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Fatigue Crack Growth Behavior of NR/EPDM Blend

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Abstract : Fatigue crack growth (FCG) behavior of natural rubber/ethylene-propylene-diene rubber (NR/EPDM) blend vulcanizates under dynamic tearing condition was investigated by using a fracture mechanics approach. It appeared that variation of crack growth rate with blend compositions was dependent on the level of imposed tearing energy G. At low tearing energy region, the FCG rates of the blend were lower as the EPDM content was increased, while at high tearing energy region, the trend was reversed. Over the measured range of tearing energy G, all blend compositions showed the lower crack growth rates compared to the average of properties of component elastomers. When the blends were thermally aged, the fatigue resistance of the blends was deteriorated in proportion to the concentration of EPDM phase. Fatigue crack growth behavior of the blends was supposed to be associated with the inhomogeneities of the crosslink structure of the blends arising from cure incompatibility of the EPDM and NR when they are sulphur cured.

Introduction

When a material is under a dynamic load, it is likely to be ruptured at an energy below the one required for catastrophic failure, which is referred to as the fatigue fracture. In many elastomer applications, such as tires, rubber springs and V-belts, the fatigue resistance is considered to be an important property to determine the performance of material. Fatigue failure is known to occur due to initiation and growth of one or several cracks.[1-3] In general, the initiation is originated from inherent flaw or small scale cracks embedded in polymers during preparation. Once being initiated, cracks propagate slowly but continuously until total failure occurs. A fracture mechanics approach has been employed to interpret the fatigue crack growth behavior of the elastomers.[4-7] According to this approach, the amount of cyclic crack growth (FCG) in pre-cut specimen may be described in terms of maximum tearing energy attained during a cycle: G

$$dc/dn = BG^{\alpha} \quad (1)$$

where c is the crack length, n is the number of load applications, and B and α are constants. The values of the exponent α depend strongly on the type of elastomer and to a much lesser extent on other factors such as crosslink structure.[1] It tends to be lower if the material exhibits the higher mechanical hysteresis, since the fatigue crack growth is mainly governed by viscous energy dissipation at the crack tip, particularly those arising from internal molecular motions or from stress-induced crystallization.[8]

Most of rubber compounds used in industry are based on blends in order to combine favorable properties of component elastomers. Natural rubber (NR) with superior mechanical properties has been typically blended with ethylene-propylene-diene rubber(EPDM) with ozone resistance.[9-12] Studies on the crack propagation behaviour of the NR/EPDM blends under dynamic tearing condition are necessary in order to evaluate the long-term performance of the blends as well as to gain insight on both the crack growth rate and the mechanism of fatigue failure process. In this study, fatigue properties of NR/EPDM blends under dynamic deformation condition were characterized

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Table I. Formulations(phr) and Vulcanization Conditions of NR/EPDM Blends

Ingredient	Unfilled System					Filled System	
NR	100	70	50	30	0	70	30
EPDM	0	30	50	70	100	30	70
Carbon black[a]	-	-	-	-	-	30	30
Mineral oil	-	-	-	-	-	7	7
Zinc oxide	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Stearic acid	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Sulfur	2.00	2.00	2.00	2.00	2.00	2.00	2.00
CBS	1.00	1.00	1.00	1.00	1.00	1.00	1.00
t_{90},(min/160°C)	11	14	16	22	34	8	13
Gel Content	0.978	0.978	0.968	0.953	0.969		

[a]HAF black, N-330.

in terms of crack propagation rate using tearing energy criterion. Influences of blend composition, carbon black, and thermal aging on the crack propagation behavior of the blend were investigated.

Experimental

Materials. The rubbers used in this study are natural rubber (SMR-CV60, Mardec, Malaysia) and ethylene-propylene-diene rubber (KEP-350, ENB type, Kumho E. P., Korea). Mix formulation and vulcanization conditions are given in Table I.

Sample Preparation. Mixing was carried out in a Banbury type internal mixer (Haake, Polylab 3000) at 60 rpm and at 40°C. The fill factor was 0.7. NR was masticated for 1 min and EPDM was added subsequently. When the mixing torque reached a constant value, zinc oxide, stearic acid and *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), followed by sulfur, were added.

The rubber compound was cured in an electrically heated press (Carver 2518) at 160°C for an optimum cure time (t_{95}), which was determined from an oscillating disk rheometer (Monsanto, R-100). Aging of the vulcanizates was carried out for 168 hrs at 100°C in an air-circulating oven.

Measurements. Fatigue test was performed by using pure-shear specimens with a length of 180 mm, a width of 20 mm and a thickness of 1.3 mm, as shown in Figure 1. A specimen with a sharp precrack was subject to an intermittently

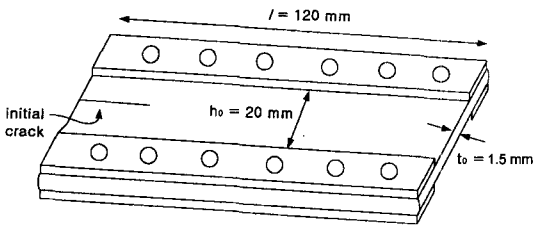

Figure 1. Geometry of pure shear specimen.

applied strain at a frequency of 2 Hz at room temperature. The magnitude of applied deformations was varied from 10% to 60%. The crack length was measured by traveling microscope after various cycling intervals. The tearing energy of pure-shear specimen was determined at a deformation rate of 10 mm/min at room temperature using universal testing machine (United Co., STM-10E). For this geometry tearing energy of elastomer (G) is given by

$$G = U \cdot h_o \quad (2)$$

where h_o is the unstrained width of the specimen, and U is the strain energy density.[6,7] The values of U were determined from tensile stress-strain relation for uncut specimen.

Torn surface obtained by the dynamic fatigue test was investigated by scanning electron microscopy (SEM, Akashi, WB-6). The tensile properties were determined using universal testing machine (United Co., STM-10E) at room temperature with a rate of deformation of 100 mm/min.

Results and Discussion

Effect of Blend Composition on Fatigue Behavior. The values of crack growth rates for NR/EPDM blends are measured over a wide range of values of tearing energy G, and the results are given on a logarithmic scale in Figure 2. It is observed that the value of dc/dn decreases with G and the fatigue crack growth rate depends on material properties such as type of elastomer and blend composition. At low values of tearing energy (G<ca. 300 J/mol), EPDM shows the better fatigue property than NR. However, as G is increased over ca. 300 J/mol, NR exhibits much lower rates of crack growth than EPDM, which has been observed by other researchers.[1,14] It is interesting to observe that the variation of fatigue crack growth rates of the blends is not proportional to EPDM content over a wide range of tear energy G. As is shown in Figure 3 where the values of dc/dn are plotted against blend composition at a given tearing energy G, all blend compositions show the superior fatigue properties as compared to the average of the properties of the two component elastomers over the whole measured range of tearing energy G. When G = 1000 J/m^2 or above, the crack propagation rate of NR/EPDM (70/30) blend is almost same as that of NR alone. This is contrasted with tensile properties of the blends, which are deteriorated in proportion with EPDM concentration in the blends (see Table II).

It is conjectured that the fatigue behaviour of blend may be associated with its morphology. Since NR has the greater cure rate as well as curative affinity than EPDM for conventional sulfur cured

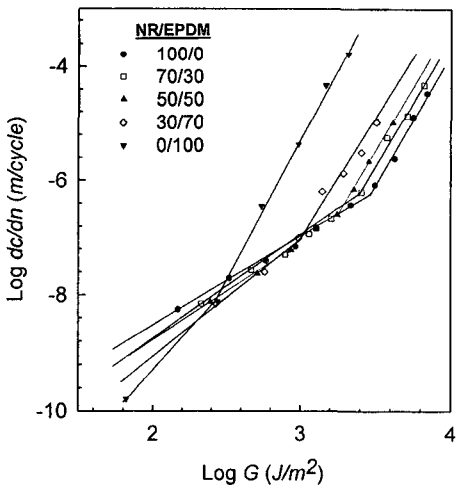

Figure 2. Crack growth rate versus tear energy G for unfilled NR/EPDM blends.

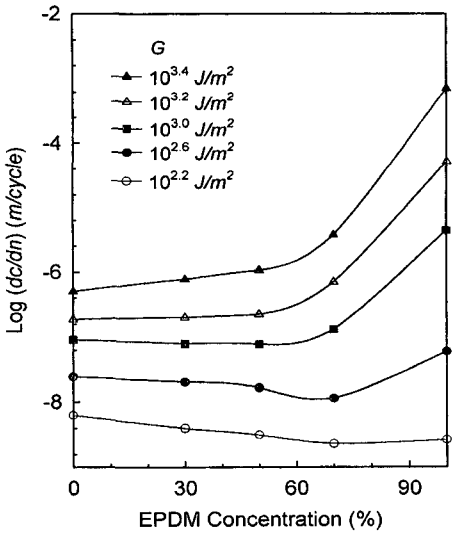

Figure 3. Crack growth rate versus blend composition at a given tear energy G for unfilled NR/EPDM blends.

Table II. Tensile Stress-strain Behaviours of NR/EPDM Blends

	Unfilled System					Filled System			
						Blend A[a]		Blend B[b]	
NR/EPDM	100/0	70/30	50/50	30/70	0/100	70/30	30/70	70/30	30/70
Tensile Stress, MPa	20	15	8	5	2.5	16	20	18	23
Tensile Strain,%	760	670	580	490	200	530	580	620	620
300% Modulus, MPa	1.57	1.67	1.76	1.78	-	6.08	5.88	4.31	6.17

[a]Carbon black was mixed with pre-blended NR/EPDM.
[b]NR was mixed with EPDM pre-loaded with carbon black.

system, the blend morphology should be consisted of lightly-cured EPDM phase and completely or over-cured NR phase.[12] When the blend is under the repeated deformation, a crack propagation may be impeded in very strong NR phase. The crack growth may be also restrained in the lightly-crosslinked EPDM phase, since the amount of viscoelastic energy dissipation, the major strengthening mechanism in amorphous elastomer, become greater as the crosslink density in the elastomer is decreased.[15,16] The high degree of energy dissipation that occurred at the localized crack tip in both phases is considered to lead to the fatigue properties of the blends superior to the average value for the constituent elastomers. However, the lightly-crosslinked EPDM phase is unable to stand for the high value of repeated stress, even though it is supported by the strong NR phase. This explains that FCG rates for the blend with the higher concentration of EPDM are increased more significantly with the increment of G, as can be seen in Figure 2.

The fractured surfaces obtained from elastomers subject to the cyclic stress of G = 1000 J/mol are given in Figure 4 and 5. Figure 4(a) and (b) shows

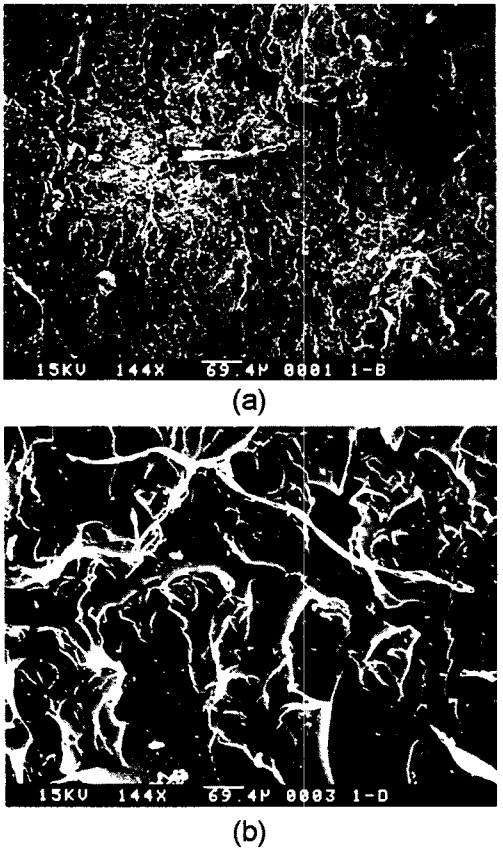

Figure 4. Scanning electron micrographs of torn surface for separately cured NR and EPDM vulcanizates: (a) NR and (b) EPDM.

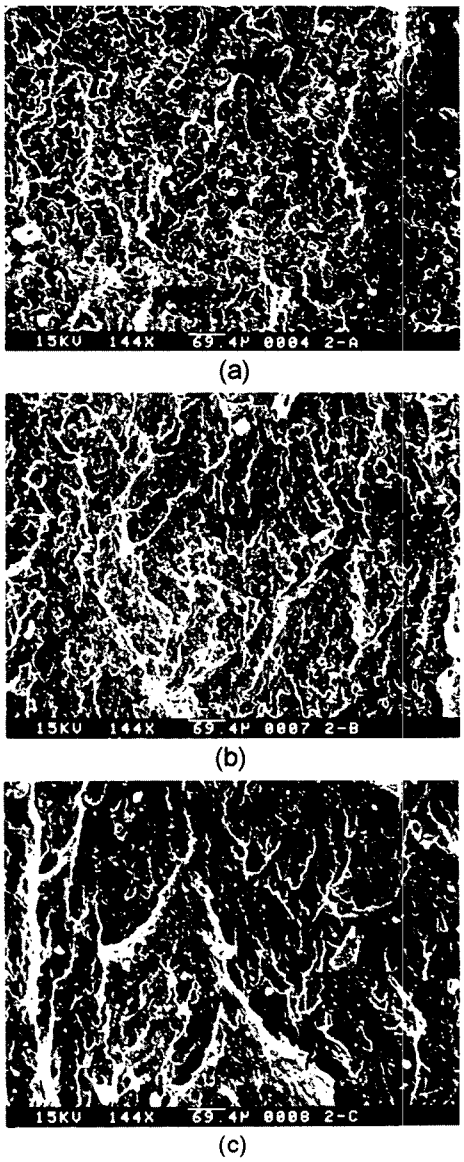

Figure 5. Scanning electron micrographs of torn surface for NR/EPDM blend vulcanizates: (a) 70/30, (b) 50/50, and (c) 30/70.

the torn surfaces of the fully-cured NR and EPDM, respectively. The figures clearly manifest different failure mechanism of the two elastomers. The torn surface of NR is relatively rough and consists of small-featured step compared to that of EPDM, which should be due to bluntness of the tear tip of NR arising from strain-induced crystallization.[17] In contrast, EPDM shows much smoother torn surface, implying that the fatigue crack propagates fast without any serious resistance. The fracture surfaces of the blends shown in the Figure 5(a), (b) and (c) exhibit that as EPDM concentration of blend is increased, the texture of torn surface is less dense whereas the large-scale deformation seems to occur. This observation can not be seen in fully cured EPDM (Figure 4(b)) and probably arises from the higher deformability of lightly-cured EPDM phase.

Effect of Thermal Aging on Fatigue Behavior. The variations of fatigue resistance for NR/EPDM blend were determined after unfilled vulcanizates had been aged at 100°C in air. Figure 6 shows that upon the exposure to thermo-oxidative condition, the values of *dc/dn* of all elastomeric systems are increased over the whole range of tearing energy. This indicate that the crack resistance of aged elastomers is significantly reduced, especially at high tearing energy region.

Figure 7 illustrates that the fatigue crack growth rates of the thermally-aged blends is more highly dependent on the content of EPDM in the blend as compared to unaged blends: the fatigue resistance of the thermally-aged blend decreases in proportion to the concentration of EPDM in the blend. This observation may be related with the fact that the resistance of thermal aging depends on the crosslinking density of elastomer, in addition to the molecular structure of repeating unit. That is to say, the lightly-cured EPDM in the blend may be deteriorated significantly upon exposure to heat, more seriously than fully-cured NR and cannot dissipate mechanical energy.

Fatigue Behavior of Filled Blends. The values of *dc/dn* for filled rubber blends (blend A in Table II) are measured and compared with the corresponding unfilled blends. Figure 8 illustrates that the fatigue property of blend is enhanced in the presence of carbon black over the whole measured range of tearing energy and the effect of filler on fatigue crack growth rate seems to be more significant in NR/EPDM (30/70) than in (70/30) blend. The reinforcement of filled elastomers may be associated with (1) an additional sources of hysteresis and (2) an increased propensity to crack tip blunting and branching in the presence of car-

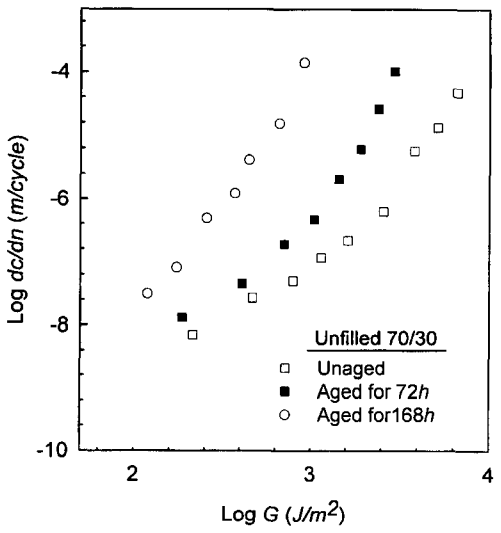

Figure 6. Effect of thermal aging on fatigue crack growth rate for unfilled NR/EPDM (70/30) blends.

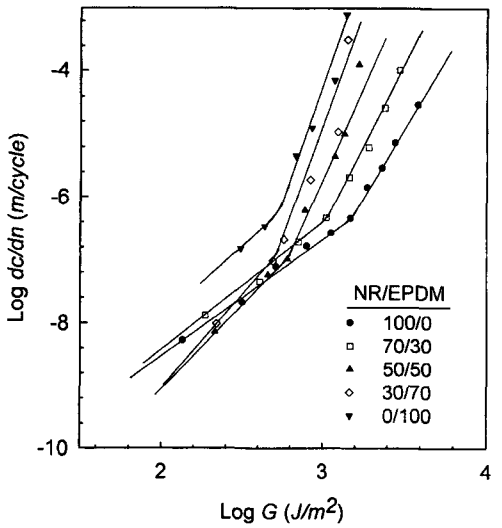

Figure 7. Crack growth rate versus tear energy G for unfilled NR/EPDM blends after aging at 100 °C for 72 hrs.

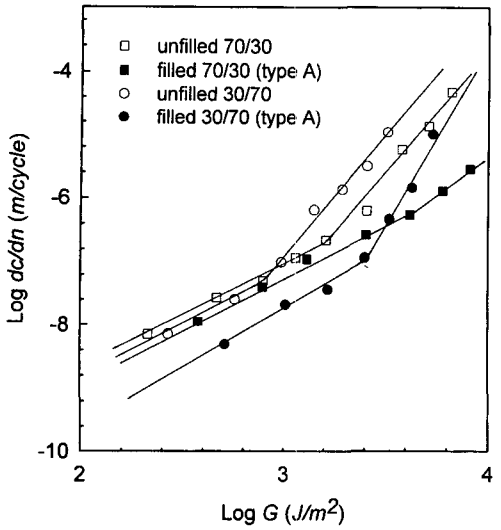

Figure 8. Crack growth rate versus tear energy G for filled NR/EPDM blends.

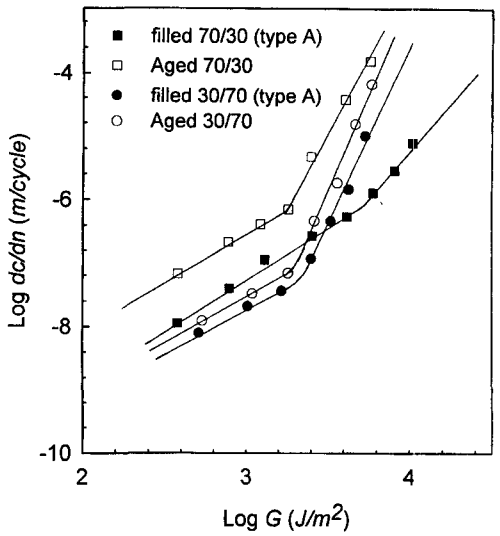

Figure 9. Crack growth rate versus tear energy G for filled NR/EPDM blends after thermal aging at 100 °C for 72 hrs. For comparison, crack growth rate of corresponding unaged blends are given together.

bon black.[1,16] For the filled blends, FCG rate of NR/EPDM (30/70) blend is obviously lower than that of (70/30) blend until the tearing energy reachs 3000 J/mol. In the case of unfilled system, on the other hand, (30/70) blend shows the slightly lower FCG rates than (70/30) blend within the more limited range of tearing energy region ($G \leq$ 1000 J/mol). These facts suggest that lightly-crosslinked EPDM phase is more influenced by carbon black than fully-cured NR phase is. The carbon black might lead the lightly-cured EPDM to be more resistant to plastic flow (permanent deformation) under the repeated stress, provided that the applied tearing energy is not too high. Furthermore it is well known fact that the crystallizable elastomer (i.e., NR) is not reinforced very much by the addition of carbon black.[16] Thus elastomer blends with the higher concentration of EPDM, such as 30/70 blend, may be reinforced substantially in the presence of carbon black, at least in low tearing energy region.

Figure 9 illustrates the effects of thermal aging on the FCG rates of carbon black filled blend (blend type A referred in Table II). It can be observed that for the thermally aged filled blends, the FCG rates increased more significantly in 70/30 blend than in 30/70 blend. It is contrasted with unfilled blends: it should be reminded that for unfilled blends the effect of thermal aging on FCG rates is more serious as the EPDM content in the blend is increased. Also, within the measured range of tearing energy, aged 30/70 blend exhibits the higher resistance to fatigue crack growth than 70/30 blend. The increased aging resistance of NR/EPDM (30/70) blend indicates that the reinforcing effect of the filler is greater in lightly-cured EPDM than in fully-cured NR.

As described in experimental section, filled NR/EPDM blends were prepared in two different methods to see the effect of filler addition mode on the mechanical properties of the blends. It has been reported that the distribution of the carbon black in elastomer blends is affected by mixing methods: if carbon black is added to pre-mixed NR/EPDM blends (type A), the black is preferentially located in NR phases, due to the higher affinity of NR toward carbon black. By mixing all the fillers into EPDM first (type B) and then blending the EPDM masterbatch with NR, more uniform distribution of the fillers in the blends can be obtained.[13] The effects of carbon black distribution on tensile properties of the blends are obvious, as shown in Table II. Ultimate tensile stress and elongation of filled-blend of type B are greater than

those of the filled-blend of type A, irrespective of blend composition. Tensile modulus of the blend appears to be governed by the major component in the blend. In the case of NR/EPDM (70/30) blend, the tensile modulus of type A blend is higher than that of type B blend, since the major component (i.e. NR) in the blend of type A contains higher amount of carbon black than in the blend of type B. For NR/EPDM (30/70) blend, in which EPDM is a major component, the blend of type B shows the higher modulus than the blend of type A, due to the higher filler content in EPDM phase for type B blend.

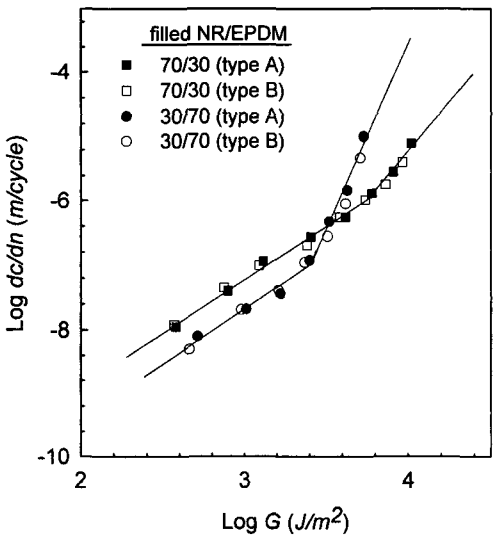

Figure 10. Influence of carbon black distribution on crack growth rate for NR/EPDM blends.

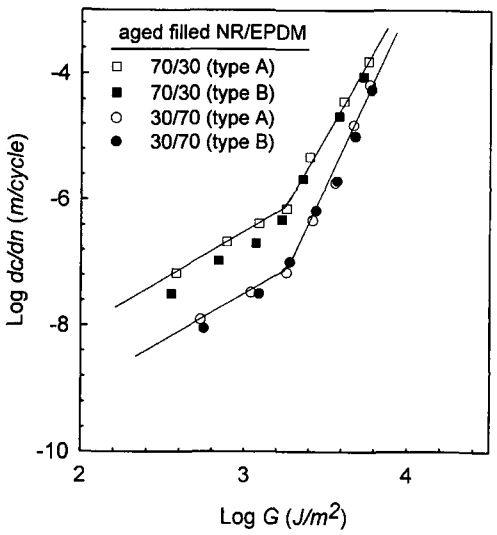

Figure 11. Influence of carbon black distribution on crack growth rate for NR/EPDM blends which were thermally aged at 100 °C for 72 hrs.

However, the fatigue behavior of the blends appears not to be affected by the filler distribution. Figure 10 shows that FCG rates of the two types of filled-blends are virtually same each other over the measured range of tearing energy, irrespective of blend composition. Little influence of the method of filler loading on the fatigue behavior is also observed for the thermally aged filled blends, as can be seen in Figure 11. These observations suggest that the filler distribution may not be a necessary condition in optimizing the resistance to fatigue crack growth for NR/EPDM blend. More detailed studies to understand the filler effects are under way.

Conclusions

1. Fatigue crack growth behavior of NR/EPDM blend with various compositions was investigated. The resistance to fatigue crack growth for all blends is shown to be greater as compared to the average of properties of the two component elastomers over the whole measured range of tearing energy G. The fatigue behaviour of the blends may be associated with high degree of viscoelastic energy dissipation at the localized crack tip in both phases: strain-crystallization of the NR phase and high degree of hysteresis in lightly-crosslinked EPDM phase.

2. The values of FCG rates for thermally aged blends are greater than the corresponding unaged blends. Fatigue resistance of the blend is decreased in proportion to the concentration of EPDM phase. It is supposed that the low-cured EPDM phase is deteriorated more seriously than fully cured-NR phase and, as a consequence, blend can not stand for the repeated deformation.

3. It is observed that the fatigue resistance of blend is increased in the presence of carbon black over the whole measured range of tearing energy, being greater for the blend containing the higher concentration of EPDM. The trend is the same for

the blends aged at 100°C for 72 hrs. This is supposed to be due to the greater reinforcing effect of the filler on the lightly-cured EPDM than the fully-cured NR. However, the variation of carbon black distribution does not lead to any significant change on fatigue crack growth rate.

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