The Dynamic Mechanical Properties of Oil-Extended, Carbon Black-Reinforced, and Peroxide-Crosslinked EPDM Rubber

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Synopsis

The effects of aromatic, naphthenic, and paraffinic oils on the dynamic mechanical behavior of an EPDM rubber (Nordel 1560) have been investigated as have the influences of oil level, carbon black loading, and peroxide crosslinking.

INTRODUCTION

In a previous paper[1] the thermal and dynamic mechanical behavior of six commercial ethylene–propylene–diene monomer (EPDM) rubbers were reported. In EPDM rubbers the diene is present in low concentration to permit, if desired, sulfur vulcanization, whereas ethylene–propylene monomer (EPM) rubbers are peroxide vulcanized. The synthesis,[2] characterization,[3–7] and properties[1,8–12] of these types of rubber have been extensively discussed in the literature.

In this paper the influence on the dynamic mechanical properties of oil type and level, carbon black content, and dicumyl peroxide crosslinking of an EPDM rubber has been investigated. There is a rather limited amount of work in the literature dealing with the effect of these compounding variables on dynamic behavior. As EPDM rubbers can vary considerably in terms of monomer ratio, molecular weight distribution, and crystallinity, it is probably the case that all such rubbers do not respond identically.

Flanders[13] has discussed shock and vibrational energy absorption by EPDM rubber compounds, while the trade literature contains values for brittleness temperature. Dimeler et al.[14] state that the most suitable petroleum oil for oil extension depends partly on the grade of EPDM rubber employed, with some grades requiring paraffinic oils while others are better with naphthenic oils. Stout and Eaton[15] have reported that increasing the aromatic content of the extending oil reduces the low-temperature flexibility of an EPDM rubber compound. Roche[16] has commented on the Yerzley resilience of EPDM rubber vulcanizates containing 50 parts oil, showing that the resilience decreases from paraffinic to naphthenic to aromatic oils. Hazelton and Puydak[17] consider naphthenic oils to impart greater resilience than paraffinic oils of the same viscosity.

McDuff[18] concluded from rebound resilience tests that oil content has only a small effect on resilience, with the most influence occurring with compounds having low carbon black loadings. Kochmit[19] and Walker and Louthan[20] have

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investigated black-filled and oil-extended ethylene–propylene rubbers. The effect of loading levels of both carbon black and other types of fillers on dynamic properties has also been reported.[16,17]

A number of publications[16,17,21,22] on sulfur and peroxide curing of ethylene–propylene rubbers exist.

EXPERIMENTAL

Materials

All the compounds are based on the EPDM elastomer Nordel 1560, which is manufactured by du Pont de Nemours Inc. Characterization data for this relatively crystalline[1] rubber are given in Table I.

The oils were Burmah Oil Ltd. products. For compounds A50 and W50 an aromatic oil (Poly-x A65) and a paraffinic oil (Poly-x W60), respectively, were added to extend Nordel 1560. For all other compounds, a naphthenic oil (Poly-x N65) with the same viscosity as the other two was used. See Table II for details of compounds prepared.

An FEF-grade carbon black (Sterling SO) was used in all the reinforced compounds. For the samples containing 50 parts naphthenic oil, three black levels (50, 100, and 150 parts) were used, but for the compounds containing 100 parts oil, an extra level (250 parts) of carbon black was investigated (see Table II).

Crosslinking was effected using dicumyl peroxide. The amount (2.5 parts) was kept constant irrespective of oil and black levels (see Table II).

Fabrication of Sheet

The oil and carbon black were mixed with the Nordel 1560 using a steam-heated Banbury mixer. In the cases of compounds containing 100 parts oil, the oil and the carbon black were added in two separate parts. The total mixing time was 8 min. The compounds were sheeted for 5 min at 90°C on a Bridge two-roll mill prior to final sheeting in a steam-heated press at 140°C for 5 min. The sheets (1 mm thick) were allowed to cool in the press. For compounds containing dicumyl peroxide, optimum cure times were determined using a Monsanto rheograph.

TABLE I
Characterization Data for Nordel 1560

Property	Magnitude
$\overline{M}_n \times 10^{-3}$ [a]	98
$\overline{M}_w/\overline{M}_n$ [b]	6.4
E/P [c]	82:18
Blockiness factor [d]	1.54

[a] Mecrolab high-speed membrane osmometer (Model 501); toluene at 37°C as solvent.
[b] Waters Associates gel permeation chromatograph (Model 502).
[c] Ethylene–propylene ratio (weight).[1]
[d] ^{13}C–NMR.[1]

TABLE II
Composition of Compounds

| Code | Composition, phr[a] | | |
	Oil	Carbon black	Peroxide
A50	50 (aromatic)		
W50	50 (paraffinic)		
A1	50 (naphthenic)		
B1	50	50	
C1	50	100	
D1	50	150	
A2	50		2.5
B2	50	50	2.5
C2	50	100	2.5
D2	50	150	2.5
F1	100		
G1	100	50	
H1	100	100	
I1	100	150	
J1	100	250	
F2	100		2.5
G2	100	50	2.5
H2	100	100	2.5
I2	100	150	2.5
J2	100	250	2.5

[a] All based on 100 parts by weight of Nordel 1560.

Dynamic Mechanical Measurements

A Rheovibron dynamic viscoelastometer (Model DDV-II-B) was used at a frequency of 110 Hz. The temperature range covered was scanned at a rate of about 1°C/min.

RESULTS AND DISCUSSION

Influence of Type and Amount of Oil

Table III shows the effect on the dynamic mechanical properties at 25, 30, and 40°C of adding 50 parts of the three different oils to Nordel 1560. There is a reduction in both the dynamic storage (E') and dynamic loss (E'') moduli. For both E' and E'' this decrease is greatest for the naphthenic oil followed by the paraffinic oil, and least effect in terms of modulus reduction is caused by the aromatic oil. It is also clear that there is a significant increase in tan δ (equals E''/E') between the virgin and the oil-extended rubbers, but there is no significant difference at these temperatures between the samples extended with the different types of oil, which is contrary to the findings of Roche[16] and Hazelton and Puydak.[17]

Figure 1 shows the tan δ–temperature curves in the glass transition region for the virgin polymer and for the two levels of oil extension. The glass transition temperature (T_g) shifts from −24 to −41°C for the sample containing 50 parts naphthenic oil and to −45°C for the sample with 100 parts oil. For the two oil-extended samples, tan δ has increased in both height and width relative to the unextended sample by virtually identical extents. The peak broadening is the result of polymer–oil interactions while the increase in the maximum value of

TABLE III
Influence of Type of Oil on Dynamic Properties at Various Temperatures

Property[a]	Rubber	Rubber + aromatic oil (sample A50)	Rubber + paraffinic oil (sample W50)	Rubber + naphthenic oil (sample A1)
At 25°C:				
$E' \times 10^{-6}$	19.0	7.9	7.1	6.1
$E'' \times 10^{-6}$	0.84	0.53	0.47	0.39
tan δ	0.04	0.07	0.07	0.06
At 30°C:				
$E' \times 10^{-6}$	18.0	7.3	6.7	5.6
$E'' \times 10^{-6}$	0.72	0.49	0.43	0.36
tan δ	0.04	0.07	0.06	0.06
At 40°C:				
$E' \times 10^{-6}$	12.5	5.9	4.8	4.5
$E'' \times 10^{-6}$	0.56	0.42	0.35	0.30
tan δ	0.05	0.07	0.07	0.07

[a] Modulus units are Nm^{-2}.

tan δ (tan $δ_{max}$) in the glass transition region is believed to be the result of the oil-extended samples having lower degrees of crystallinity. This has been proved at least qualitatively by x-ray diffraction experiments where it was found that the degree of crystallinity for oil-extended samples were consistently below those of the virgin rubber.

For the subsequent studies of carbon black-reinforcement and peroxide crosslinking of oil-extended Nordel 1560, the naphthenic oil was selected. As is evident from Table II, compounds containing both 50 parts and 100 parts of this oil were investigated.
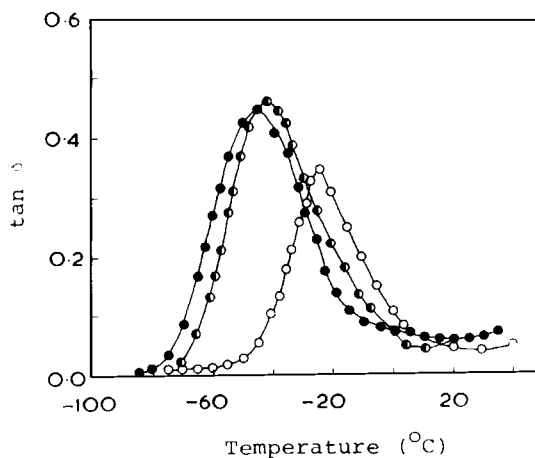

Fig. 1. tan δ-vs-temperature curves for Nordel 1560 (O) and Nordel 1560 with 50 parts (◐) and 100 parts (●) naphthenic oil.

TABLE IV
Certain Physical Properties of Compounds Based on Nordel 1560 with 50 Parts Naphthenic Oil

Code	Tensile strength, MN/m^2	100% Modulus, MN/m^2	300% Modulus, MN/m^2	E_B,[a] %
A1	—	0.8	1.4	—
B1	12.4	1.5	3.2	780
C1	9.2	3.8	8.4	460
D1	8.7	5.0	8.7	340
A2	—	1.0	1.4	—
B2	17.3	1.9	8.3	610
C2	15.4	7.3	—	230
D2	15.3	9.4	—	170

[a] Elongation at break.

TABLE V
Certain Physical Properties of Compounds Based on Nordel 1560 with 100 Parts Naphthenic Oil

Code	Tensile strength, MN/m^2	100% Modulus, MN/m^2	300% Modulus, MN/m^2	E_B,[a] %
F1	—	0.8	1.5	—
G1	—	0.8	1.6	—
H1	7.5	1.4	4.0	720
I1	7.0	2.7	6.4	380
J1	4.0	—	—	84
F2	—	0.8	1.5	—
G2	—	1.9	2.4	—
H2	9.3	1.9	6.8	510
I2	8.2	3.5	8.0	320
J2	5.6	5.0	—	100

[a] Elongation at break.

TABLE VI
T_g and Maximum Value of tan δ for Compounds Based on Nordel 1560 and 50 Parts Naphthenic Oil

Code	T_g, °C	tan $δ_{max}$[a]
A1	−41	0.47
B1	−40	0.35
C1	−34	0.21
D1	−33	0.12
A2	−38	0.53
B2	−37	0.38
C2	−38	0.20
D2	−26	0.13

[a] Value of tan δ at T_g.

Tensile Properties of the Oil-Extended Compounds

Tables IV and V show how the tensile strength, moduli, and elongation at break change with oil level, black loading, and crosslinking. The trends shown in these tables are those expected. At constant peroxide and black levels, tensile strength and moduli decrease while elongation at break increases with increase in oil content. With peroxide and oil levels constant, increasing the carbon black content leads to a decrease in tensile strength and elongation at break, but to an increase in moduli. The crosslinked samples show an increase in tensile

TABLE VII
T_g and Maximum Value of tan δ for Compounds Based on Nordel 1560 and 100 Parts
Naphthenic Oil

Code	T_g, °C	tan δ_{max}[a]
F1	−45	0.45
G1	−43	0.40
H1	−37	0.25
I1	−35	0.20
J1	−24	0.12
F2	−46	0.46
G2	−41	0.38
H2	−42	0.29
I2	−39	0.17
J2	−17	0.10

[a] Value of tan δ at T_g.

strength and moduli, but a decrease in elongation at break compared to equivalent uncrosslinked samples.

Dynamic Mechanical Behavior of the Oil-Extended Compounds

Tables VI and VII indicate that there is a shift in T_g to higher temperatures as the carbon black content is increased. For both the compounds with 50 and 100 parts oil, the shift is greater for the crosslinked samples. It is expected that

Fig. 2. tan δ-vs.-temperature curves for samples A1 (⊙), B1 (O), C1 (✕), and D1 (●). See Table II.

Fig. 3. tan δ-vs.-temperature curves for samples A2 (⊙), B2 (O), C2 (✕), and D2 (●). See Table II.

crosslinking will raise T_g, but it is only at the highest black loading for both groups of compounds that this effect is greater than the experimental error of about ±2°C.

The tan δ_{max} values for the uncrosslinked and the crosslinked samples (Tables VI and VII) show an essentially linear decrease with black content for both groups of samples up to 150 parts black. For the higher oil-content compounds the rate of decrease in tan δ_{max} is reduced significantly between 150 and 250 parts black. Tables VI and VII show that crosslinking the oil-extended rubbers leads to a small increase in tan δ_{max} as a result of the decrease in degree of crystallinity. This is in accord with the claim[1] made earlier for a range of EPDM rubbers. For the samples also containing carbon black, this trend is masked by the reinforcing action of the filler.

Figures 2 and 3 show that tan δ–temperature dispersions for the compounds with 50 parts oil in the uncrosslinked and the crosslinked forms, respectively. Apart from the reduction in tan δ_{max} and the broadening of the glass transition
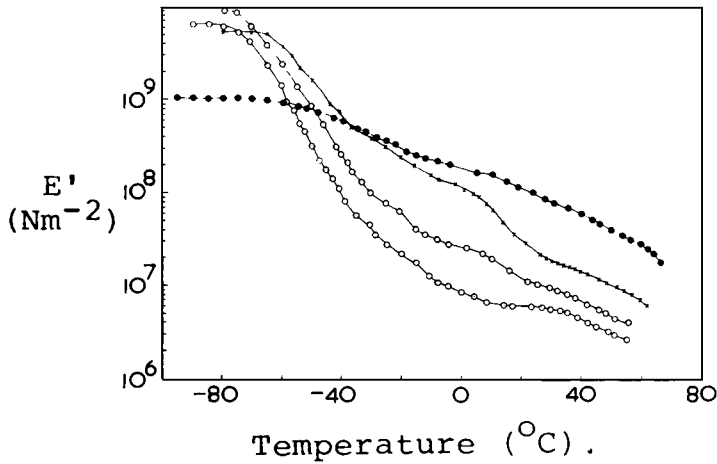

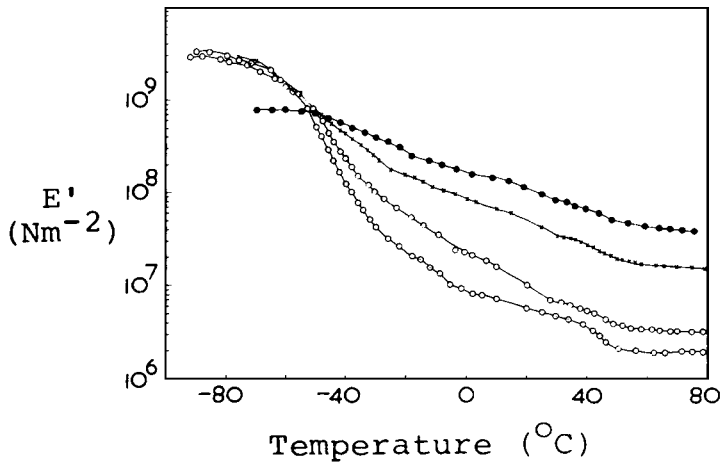Fig. 4. E'-vs.-temperature curves for samples A1 (⊙), B1 (○), C1 (×), and D1 (●). See Table II.

Fig. 5. E'-vs.-temperature curves for samples A2 (⊙), B2 (○), C2 (×), and D2 (●). See Table II.

peaks as the level of reinforcing filler is increased, the curves for the unfilled material and for the compound with 50 parts carbon black in Figure 3 show distinct evidence of crystalline melting at around 45°C. In this figure, tan δ levels off to yield an extended plateau region which is absent for the uncrosslinked materials in Figure 2. In Figure 3, the sample containing 150 parts carbon black shows a rise in tan δ at around 20°C, which may be the result of melting of poorly developed crystallites in this relatively highly filled compound.

Figures 4 and 5 show dynamic storage modulus (E')-versus-temperature plots for both sets of compounds containing 50 parts oil. In the glassy region the dynamic storage moduli are not much influenced by the presence of 50 and 100 parts carbon black. This is particularly true for the crosslinked compounds. The samples with 150 parts FEF carbon black, however, show a significant reduction in E'. In addition to the already mentioned broadening of the glass transition region, there are several regions of slope change in the E'-versus-temperature curves which cannot at this stage be interpreted. In both Figures 4 and 5 there are E'-versus-temperature slope changes at around 40°C which are believed to be associated with crystalline melting,[1] but this change is not very pronounced in the most highly filled samples. In fact, the evidence suggests that the level of crystallinity is decreasing as the filler content is raised. It is also clear from
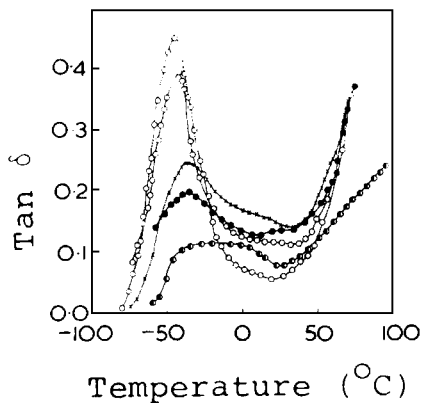

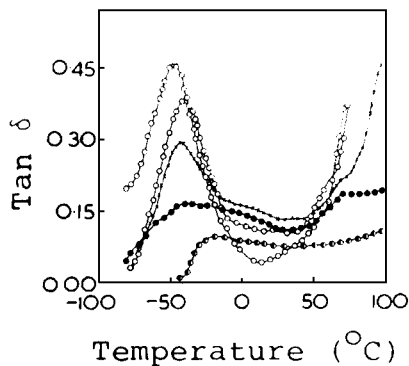Fig. 6. tan δ-vs.-temperature curves for samples F1 (⊙), G1 (○), H1 (✕), I1 (●), and J1 (◑). See Table II.

Fig. 7. tan δ-vs.-temperature curves for samples F2 (⊙), G2 (○), H2 (✕), I2 (●), and J2 (◑). See Table II.
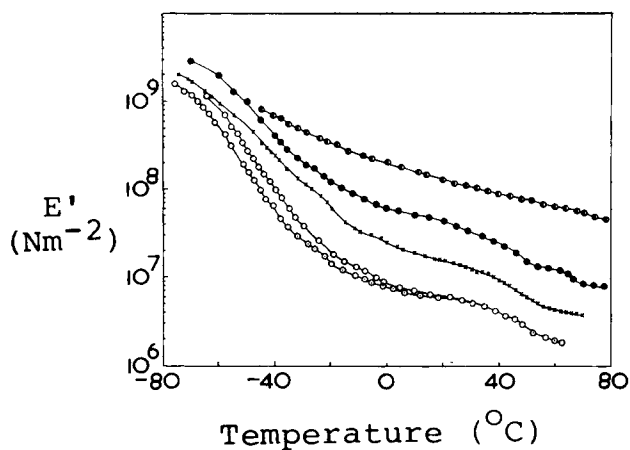
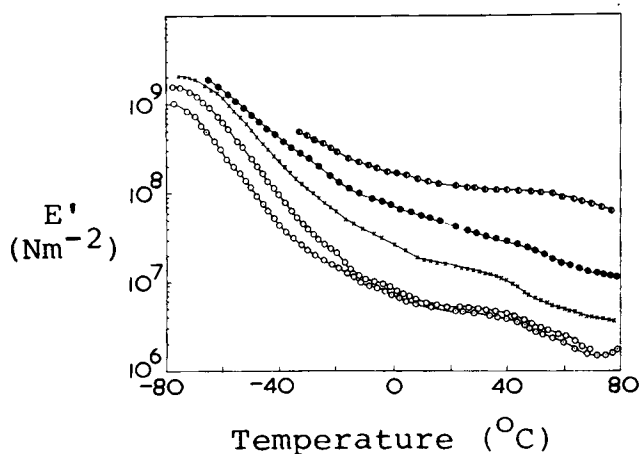Fig. 8. E'-vs.-temperature curves for samples F1 (⊙), G1 (○), H1 (×), I1 (●), and J1 (◑). See Table II.

Fig. 9. E'-vs.-temperature curves for samples F2 (⊙), G2 (○), H2 (×), I2 (●), and J2 (◑). See Table II.

Figures 3 and 5 that a significant amount of crosslinking has been achieved using 2.5 parts dicumyl peroxide in the presence of 50 parts naphthenic oil.

Figures 6 and 7 show the tan δ–temperature dispersions for the uncrosslinked and crosslinked samples, respectively. In Figure 6 there is a progressive softening at temperatures above approximately 30°C for the uncrosslinked samples, as was the case for the equivalent samples containing 50 parts oil, but for the crosslinked materials (Fig. 7) the plateau region shown in Figure 3 for the corresponding samples with 50 parts oil is absent for samples F2, G2, and H2. The samples containing 150 and 250 parts carbon black do exhibit a leveling off. This difference is likely to be the result of a less extensive degree of crosslinking in the samples with the higher oil content.

The E'-versus-temperature plots for the samples with 100 parts oil are shown in Figures 8 and 9. The E' values at 60°C are consistently marginally higher for the crosslinked samples (Fig. 9), indicating that at least some crosslinking has been obtained in the presence of 100 parts oil. These curves also show evidence

of crystalline melting at around 40°C which again becomes less marked as the carbon black level is increased.

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