Effect of Crosslink Structures on Dynamic Mechanical Properties of Natural Rubber Vulcanizates under Different Aging Conditions

RULIANG FAN,[1] YONG ZHANG,[1] CHEN HUANG,[1] YINXI ZHANG,[1] YONGZHONG FAN,[2] KANG SUN[2]

[1] Polymeric Materials Research Institute, Shanghai Jiao Tong University, Shanghai 200240, China

[2] State Key Lab of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200030, China

ABSTRACT: The effects of crosslink structures on the dynamic mechanical properties (DMPs) of unfilled and carbon black N330-filled natural rubber (NR) vulcanizates cured with conventional (CV), semiefficient (SEV), and efficient (EV) cure systems and having about the same total crosslink densities were investigated before and after aerobic and anaerobic aging at 100°C. The three unfilled NR vulcanizates cured with the CV, SEV, and EV systems had about the same mechanical loss factor (tan δ) values at about 0°C but showed some apparent differences in the tan δ values in the order EV > SEV > CV at relatively high temperatures of 40–80°C before aging. However, N330-filled NR vulcanizates gave higher tan δ values than the unfilled vulcanizates and showed little effect of the crosslink types on the tan δ at different temperatures over the glass-transition temperature (T_g) before aging. Aerobic heat aging increased the T_g and tan δ values of the vulcanizates over a wide range of temperatures from −80 to 90°C that was mainly due to the changes in the total density and types of crosslinks. The unfilled vulcanizates cured with the CV system showed the greatest change in DMP because of their poor resistance to heat aging. Aerobic heat aging of NR vulcanizates caused a more significant change in the DMP than anaerobic heat aging because of the dominant effect of the oxidative degradation during aerobic heat aging on the main-chain structure, crosslink structures, and DMPs of the vulcanizates. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 710–718, 2001

Key words: crosslink structure; dynamic mechanical property; natural rubber; vulcanizate

INTRODUCTION

The dynamic mechanical property (DMP) of a rubber vulcanizate is an important property for tire applications, as well as other dynamic rubber products. Many studies on the dynamical properties of various rubber vulcanizates have been reported, including the effects of the types and amounts of rubbers[1–3] and fillers,[4–8] as well as their interaction,[8] other compounding ingredients, and the state of cure.[8,9]

Sulfur vulcanized rubbers have network structures that are mainly composed of monosulfidic, disulfidic, and polysulfidic crosslinks. The structures including the crosslink densities and types of vulcanizates are very important parameters because of their dominant effects on the mechanical properties. The effects of the crosslink density and type on the strength of vulcanizates

were studied in depth by many authors.[10–14] Payne and Whittaker[15] investigated the DMPs of carbon black filled natural rubber (NR) compounds by varying the crosslink density and carbon black (CB) loading. They found that an increase in the crosslink density of an NR vulcanizate containing a fixed amount of CB increased the elastic modulus and decreased the values of the mechanical loss factor (tan δ). Sombatsompop[16] studied the interrelation of the degree and type of crosslink and the viscoelastic properties of sulfur-cured NR vulcanizates by altering the accelerator loading, curing time, and temperature. The results showed that the DMPs such as the elastic modulus, damping behavior, and variation of the glass-transition temperature (T_g) were not necessarily dependent on the total crosslink density but were a function of the percentage proportion of crosslink types generated in the NR compounds. However, they did not control the total crosslink densities to about the same level, and the effect of crosslink types and crosslink densities were not identified. So the effects of crosslink types such as polysulfidic, disulfidic, and monosulfidic crosslinks on the DMPs of NR vulcanizates were not well understood.

Usually, dynamic rubber products are run under a sinusoidally alternated stress. For example, the dynamic losses and heat are generated in all types of tires. At the midsections of the shoulders of heavy duty tires[17] and passenger car tires[18] the heat generated usually results in internal elevated temperatures over 100 and 60°C, respectively. Some changes in the chemical structures of the vulcanizates in the tires must have taken place, which deteriorated the physical mechanical properties of the vulcanizate, which is important to the service requirements of the tire.

It is well known that the vulcanizate undergoes anaerobic aging in the interior part of the tire tread and aerobic aging in the exterior part. Therefore, the aging resistance usually associated with the durability of dynamic rubber products is also an important performance to which great attention should be paid in developing the tire tread. Unfortunately, to our knowledge, there are few studies concerned with the effects of aging periods and environments on the crosslink structures (e.g., crosslink density and type) and the DMPs of NR vulcanizates.

Because the tensile modulus of a vulcanizate at a given elongation is proportional to the total crosslink density,[19] similar moduli can be achieved in different vulcanizates by adjusting

Table I Recipe of Three Rubber Vulcanizates with Different Curing Systems

Ingredients	CV	SEV	EV
SCR-5	100.0	100.0	100.0
N330[a]	50.0	50.0	50.0
Rhenogran ZnO-80	3.8	3.8	3.8
Stearic acid	1.5	1.5	1.5
Uop588	2.0	2.0	2.0
Rhenogran S-80	3.8	0.8	—
Rhenogran CBS-80[d]	1.3	2.5	2.0
TMTD[e]	—	1.0	1.5
DTDM[f]	—	—	1.5
Total (phr)	162.4	161.6	162.3

SCR-5, standard natural rubber made in China; Uop588, N-(1,3-dimethylbutyl)-N-phenyl-p-phenylene diamine; Rhenogran CBS-80, 80% active content of N-cyclohexyl-2-benzothiole sulfenamide (RheinChemie Corporation); TMTD, tetramethylthiuram disulfide; DTDM, 4,4′-dithiodimorpholine.

[a] N330 was not added to unfilled compounds.

the total crosslink density to the same levels. In this study, the total crosslink densities of the three types of sulfur-cured vulcanizates [conventional (CV), semiefficient (SEV), and efficient (EV) curing systems] were controlled to much the same level by changing the ratio of sulfur to the accelerators and the type of accelerators, even though they had quite different crosslink types.

The purpose of this work was to assess how the crosslink structures in these three vulcanizates affect the DMPs before and after aging at different aging conditions.

EXPERIMENTAL

The formulas of the three NR vulcanizates are listed in Table I. They were designed to make the vulcanizates have about the same total crosslink densities when cured with three distinct curing systems: the CV vulcanizate consisting mainly of polysulfidic crosslinks, the EV vulcanizate being mostly monosulfidic, and the SEV vulcanizate having a crosslink structure midway between the CV and the EV vulcanizates.

All the ingredients including sulfur and accelerates were mixed on a laboratory-scale 6-in. roll mill. The mixing temperature was controlled between 80 and 90°C. The optimum cure time (T_{90}) at 150°C was determined by using a Monsanto ODR2000 viscometer. The specimens were vulcanized on a laboratory press at 150°C for T_{90}.

To evaluate the effects of aging on the DMP, total density, and types of crosslinks, the samples were aged for 24, 72, and 120 h at 100°C under aerobic and anaerobic conditions by intentionally covering the surfaces of the samples with aluminum sheets.

The DMPs of all three vulcanizates were measured under a multiwave compression mode at a frequency of 11 Hz with 23-kPa static stress and 20.7-kPa dynamic stress for the N330-filled NR vulcanizates and 10-kPa static stress and 9-kPa dynamic stress for the unfilled vulcanizates on a Rheometric Scientific™ DMTA IV. It should be noted that the static and dynamic stresses imposed on the N330-filled vulcanizates were greater than those imposed on the unfilled vulcanizates in order to obtain a similar dynamic strain through the whole range of temperatures in this study. The dimensions of the specimens were about 10 mm in height and 6 mm in diameter. The temperature dependencies of the tan δ, elastic modulus G', and viscous modulus G'' were measured simultaneously.

The total densities and types of crosslinks of the vulcanizates were measured by the n-decane swelling method developed by NRPRA (now MR-PRA) and described by Cunneen and Russell.[17] Prior to swelling, each sample was preextracted with acetone for 24 h and then dried to a constant weight in a vacuum oven at 50°C. Propane-2-thiol and n-hexanethiol were used as the chemical probes to cleave polysulfidic crosslinks only and both polysulfidic and disulfidic crosslinks, respectively. Piperidine was added to the propane-2-thiol and n-hexanethiol to enhance the nucleophilic properties of sulfur atoms in the piperidium thiolate ion pair. The samples were treated for 2 h in propane-2-thiol and 48 h in n-hexanethiol at 25°C, then extracted with acetone for 12 h, and finally dried to constant weight in a vacuum oven at 50°C.

The values of (v_r) the corrected volume fraction of the rubber network in the swollen samples containing CB were calculated by the following equation[17,20]:

$$\frac{v_r}{v_r'} = 0.56e^{-z} + 0.44 \quad (1)$$

where v_r' is the measured volume fraction of rubber in the swollen vulcanizate samples and z is the weight concentration of CB in the vulcanizate. The density of the gum rubber vulcanizate was
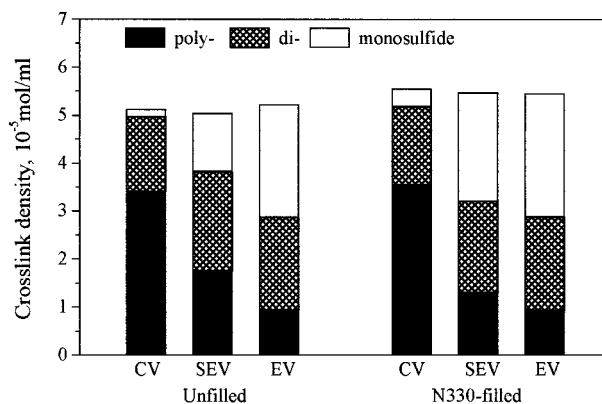

Figure 1 Comparisons of the crosslink densities and types of unfilled and N330-filled vulcanizates before aging.

assumed to be 0.93 g/mL. The elastic constant C_1 was then calculated by eq. (2).[21]

$$-\ln(1 - v_r) - v_r - \chi v_r^2 = 2c_1V_0(v_r)^{1/3}/RT \quad (2)$$

where χ is the rubber–solvent interaction parameter (assumed to be 0.43), V_0 is the molar volume of n-decane (194.92 mL/mol), R is the gas constant [8.29 N m/(mol K)], and T is the absolute temperature (298 K). The calculated C_1 value can be converted into the concentration of chemical crosslinks $[2M_{c,\text{chem}}]^{-1}$, which is referred to crosslink density using eq. (3).[22]

$$C_1 = (0.5\rho RTM_{c,\text{chem}}^{-1} + 0.78 \times 10^6)$$
$$\times (1 - 2.3M_{c,\text{chem}}M_n^{-1}) \quad (3)$$

where ρ is the density of the gum rubber vulcanizate (0.93 g/mL) and M_n is the number-average molecular weight of the masticated NR before vulcanization, which was found to be 5×10^5 by the GPC method.

RESULTS AND DISCUSSION

Effect of Crosslink Types

Comparisons between the unfilled and the N330-filled vulcanizates with CV, SEV, and EV curing systems corresponding to very different crosslink types are shown in Figure 1. The CV vulcanizate has mainly polysulfidic crosslinks (66.6% for the unfilled and 64.0% for the N330 filled), the EV vulcanizate has mainly monosulfidic crosslinks

Table II   Total Crosslink Density (v_T) and Moduli (M) of Unfilled and N330-Filled Vulcanizates

	Unfilled			N330 Filled		
	CV	SEV	EV	CV	SEV	EV
v_T ($\times 10^5$ mol/mL)	5.12	5.04	5.23	5.55	5.47	5.46
M_{25} (MPa)	0.38	0.35	0.37	1.06	1.08	1.10
M_{50} (MPa)	0.61	0.52	0.56	1.56	1.58	1.60
M_{75} (MPa)	0.77	0.63	0.70	2.11	2.13	2.17

M_{25}, M_{50}, and M_{75}, moduli at 25, 50, and 75% elongation, respectively, obtained from stress–strain curves by using an Instron 4465 tensile machine at a crosshead speed of 50 mm/min.

(45.1% for the unfilled and 47.3% for the N330 filled), and the SEV vulcanizate consists of a network structure midway between the CV and the EV vulcanizates. Figure 1 and Table II also show that these three vulcanizates have similar levels of moduli at low elongation and similar total crosslink densities of $(5.13 \pm 0.10) \times 10^{-5}$ mol/mL for the unfilled rubbers and $(5.49 \pm 0.06) \times 10^{-5}$ mol/mL for the CB filled rubbers. Judged by the percent differences, the tolerances of the above crosslink densities correspond to 2.0% for the three unfilled rubbers and 1.4% for the three N330-filled rubbers.

As shown in Table II, the unfilled vulcanizates with the three cure systems have similar moduli at the same elongation before aging, reflecting that they have similar crosslink densities. The N330-filled vulcanizates of the three types of cure systems also show a similar modulus at 25, 50, and 75% elongation, respectively, before aging. Therefore, the DMPs of the vulcanizates of the

three types of cure systems was not significantly influenced by modulus differences under stress-controlled deformations before aging in this study, which is different from the influence imposed by crosslink types.

When a compression stress is imposed periodically with a sinusoidal alternation at some frequency on rubber specimens that possess viscoelastic behavior, the strain will also alternate sinusoidally but will be out of phase (i.e., the strain lagging the applied stress).[23] Thus, the dynamic losses are usually associated with hysteresis and some specific mechanisms of molecular or structural motions in the rubber materials. The damping characteristics are extensively measured as "the tangent of the phase angle (tan δ)" and defined by

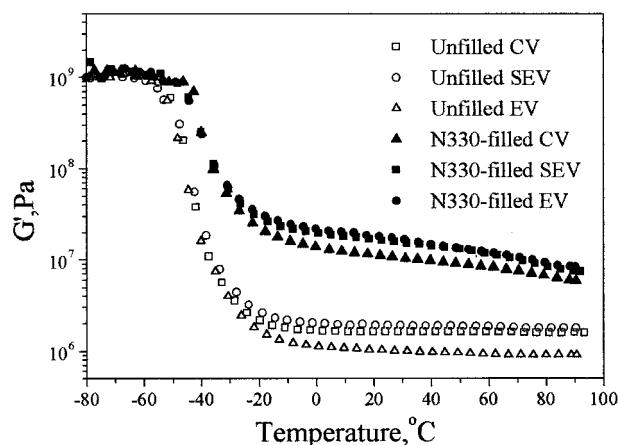$$\tan\delta = \frac{G''}{G'} \qquad (4)$$

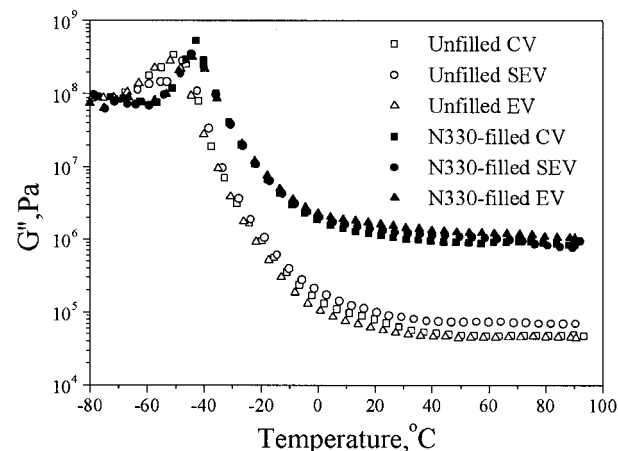**Figure 2** Changes in G' as a function of temperature for the unfilled and N330-filled NR vulcanizates before aging.

Figure 3 Changes in G'' as a function of temperature of unfilled and N330-filled NR vulcanizates before aging.
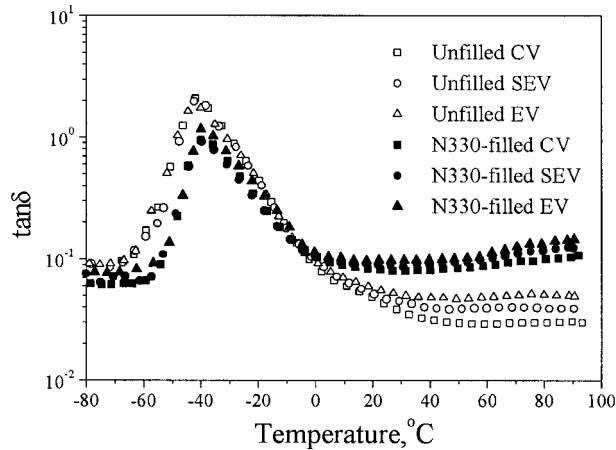
Figure 4 Changes in tan δ as a function of temperature of unfilled and N330-filled NR vulcanizates before aging.

Figure 5 The effect of aerobic heat aging at 100°C on the tan δ for the unfilled CV vulcanizate.

where G' is the storage modulus or elastic modulus representing the stored elastic energy in the materials and G'' is the loss modulus or viscous modulus due to viscous dissipation.

The tan δ of the tread rubber at about 0°C and about 10 Hz was found to be the best indication of wet skid resistance according to the frequency and temperature transformation rule.[24,25] However, the tan δ at about 60°C and 10–110 Hz is considered to be the best indication of rolling resistance.

Figures 2, 3, and 4 show the G', G'', and tan δ, respectively, of the unfilled and N330-filled vulcanizates with CV, SEV, and EV cure systems as functions of the temperature before aging. The tan δ values at 0 and 60°C are listed in Table III.

The conclusion that may be drawn from the results in Figures 2, 3, and 4 is that the tan δ and moduli of the N330-filled NR vulcanizates are greater than those of the unfilled NR vulcanizates. This result can be explained in terms of Wang's viewpoint.[6] In fact, the dynamic properties with regard to the tire application can be
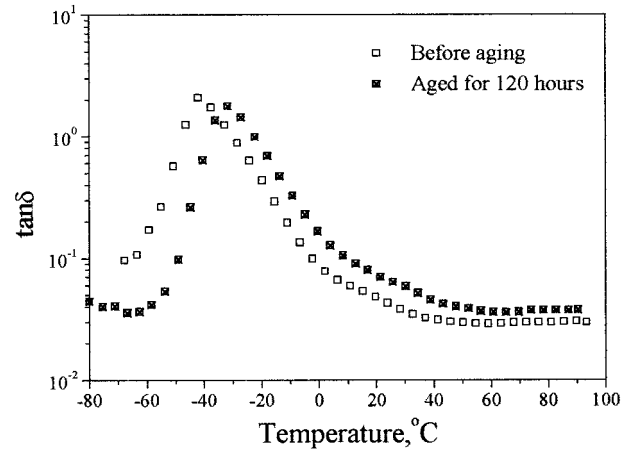
satisfied at least from the viewpoint of hysteresis by simply reducing the filler loading, because the gum rubber gives a lower hysteresis at relatively high temperature. However, in tire compounding enough filler must be incorporated to meet the requirements for stiffness, wear resistance, tearing resistance, and strength of the vulcanizate. These properties not only influence the service life of the tire but can also affect driving safety because hysteresis properties may not be the only factor to govern the skid resistance and cornering performance.

Also, it can be seen from Figures 2, 3, and 4 that the effects of the crosslink types on the DMPs at different temperature regions are dominated by different mechanisms. It seems that at temperatures near the tan δ peak in the glass-transition zone, even near 0°C, the unfilled CV, SEV, and EV vulcanizates samples give values similar to the tan δ and T_g. This may be accounted for by the fact that they have the same gum NR structure and nearly the same total crosslink densities that relate to similar motion characteristics of the chain segment. If this interpretation is reason-

Table III   Changes in Glass-Transition Temperature (T_g) and Mechanical Loss Factor (tan δ) Values of Vulcanizates at 0 and 60°C

Vulcanizates	T_g (°C)		tan δ at 0°C		tan δ at 60°C	
	Unfilled	Filled	Unfilled	Filled	Unfilled	Filled
CV	−42.0	−40.1	0.089	0.110	0.029	0.088
SEV	−40.2	−39.8	0.094	0.104	0.039	0.098
EV	−40.2	−40.1	0.091	0.110	0.047	0.107

Table IV Effect of Aerobic Aging at 100°C on Glass-Transition Temperature (T_g) and Mechanical Loss Factor (tan δ) Values of Unfilled Vulcanizates with Different Curing Systems at 0 and 60°C

Vulcanizates	Aging Time (h)	T_g (°C)	tan δ at 0°C	tan δ at 60°C
CV	0	−42.0	0.089	0.029
	120	−31.7	0.166	0.036
SEV	0	−40.2	0.094	0.039
	120	−35.1	0.121	0.045
EV	0	−40.2	0.091	0.047
	120	−36.0	0.122	0.051

Aging time 0 means before aging.

able for hysteresis in the glass-transition zone, it may not be true at high temperatures, especially near 60°C (also shown in Table III), where the hysteresis decreases in the order EV > SEV > CV. It was routinely demonstrated in NR compounding that, when the vulcanizates have the same total crosslink densities, various cure systems with different concentrations of polysulfidic, disulfidic, and monsulfidic crosslinks give different responses to the temperature dependence of the dynamic hysteresis. The polysulfidic crosslink has a longer crosslink and a more flexible structure; the dynamic hysteresis of the vulcanizate with more polysulfidic crosslinks is certainly lower.

We conclusively postulated that lower tan δ values at 60°C and lower heat buildup of NR vulcanizates can be obtained by reaching a relatively high concentration of polysulfides, leading to a greater flexibility of the network structure. Thus, for practical purposes, the use of cure systems that could form a relatively high content of polysulfides enables the preparation of a low hysteresis compound for predictive tire lower rolling resistance as evidenced by the tan δ at 60°C.

Effect of Heat Aging

Figure 5 shows the tan δ values of the unfilled CV vulcanizates before and after heat aging at 100°C for 120 h as a function of the temperature. The results, including those of the unfilled SEV and EV vulcanizates, are also listed in Table IV. The DMPs including the moduli (elastic and viscous), T_g, and tan δ of the unfilled vulcanizates varied significantly after aging at 100°C for 120 h. The

aging in the presence of oxygen in air at elevated temperature (100°C) caused very apparent increases in the T_g, and tan δ values at 0 and 60°C for unfilled vulcanizates with CV, SEV, and EV cure systems because of the changes in the crosslink structures. The differences that can be found in these results might be described as follows.

The unfilled CV, SEV, and EV vulcanizate specimens had similar T_g and tan δ values at temperatures near the tan δ peak, even near 0°C; the tan δ values at high temperatures, especially near 60°C, clearly increased in the order EV > SEV > CV before aging. After aging, the T_g and tan δ values of the unfilled CV, SEV, and EV vulcanizates decreased to varied extents in the order CV > SEV > EV. These results demonstrate that CV cured NR has the largest change in the DMP after aging, while the SEV and EV vulcanizates show similar changes in the DMPs. This can be considered a characteristic of polysulfidic crosslinks: namely, poor heat stability. That is to say, based on the different changes in the DMP for the three curing systems, it is reasonable that the dominant factor was the different aging resistances of the vulcanizates that were due to the different crosslink structures.

The heat aging of crosslinked rubber inevitably gives rise to changes in the crosslink structures as listed in Table V. The effect of the aging time on

Table V Crosslink Densities and Types for Three Unfilled Vulcanizates before and after Aerobic Aging at 100°C

Vulcanizates	Aging Time (h)	v_T	v_M	v_D	v_P
			($\times 10^5$ mol/mL)		
CV	0	5.12	0.15	1.56	3.41
	24	6.01	1.76	2.66	1.59
	72	6.12	2.64	2.72	0.76
	120	5.88	2.88	2.44	0.56
SEV	0	5.04	1.21	2.07	1.76
	24	6.13	3.08	2.17	0.88
	72	5.68	2.72	2.14	0.82
	120	4.74	2.08	1.90	0.76
EV	0	5.23	2.36	1.93	0.94
	24	6.28	4.20	1.51	0.57
	72	5.89	3.43	1.50	0.50
	120	4.32	2.41	1.51	0.50

v_M, Monosulfidic crosslink density; v_D, disulfidic crosslink density; v_P, polysulfidic crosslink density; and aging time 0 means before aging.
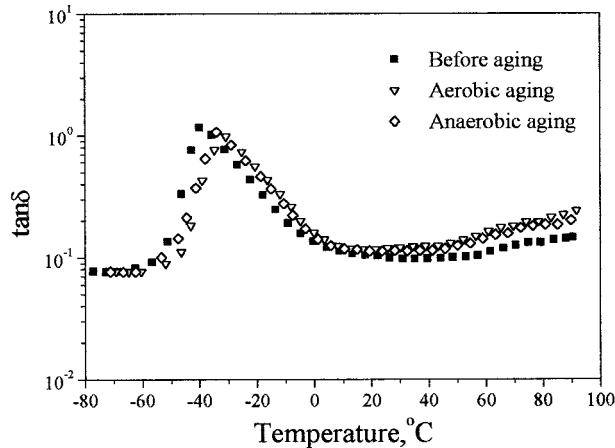
Figure 6 Comparisons of the tan δ before aerobic and anaerobic aging for 120 h at 100°C as a function of temperature for the N330-filled CV vulcanizate.

Figure 7 Comparisons of the tan δ before aerobic and anaerobic aging for 120 h at 100°C as a function of temperature for the N330-filled SEV vulcanizate.

the DMP for each cure system correlated well with the resistant to aging at 100°C in air. From this viewpoint, the large change in the total crosslink density and crosslink types of the CV vulcanizate can be considered as the major reasons for its greatest changes in DMP values in contrast with the other vulcanizates after aging for 120 h at 100°C in air.

However, it is not reasonable to simply connect the variation of the total crosslink density after aging with the DMP change. The very complicated degradation processes of the networks such as main chain scissions, and configuration changes, as well as changes of crosslink densities and types, should be occurring during the aging.

Effect of Aging Environments

Figures 6, 7, and 8 show the differences in the tan δ values for CV, SEV, and EV cured N330-filled vulcanizates, respectively, as a function of temperature before and after aging for 120 h at 100°C under aerobic (in air) and anaerobic (isolation from air) conditions. Their results including T_g and tan δ values at 0 and 60°C are listed in Table VI. The changes in the crosslink densities and types are given in Table VII.

In general, all three vulcanizates had higher T_g and tan δ values at 0 and 60°C when aged under aerobic conditions than under anaerobic conditions. This result indicated that the heat aging of NR vulcanizates at 100°C under aerobic and anaerobic conditions caused an apparent increase in the DMPs due to the change in the crosslink structures.
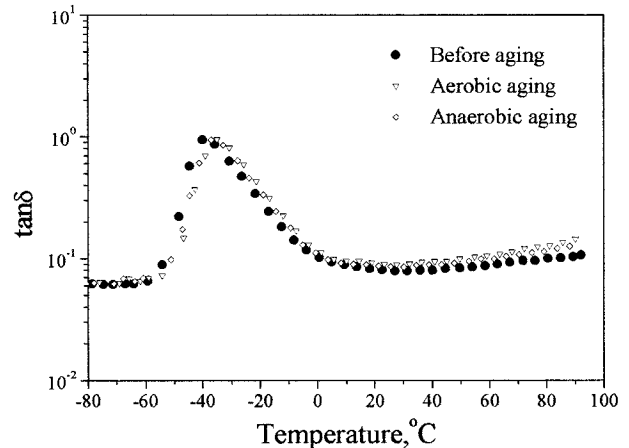
The aerobic heat aging of the CB-filled vulcanizates gave relatively higher T_g and tan δ values at 0 and 60°C than the anaerobic heat aging because the oxidative degradation of rubber vulcanizates caused the large changes in the network structures including the density, crosslink types, and chain scissions as shown in Table VII.

The filled CV vulcanizates showed a large change in T_g and tan δ values at 0 and 60°C compared with SEV and EV vulcanizates after aging for 120 h under aerobic and anaerobic conditions. Those values decreased in the order of filled EV > SEV > CV, which can be attributed to the fact that the highest concentration of polysul-
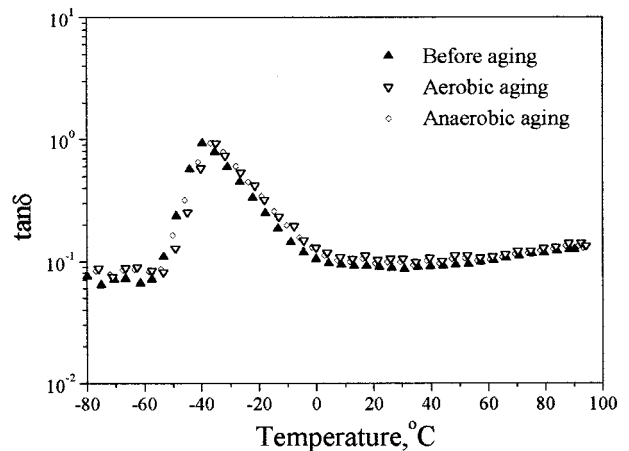

Figure 8 Comparisons of the tan δ before aerobic and anaerobic aging for 120 h at 100°C as a function of temperature for the N330-filled EV vulcanizate.

Table VI   Glass-Transition Temperature (T_g) and Mechanical Loss Factor (tan δ) at 0 and 60°C of N330-Filled Vulcanizates for Different Curing Systems before and after Anaerobic and Aerobic Aging at 100°C

Vulcanizates	Aging Time (h)	T_g (°C)		tan δ at 0°C		tan δ at 60°C	
		Aerobic	Anaerobic	Aerobic	Anaerobic	Aerobic	Anaerobic
CV	0		−40.1		0.110		0.088
	120	−30.0	−34.0	0.159	0.140	0.162	0.143
SEV	0		−39.8		0.104		0.098
	120	−35.0	−37.1	0.115	0.110	0.106	0.100
EV	0		−40.1		0.110		0.107
	120	−35.0	−36.8	0.117	0.113	0.109	0.109

Aging time 0 means before aging.

fidic crosslinks corresponds to the poorest resistance to heat aging.

CONCLUSIONS

The following conclusions can be drawn in the stress controlled DMP experiments for the unfilled and N330-filled vulcanizates cured with CV, SEV, and EV cure systems having similar levels of total crosslink densities and moduli and quite different crosslink types.

1. Unfilled vulcanizates cured with the CV, SEV, and EV curing systems had about the same T_g and tan δ values at about 0°C. The different tan δ values at relatively high temperatures such as 60°C before heat aging and their tan δ values decreased in the order EV > SEV > CV. However, the

N330-filled vulcanizates cured with the three curing systems had about the same T_g and tan δ at 0°C, and the tan δ varied at 60°C in the decreasing order EV > SEV > CV. The presence of CB in the filled NR vulcanizates made the moduli, T_g, and tan δ values through the whole range of temperatures higher than the unfilled vulcanizates before aging.

2. Aerobic heat aging in the surrounding air led to the increase of T_g and tan δ through the whole range of temperatures that was mainly due to the changes in the total crosslink density and crosslink types. The CV vulcanizate showed the highest change in DMPs, which was attributable to the poorest resistance to heat aging of the polysulfidic crosslinks.

3. Aerobic heat aging of the N330-filled vulcanizates caused more apparent change in the DMPs than anaerobic heat aging of the same specimens because the oxidation of the rubber caused a high level of reversion and had a dominant effect on the DMPs.

Table VII   Moduli, Crosslink Densities, and Types of Three N330-Filled Vulcanizates before and after Aerobic Aging for 120 h at 100°C

Vulcanizates	Aging Condition	v_T	v_M	v_D	v_P
			($\times 10^5$ mol/mL)		
CV	None	5.55	0.37	1.63	3.55
	Anaerobic	7.11	3.07	2.75	1.29
	Aerobic	6.38	2.88	2.58	0.92
SEV	None	5.47	2.26	1.91	1.30
	Anaerobic	7.48	5.35	1.65	0.78
	Aerobic	7.12	4.43	1.88	0.81
EV	None	5.46	2.58	1.95	0.93
	Anaerobic	7.51	5.75	1.36	0.60
	Aerobic	7.23	4.55	1.76	0.92

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