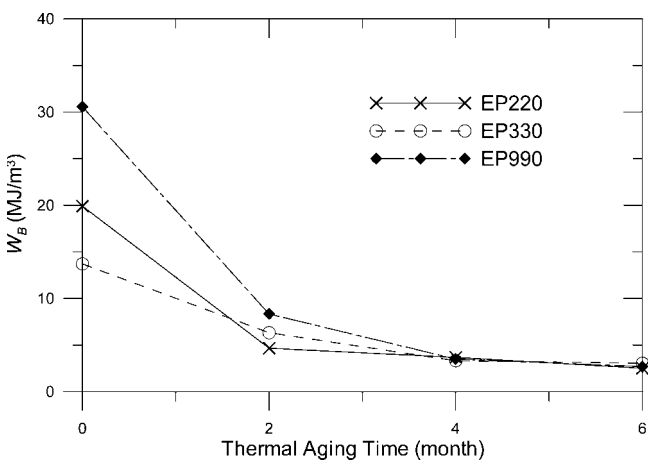

Figure 3 Variation in energy to break, W_B, of rubber compounds EP220, EP330, and EP990 before and after 2, 4, and 6 months of thermal aging.

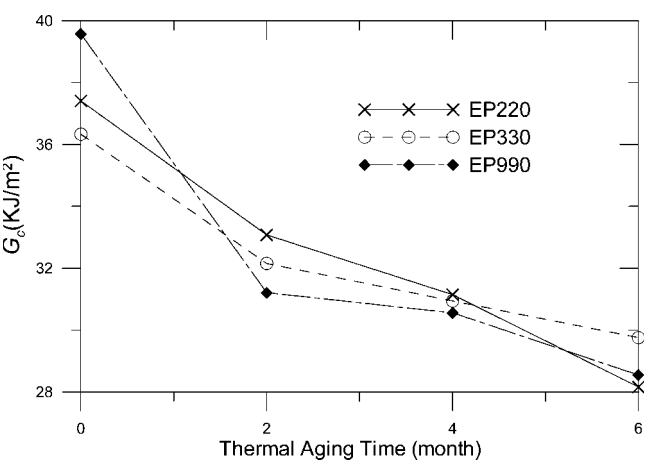

Figure 4 Variation in tear strength, G_c, of rubber compounds EP220, EP330, and EP990 before and after 2, 4, and 6 months of thermal aging.

TABLE II
Fatigue Parameters of Rubber Compounds EP220, EP330, and EP990 Calculated from Static and Fatigue Failure Tests

		W_B (MJ/m^3)	G_c (kJ/m^2)	E (MPa)	a	b	c_0 (μm)
EP220	No aging	19.9	37.4	19.7	543	2.72	17.25
	After aging 6 months	2.5	28.2	27.8	1.12×10^{13}	4.85	11.65
EP330	No aging	13.7	36.3	25.7	12535	3.66	105.71
	After aging 6 months	3.0	29.8	38.6	4.29×10^{10}	4.77	38.74
EP990	No aging	30.5	39.6	18.9	15	2.55	59.52
	After aging 6 months	2.7	28.6	29.5	45,826	2.62	11.06

compounds subjected to a prescribed energy release rate in service. To evaluate the effects of carbon black and thermal aging on intrinsic flaw size, the fatigue lives of carbon black–reinforced rubber compounds before and after 6 months of thermal aging were obtained from cyclic extension tests.

Eq. (4) can be further rearranged as:

$$\log N = -b \log(2\pi\lambda^{-1/2}W) + \log\left[\frac{1}{a(b-1)c_0^{b-1}}\right] \quad (5)$$

Eq. (5) indicates that the slope of the straight line closely passing through experimental data is $-b$ when the fatigue life of rubber compounds is plotted against the parameter $2\pi\lambda^{-1/2}W$ in a double logarithmic figure. Hence, the fatigue parameter, b, of rubber compounds can be obtained from the slope of this straight line. The experimentally determined fatigue parameters of rubber compounds EP220, EP330 and EP990 are listed in Table II. To determine the fatigue crack growth parameter, a, a small cut of less than 1 mm was introduced in each specimen[7] before cyclic extension testing. Then a could be calculated by substituting the previously determined fatigue parameter, b, and the length of the small cut that had been introduced in eq. (4); the fatigue parameters of rubber compounds EP220, EP330, and EP990 are listed in Table II. Once fatigue parameters a and b are known and the fatigue life of each rubber specimen is measured, its intrinsic flaw size, c_0, can easily be calculated from eq. (4). The intrinsic flaw sizes of rubber compounds EP220, EP330, and EP990 are also listed in Table II.

For comparison, the fatigue lives of rubber compounds EP220, EP330, and EP990 before and after 6 months of thermal aging are shown in Figure 5(a–c), respectively, from which it can be seen that the fatigue life of rubber compounds after 6 months of thermal aging was dramatically reduced, to less than a tenth of that before thermal aging. Meanwhile, fatigue parameter b apparently increased for rubber compounds after 6 months of thermal aging. For rubber compounds with a larger value of b, their fatigue life decreased more rapidly with the imposed strain energy density. In other words, the effect of thermal aging on the fatigue life of a rubber compound becomes more significant when subjected to a larger strain energy density. At the same time, the other fatigue parameter, a, increased substantially for the three rubber compounds after 6 months of thermal aging, leading to a severe reduction in fatigue life. Therefore, it can be concluded that the fatigue resistance of rubber compounds with different carbon blacks was consistently reduced because of the changes in molecular structure and crosslink density caused by thermal aging.

From Table II, it can be seen that the intrinsic flaw sizes of rubber compounds EP220, EP330, and EP990 decreased after 6 months of thermal aging. This occurred because of the increased crosslink density of the rubber compounds. It was suggested that the pendent groups binding to rubber chains and further vulcanization caused by thermal aging made the structure of rubber compounds denser to reduce the intrinsic flaw size within them.[2] Hence, intrinsic flaw size decreased with increasing crosslink density in rubber compounds after 6 months of thermal aging.

Fatigue crack growth rate

The fatigue crack growth rate of the three rubber compounds was measured to determine the corresponding fatigue parameters in regimes 2 and 3. The fatigue crack growth rate, dc/dn, plotted against the maximum energy release rate, G, of rubber compounds EP220, EP330, and EP990 before and after 6 months of thermal aging is shown in Figures 6–8, respectively. The fatigue parameters of the three rubber compounds in regimes 2 and 3 can be determined from eqs. (1) and (2) and are listed in Table III. From Figures 6–8, it can be seen that the curves employed to describe the relationship between crack growth rate and energy release rate in regime 3 for rubber compounds EP220, EP330, and EP990 after 6 months of thermal aging shifted consistently toward the upper left. In other words, the fatigue crack growth rates of the rubber compounds after 6 months of thermal aging increased much more than those before thermal aging. At the same time, the slopes of the curves after 6 months of thermal aging were steeper than those before thermal aging. As a result, in regime 3 fatigue parameters a and b of the three rubber compounds increased simultaneously after 6 months of thermal aging. It was expected that the

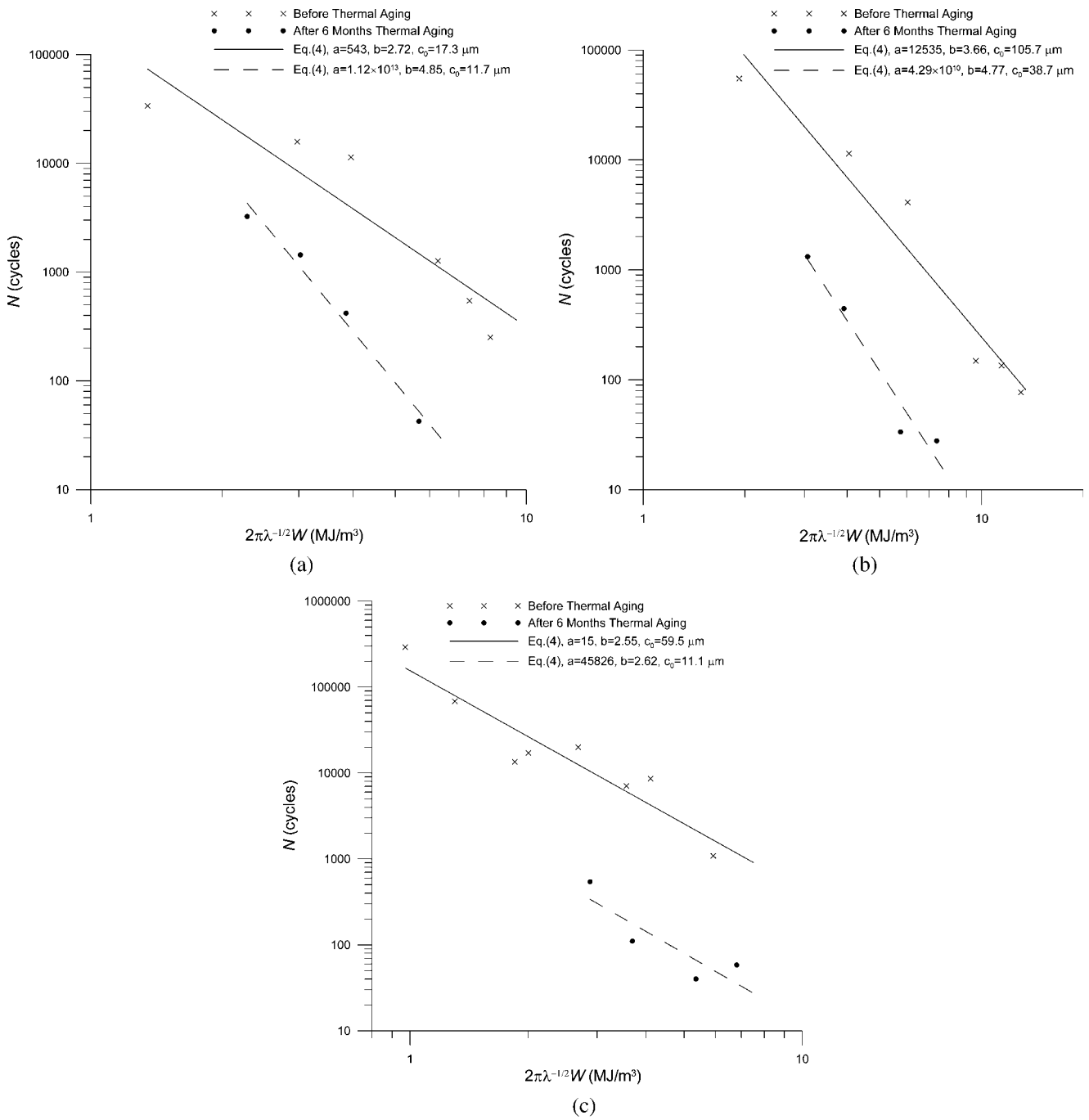

Figure 5 Effects of 6 months of thermal aging on the fatigue lives of rubber compounds (a) EP220, (b) EP330, and (c) EP990.

fatigue life of rubber compounds EP220, EP330, and EP990 after 6 months of thermal aging would be significantly reduced. On the other hand, in regime 2 fatigue parameter A of the three rubber compounds increased after 6 months of thermal aging when subjected to a lower rate of energy release. Consequently, the fatigue crack growth rate increased, reducing fatigue life.

From Figures 6–8 and Table III it can also be noted that the three rubber compounds had a larger threshold value, G_0, after 6 months of thermal aging than before thermal aging. Rubber compound EP990 had a G_0 up to 3 times larger, whereas that of rubber compounds EP220 and EP330 was around 25%. Hence, the fatigue crack growth rate of rubber compounds after 6 months of thermal aging could be slightly reduced when subjected to an energy release rate within the range of the threshold value, G_0, before and after thermal aging. However, the transition value, G_t, of rubber compounds after 6 months of thermal aging was slightly lower than that before thermal aging. Nevertheless, the effect of thermal aging on G_t was relatively insignificant. Because the G_0 increased significantly but the G_t

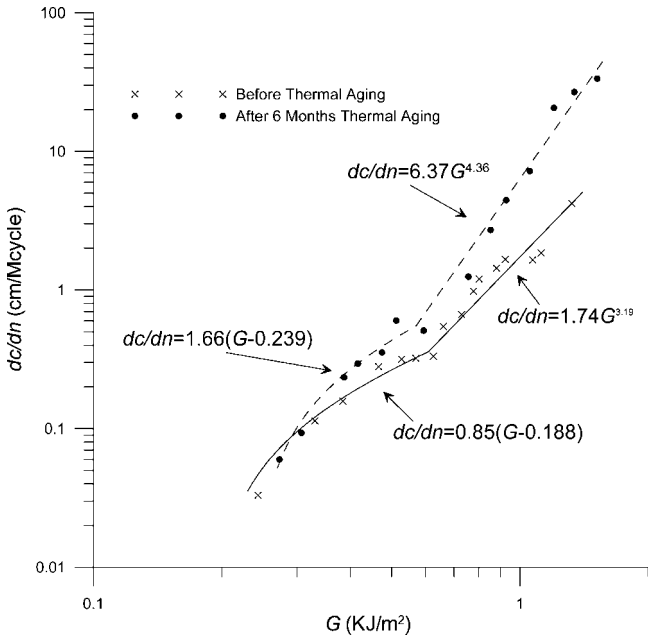

Figure 6 Effects of 6 months of thermal aging on the fatigue crack growth rates of rubber compound EP220.

decreased only slightly in regime 2, it can be said that the energy release rate range narrowed after 6 months of thermal aging. For some of the energy release rates we imposed on rubber compounds, their fatigue crack growth rates were governed by regime 3 instead of regime 2 because of the effect of thermal aging. In addition, the ultimate stretch and tear resistance of rubber compounds decreased when they were shifted from regime 2 to regime 3. Therefore, an unexpected catastrophic failure of rubber compounds is very likely to occur when successively subjected to the environmental attack of thermal aging.

CONCLUSIONS

The energy to break of rubber compounds EP220, EP330, and EP990 after 6 months of thermal aging decreased substantially, and tear strength was reduced by as much as 25%. Meanwhile, the fatigue life of the three rubber compounds after 6 months of thermal aging was dramatically reduced, to less than a tenth of what it was before thermal aging. Hence, the fatigue resistance of rubber compounds with different carbon blacks was consistently reduced because of the changes in molecular structure and crosslink density caused by thermal aging. However, the rubber compounds had smaller intrinsic flaws after 6 months of thermal aging. Again, this occurred because of the increased crosslink density of the EPDM rubber compounds, which resulted from thermal aging.

In contrast, the slopes of the curves that described the relation between crack growth rate and energy release rate for rubber compounds in regime 3 after 6 months of thermal aging were steeper than those before thermal aging. Also, when the rubber compounds in regime 2 were subjected to a lower rate of energy release over 6 months of thermal aging, fatigue parameter A increased. Consequently, the fatigue crack growth rate increased and fatigue life was reduced. It was also found that the threshold value, G_0, of rubber compounds was larger after 6 months of thermal aging than before thermal aging. The G_0 of

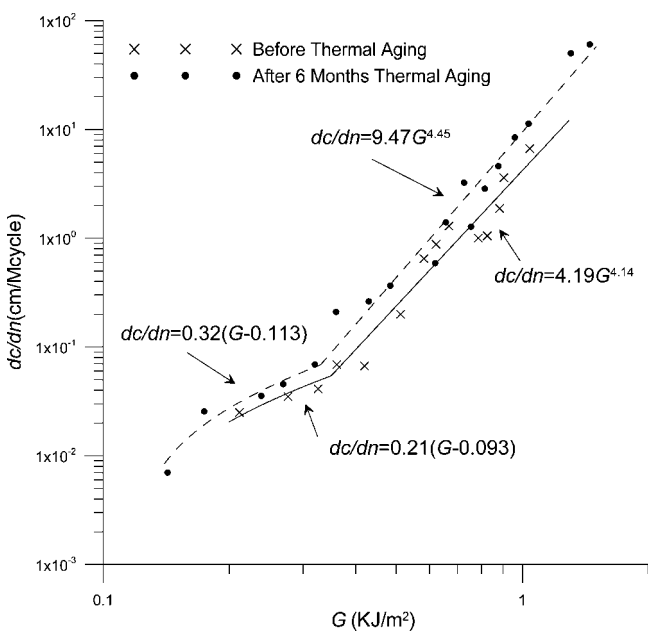

Figure 7 Effects of 6 months of thermal aging on the fatigue crack growth rates of rubber compound EP330.

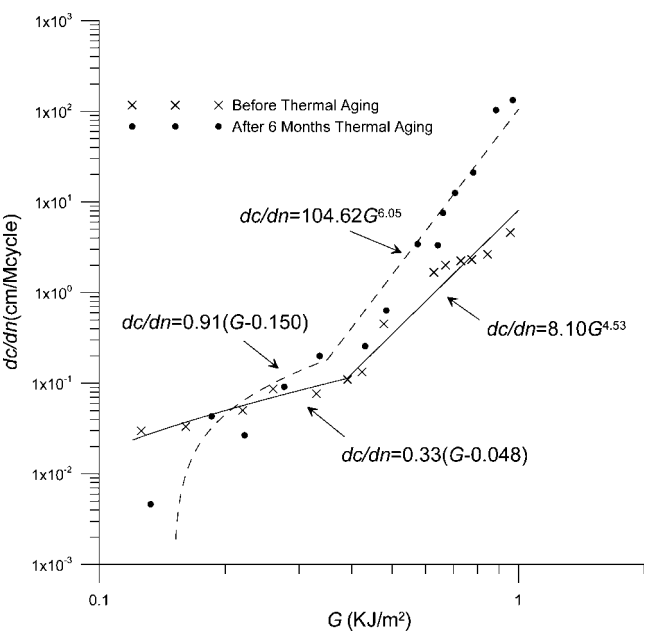

Figure 8 Effects of 6 months of thermal aging on the fatigue crack growth rates of rubber compound EP990.

TABLE III
Fatigue Parameters of Rubber Compounds EP220, EP330 and EP990 Calculated from Fatigue Crack Growth Rate Tests

		Regime 2		Regime 3		
		G_0 (kJ/m^2)	A	G_t (kJ/m^2)	a	b
EP220	No aging	0.188	0.85	0.61	1.74	3.19
	After 6 months aging	0.239	1.66	0.57	6.37	4.36
EP330	No aging	0.093	0.21	0.35	4.19	4.14
	After 6 months aging	0.113	0.32	0.33	9.47	4.45
EP990	No aging	0.048	0.33	0.39	8.07	4.53
	After 6 months aging	0.150	0.91	0.35	104.62	6.05

rubber compound EP990 was up to 3 times larger, whereas that of rubber compounds EP220 and EP330 was around 25%. However, the transition value, G_t, of the three rubber compounds after 6 months of thermal aging was slightly lower than that before thermal aging. As a result, it can be said that the energy release rate range in regime 2 narrowed after 6 months of thermal aging.

From the experimental results of a series of static and cyclic loading tests, it is clear that the effects of thermal aging on the fatigue parameters of carbon black–reinforced EPDM rubber compounds are significant and should be taken into account in designing rubber components.

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