Tensile Retraction Measurements. V. The Effect of Carbon Black on the Cross-Link Density of Cured Rubber

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SYNOPSIS

Tensile retraction measurements have been made on the same SBR filled with 50 phr of 10 different carbon blacks. The slopes and intercepts determined from the plots against λ_{max} were determined in three different elongation ranges. These carbon blacks were chosen to have a variety of different surface areas and structures such that the influence of these features on the slopes and intercepts could be measured. The tensile retraction parameters determined were also evaluated at elevated temperatures and Arrhenius plots were made. The activation energies calculated from these plots showed that the structure and surface area of the carbon blacks had no effect on the process being measured. A series of different molecular weight SBRs were also made by anionic techniques to have 0, 1, and 2 tributyltin end groups. The changes in the constants determined from tensile retraction measurement on these cured filled stocks were explained in terms of the number of loose end groups still present after reaction with the carbon black. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, an improved method to measure the molecular weight between cross-links (M_c) of elastomers has been developed using the retractive portion of a tensile stress–strain (σ–λ) curve and the rubber elasticity theory.[1–3] The initial work of Fedors,[1] with gum stocks, concluded that the M_c was best determined after extension to a λ_{max} = 2.6. Hergenrother[2] later showed that fillers could be accounted for in the calculations by using strain amplification (Λ).[4,5] He also showed that the most meaningful results were obtained by measuring M_c at different values of Λ_{max} and then extrapolating these values to a Λ_{max} = 1. This treatment gave a characteristic intercept (M_r), which was defined as the molecular weight between chain restrictions. The slope (S) of this plot gives a measure of the mobility of the nonchemical cross-links with changes in the Λ_{max} employed. Eisele and Muller[3] exercised filled stocks at high values of Λ_{max} before measuring the M_c. These stocks were then tested at lesser extensions, thereby eliminating the need to extrapolate

to Λ_{max} = 1 and the associated slope. In all cases, the M_c was calculated by some form of eq. (1)[6]:

$$M_c = \frac{dXRT(\Lambda - \Lambda^{-2})}{\sigma} \quad (1)$$

where d is the density of the stock; X, the Guth-Gold[4] filler factor; Λ, the actual strain associated with the stress (σ) that was measured after being corrected for strain amplification[5]; R, the gas constant; and T, the absolute temperature. The results obtained from these tensile retraction measurements showed the procedure to give a rapid, accurate, and reproducible measure of M_c in a nondestructive fashion.

If the samples being tested were carefully handled, such that they were not prestrained, additional information could be extracted from the retraction curve. This included a measurement of the interaction between the polymer chains[7] as well as the pulling out of loose ends through the cross-linked matrix.[8]

Originally, the effect of fillers on the slopes and intercepts was observed only in the high-strain test region.[2] With the advent of improved testing procedures, it is now possible to look at results in both the low and intermediate elongation[8] regions. Cured

gum stocks were shown over these lower elongation ranges to give information as to the interactions of the polymer chain with itself or with the loose end group that was being pulled out of the cured matrix. The effect of inert or reinforcing fillers on the M_c determined in these ranges will be described.

Thus, identically compounded SBRs were cured with carbon blacks in which the structure and surface area was varied over a wide range, so that the effect on the full tensile retraction measurements could be made. In addition, dynamic properties were also measured and related to the parameters determined by tensile retraction.

Also of interest was the effect that the molecular weight of the polymer and the introduction of functional end groups would have on the tensile retraction measurements. For this study, a series of SBR polymers were prepared at the same T_g and varying number average molecular weight, with 0, 1, or 2 tributyltin end groups per polymer chain. Identical compounding and curing with the same carbon black gave a series of stocks that had a different number of end groups that were chemically reacted with carbon black.[9] The effect that these changes had on tensile retraction measurements and dynamic properties will be discussed.

EXPERIMENTAL

Test Procedure

The procedure described previously[8] was used except that a straightening routine was incorporated into the program to remove any slack that was introduced during the mounting of the cylindrical ribs on the end of the test piece into the fixture. This resulted in the test specimen being preloaded with 0.01 lb prior to testing. The additional travel measured by this preloading was then added to the initial span to give the true original length, l_0, that was then used in the calculations. This modification prevented loss of the low extension data by assuring that all the travel associated with these measurements was accompanied by loading the sample to the measured elongation. All the equations and calculations were done as before.[7,8]

The dynamic properties of the vulcanizate were measured on a 14 × 9 mm-diameter button on the Rheometrics dynamic mechanical spectrometer (RDA II) at a frequency of 0.5 Hz from 0.25 to 14.6% strain at either 25 or 65°C.

Black Study

These stocks were prepared with an emulsion polymerized SBR that had a number average molecular weight of 84,000 g/mol and a molecular weight distribution of 4.94. The copolymer contained 23.9% styrene, of which 2.2% was present as blocks of, at least, 4 monomer units. The polybutadiene portion consisted of a microstructure of 20% 1,2-, 5% cis-1,4-, and 75% trans-1,4-. The T_g of this copolymer was −50°C. This rubber was used to evaluate the effect of different structures and surface areas of the carbon black on the tensile retraction constants.

Compounding of the emulsion SBR was done in a 320 g Brabender with 50 parts per hundred (phr) of carbon black, 1.8 phr of sulfur, 1.0 phr of an accelerator, 3 phr of zinc oxide, 2 phr of stearic acid, and 1 phr of an alkylated para-phenylenediamine antioxidant (AO). These stocks, which are designated by the letter for the carbon black used, were cured at 150°C for 40 min. Table I gives the ASTM D-1765 designation of the I_2 absorption, DBP structure, and N_2 surface area values of the carbon blacks used. Because of the similarity between the I_2 and the N_2 values, only the N_2 surface area correlations are made in the remainder of the paper.

Samples were prepared with less than 50 phr of carbon black and will be designated with the sample letter, as in Table I, followed by the level of black charged in the parentheses. Thus, a cured copolymer with 25 phr of N339 black would be sample G(25). The level of sulfur was increased slightly with these stocks to increase the strength of those containing little or no filler to a level that would give an adequate deflection on the 1 lb load cell used.

Table I   Characterization of the Different Carbon Blacks Used

Sample No.	Type N	I_2 (g/kg)	DBP (10^{-5} g/kg)	N_2 (10^3 m²/kg)
A	990	10	36	10
B	880	13	35	12
C	762	23	65	24
D	650	36	122	36
E	351	67	120	72
F	343	92	130	100
G	339	90	120	104
H	299	108	124	109
I	220	121	116	121
J	110	147	112	148

Molecular Weight Study

A series of anionically polymerized SBRs were prepared in solution by standard techniques. These 20% styrene and 60% vinyl PBD copolymers were prepared over a range of molecular weights with T_g's of about $-36°C$. Termination of the live cement was done with either tributyltin chloride or alcohol to give the desired number of tin end groups. The characteristics of these polymers by GPC, IR, and thermal analysis are listed in Table II.

These polymers were mixed in a 240 g Brabender with 55 phr of N351 carbon black, 10 phr oil, 3 phr ZnO, 2 phr wax, and 1 phr AO. The curatives of 1.5 phr sulfur, 2 phr stearic acid, and 1 phr accelerator were added on a warm mill. The stocks were cured 25 min at 166°C.

RESULTS AND DISCUSSION

Tensile retraction measurements were made on samples A–J at ambient temperature in the manner described. The experimental curve was best fit by the three linear equations[6-8] that were previously used to evaluate these types of relationships. The results obtained are summarized on Table III. In all cases, the linear least-squares correlation coefficient (r) was, at least, .99 or better.

A typical tensile retraction curve can be seen in Figure 1 for the data collected with **G**. At the highest strains region, i.e., for the data above 36% E (λ_1), an excellent linear relationship was obtained by eq. (2):

$$M_c = M_r + S \, (\Lambda_{max} - 1) = d/\nu_e \qquad (2)$$

where M_c is the molecular weight between crosslinks in g/mol; M_r, the molecular weight between chain restrictions in g/mol; S, the slope in g/mol; Λ_{max}, the maximum strain for the measurement being made corrected for strain amplification; ν_e, the effective cross-link density in mol/cc; and d, the density of the stock. This equation holds for the data collected from λ_1, the lowest λ level that still was described by eq. (2), to the maximum λ used for the test. The changes occurring in this region have been attributed to the cross-links due to covalent bonds and entanglements.

In the intermediate strain range used for this sample, from 5% to 36% E, the deviation from eq. (2) can be expressed as $\Delta\nu_e$, which is the difference between the ν_o (observed cross-link density) and the ν_c (calculated cross-link density) from eq. (2). These data points are plotted in Figure 2 from which the linear region can be described by eq. (3):

$$\log(\Delta\nu_e) = m + s(\Lambda_{max} - 1) \qquad (3)$$

Table II   Characterization of Solution-polymerized SBRs Used in This Study

Polymer No.	Sn End Groups	STY (%)	V-PBD (%)	T_g (°C)	$M_n \times 10^{-3}$ (g/mol)	M_w/M_n
1	0	21.4	57.3	−34.6	80.2	1.11
2	0	20.9	58.5	−36.0	94.4	1.11
3	0	21.0	58.1	−34.7	115.1	1.13
4	0	21.1	52.9	−37.8	178.8	1.32
5	0	20.4	53.6	−37.0	188.4	1.24
6	1	20.1	62.0	−35.4	65.8	1.16
7	1	21.7	62.2	−33.4	75.7	1.22
8	1	22.4	60.2	−31.2	134.0	1.23
9	1	22.0	64.6	−29.8	156.0	1.27
10	1	21.5	66.2	−34.1	181.1	1.37
11	1	21.5	62.2	−34.1	263.9	1.49
12	1	21.8	60.7	−37.8	384.9	1.50
13	2	21.4	60.8	−33.8	76.4	1.17
14	2	22.3	58.0	−33.5	95.8	1.23
15	2	21.0	58.6	−33.1	136.5	1.24
16	2	20.6	53.4	−36.2	167.9	1.24
17	2	20.6	53.4	−36.1	182.5	1.30

Table III   Summary of Constants from Cured Samples Containing Various Blacks

Sample No.	M_r (g/mol)	S (g/mol)	β (g/mol)	s	γ (g/mol)	t
A	14,500	1,070	300,000	−5.230	120,000	−42.51
B	14,300	1,210	93,900	−3.737	152,000	−33.82
C	10,200	1,040	118,000	−3.635	90,000	−44.04
D	8,000	1,360	22,100	−5.146	29,200	−35.25
E	8,450	1,370	13,500	−3.748	21,300	−34.24
F	8,040	1,420	16,900	−2.003	10,900	−15.63
G	8,620	1,370	20,100	−1.772	10,600	−16.51
H	8,420	1,370	16,700	−1.679	15,100	−13.33
I	8,400	1,460	13,600	−1.727	7,890	−14.75
J	8,640	1,450	16,100	−1.638	10,900	−11.56[a]

[a] A fourth linear first-order region was detected with this sample that covered the first 6 pulls (0.5–1.5% elongation) of the test. A slope of −55.08, intercept of −3.816, and a linear least-square correlation coefficient of −.9838 was determined.

where s is the slope and m is the intercept. The intercept can be expressed as an M_c characteristic of this region by, $\beta = 10^{-m}$, which is in g/mol. The phenomena measured by this strain region have been postulated[8] as being due to rearrangements of the polymer chain and the frictional forces acting on the chain as it is being pulled through the cross-linked network.

The lowest strain region, below about 5–0.5% E, also deviates from the relationship described by eq. (3). The calculation of the difference between the observed and calculated values of eq. (3) gave a $\Delta\Delta\nu_e$

in the same fashion as above. Plotting these data in Figure 3 gave the linear region described by eq. (4):

$$\log(\Delta\Delta\nu_e) = n + t(\Lambda_{max} - 1) \qquad (4)$$

where t is the slope and n is the intercept. The intercept can be expressed as an M_c characteristic of this region by, $\gamma = 10^{-n}$, which is in g/mol. The process measured here probably is due to the pullout of the loose ends of the polymer both from the filler and through the cross-linked network.

The values of the intercepts (M_r, β, and γ) and slopes (S, s, and t) that are listed in Table III were
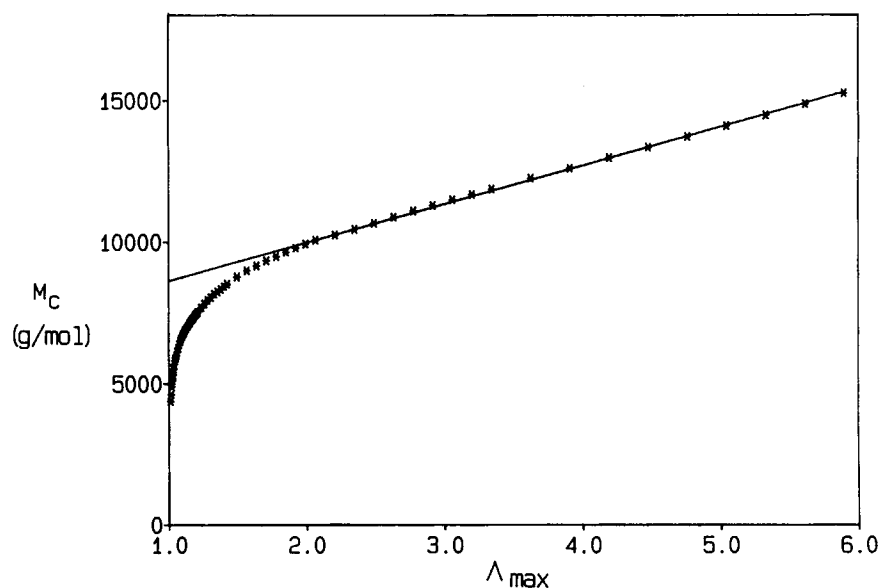

Figure 1 M_c vs. Λ_{max} for **G** at 24°C, where the line was drawn using eq. (2) with M_r = 8620 g/mol, S = 1370 g/mol, and r = .9996.
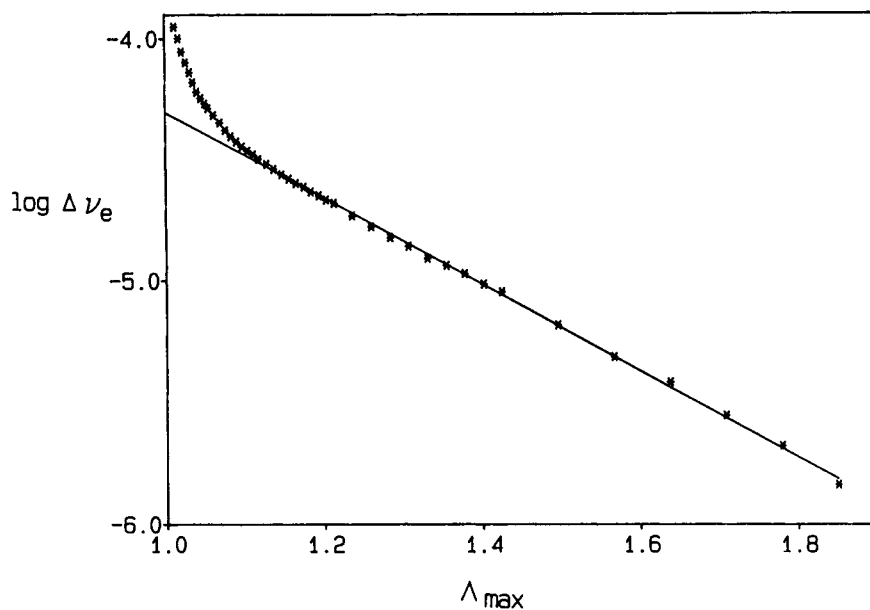
Figure 2   Log $\Delta\nu_e$ vs. Λ_{max} for **G** at 24°C, where the line was drawn using eq. (3) with m = -4.304, $s = -1.772$, and $r = -.9995$.

observed to change depending upon the characteristics of the carbon black that were used (see Table I). Linear plots with $r \geq .92$ were obtained when the structure as determined by DBP or the N_2 surface area of the carbon blacks were plotted against these parameters. Table IV shows the slope and intercept of the associated linear least-squared line, along with the value of r for these relationships. In general, the structure of the carbon had the largest influence on the parameters determined by eqs. (2) and (3), whereas the surface area of the filler had a larger effect on λ_1 and the parameters in eq. (4).
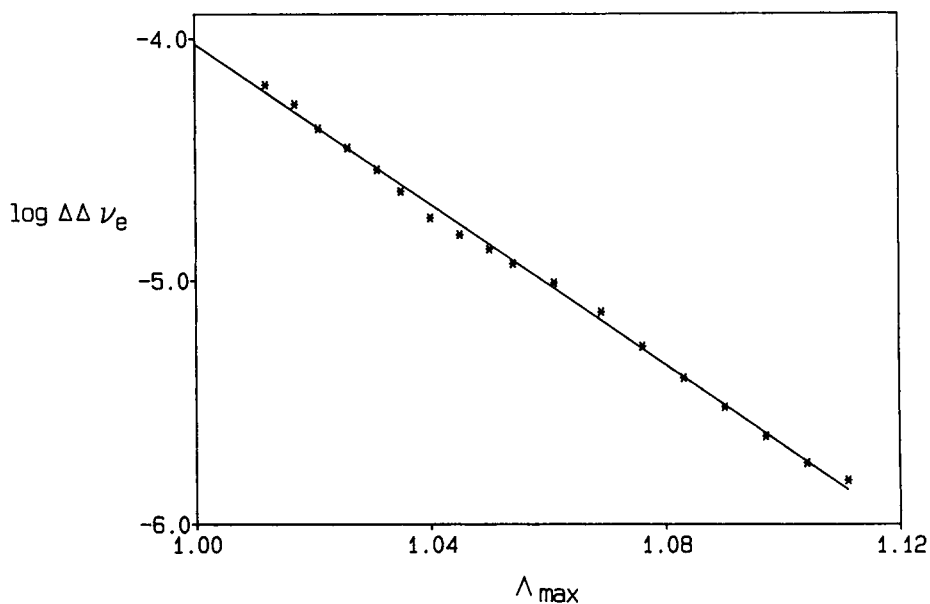

Figure 3   Log $\Delta\Delta\nu_e$ vs. Λ_{max} for **G** at 24°C, where the line was drawn using eq. (4) with $n = -4.025$, $t = -16.511$, and $r = -.9988$.

Table IV Linear Least-square Fits for Tensile Retraction Parameters vs. Carbon Black Characteristics

Parameter	Slope	Intercept	r
For plots vs. DBP no.			
M_r (g/mol)	-64.52	16,100.	-0.9647
m	0.0119	-5.681	0.9356
γ	$-1393.$	183,000.	-0.9724
S/M_r	0.00102	0.0426	0.9780
$\nu_e \times 10^5$ (mol/g)	0.0557	5.283	0.9823
$\Delta\nu_e \times 10^6$ (mol/g)	0.645	-18.98	0.9000
For plots vs. N_2 surface area			
λ_1	0.00644	1.074	0.9414
t	0.239	-43.82	0.9277
n	0.00939	-5.093	0.9588
$\Delta\Delta\nu_e \times 10^5$ (mol/g)	0.0891	-0.3473	0.9209

Different Carbon Black Levels

When the level of carbon black loading was varied from 0 to 50 phr in formulation **G**, the values listed in Table V were measured at ambient temperature by tensile retraction. Only small variations in M_r and S were observed with the increase in the level of filler. The decrease in the M_r measured with these samples, compared to sample **G**, was caused by a small increase in the sulfur level to 2 phr for this series. This change was made so that the stocks with low filler levels would be in a higher and more convenient range of stress, thereby minimizing errors in reading the load cell for this measurement.

At intermediate strain, the interactions, β and s, showed a steady decrease with the increasing filler content. This seems most reasonable since the presence of additional filler enhances the interaction of chain ends with the cross-linked matrix. Although the lowest strain region shows an apparent random variation with filler level, it must be remembered that two processes are most probably occurring simultaneously. These are the previously observed pullout of loose chain ends and the debonding of the polymer chain absorbed on the carbon black. Both of these processes have been seen with sample **J** (see footnote to Table III).

Arrhenius Relationships

A number of stocks containing different types of carbon black were tested at elevated temperatures. The value of the constants evaluated from such testing are summarized on Table VI. When the logarithm of the constants evaluated was plotted against the reciprocal of the absolute temperature, good Arrhenius plots were obtained in most cases. The Arrhenius plots that were obtained included the data listed in Table III in order to give the largest temperature range possible. The slopes obtained from the plots are given in Table VII. Some sample-to-sample variations were observed for each tensile retraction constant that was evaluated, but no significance was attached to it because of the errors associated with the measurements. The slopes that

Table V Tensile Retraction Constants from Emulsion SBR Containing Varying Levels of Black (N339)

Sample No.	M_r (g/mol)	S (g/mol)	β (g/mol)	s	γ (g/mol)	t
G(0)	5,820	1,090	42,500	-2.686	60,900	-29.75
G(12.5)	6,330	986	37,700	-2.419	24,500	-28.29
G(25)	6,930	1,300	23,200	-2.340	113,000	-13.15
G(37.5)	6,090	1,110	17,800	-2.336	17,700	-14.15
G(50)	6,580	1,220	10,500	-1.886	8,470	-14.51

Table VI   Tensile Retraction Values from Testing at Elevated Temperatures

Sample at °C	M_r (g/mol)	S (g/mol)	β (g/mol)	s	γ (g/mol)	t
A-100	16,670	784				
A-74	15,760	728				
B-100	14,810	740				
B-75	15,510	879				
B-50	14,840	1050				
F-100	8,580	1980	36,100	−12.060		
F-75	9,380	1040	32,200	−2.702	17,750	−37.390
F-50	8,870	1160	23,600	−2.655	25,300	−23.200
F-23	8,060	1340	18,100	−1.710	9,860	−15.460
G-126	10,420	1030				
G-100	8,900	830				
G-76	9,910	1130	33,300	−5.427		
G-52	9,020	1290	15,100	−4.558		
G-25	8,480	1480	17,600	−2.710	13,400	−16.260
I-100	9,890	1130	49,100	−2.584	27,500	−21.580
I-75	9,610	1190	22,900	−3.317	24,200	−23.390
I-51	8,980	1340	17,060	−2.967	20,730	−20.730
I-23	8,330	1480	13,000	−1.849	6,780	−16.270
J-126	10,700	1390	56,600	−2.955	103,000	−15.380
J-101	10,400	1060	50,000	−2.609	59,000	−13.490
J-50	9,690	1300	32,800	−1.681	26,700	−5.174

ranged from −44 to −626 deg^{-1} would represent processes with activation energies in the range of 0.2–2.9 kcal/mol. This is the same energy range that was previously measured for these activation energies in gum vulcanizates.[8] Previously, the low activation energies measured were attributed to the pullout of loose chain ends, the interaction of these loose chain ends with the cross-linked matrix, and the deformation of the cross-linked network. These data are consistent with that postulate. Thus, it must be concluded that the type of carbon black used does not affect the temperature response of the constants measured by tensile retraction.

The measurable interactions of the various carbon blacks with the polymer chain in the low-strain regions were observed to be rapidly lost as the temperature was increased. This happened more readily as the reinforcing nature of the black was reduced (e.g., higher N values). These interactions, which are at most 3 kcal/mol, must be interfering with the measurement of a stronger reinforcing mechanism that must also be present. By inference, the reinforcement imparted by the black must have a much higher activation energy, which would suggest that it may be in the order of a chemical bond.

Molecular Weight and Reactive End Study

The testing of Samples 1–17 by tensile retraction gave the constants of eqs. (2)–(4), which are listed in Table VIII. As the molecular weight of the copolymer was increased, the measured M_r and S decreased. This was the expected response since a higher molecular weight polymer would require fewer cross-links to reach the gel point. Thus, if the same number of cross-links are produced in each

Table VII   Slopes from the Arrhenius Plots of Constants Evaluated Using Different Carbon Blacks

Sample No	Value of the Slope (deg^{-1})					
	M_r	S	m	s	n	t
A	−84	221				
B	−71	297				
F	−131	218	−44	−406	−58	−625
G	−136	246	−52	−626		
I	−111	175	−78	−515	−90	−315
J	−104	201	−59	−328	−105	−290

Table VIII Tensile Retraction Constants from Testing Polymers with Different Molecular Weights and End Groups Filled with N-351

Sample No.	M_r (g/mol)	S (g/mol)	β (g/mol)	s	γ (g/mol)	t
1	14,620	3,015	9,195	-1.343	3,784	-11.585
2	12,350	2,743	9,211	-1.373	3,696	-11.657
3	11,630	2,375	10,350	-1.329	4,716	-11.596
4	11,110	1,963	15,290	-1.267	7,641	-11.418
5	10,760	1,831	15,750	-1.272	8,101	-11.418
6	16,810	3,261	18,980	-1.294	11,100	-10.576
7	15,410	2,519	26,040	-1.163	15,890	-9.024
8	12,050	1,845	24,440	-1.214	15,720	-9.522
9	11,810	1,632	23,230	-1.155	14,390	-9.272
10	11,480	1,532	23,860	-1.151	15,830	-8.830
11	11,010	1,384	23,710	-1.057	12,320	-8.162
12	10,890	1,518	19,680	-1.099	10,100	-8.357
13	14,440	2,042	41,220	-1.067	36,850	-6.682
14	12,380	1,900	70,890	-1.004	48,310	-7.287
15	12,150	1,510	53,800	-0.958	34,650	-8.879
16	11,750	1,495	48,110	-1.043	35,320	-8.879
17	11,490	1,475	36,210	-1.088	19,020	-8.226

stock during cure, then the higher molecular weight polymer will have a larger portion of effective cross-links. The linear least-squares straight line obtained from the plot of $1/M_n$ vs. M_r had $r = .92$.

The shift factors,[7] which have been used to correct the tensile retraction measurements to a constant test rate of 5% per minute, also gave a linear plot with M_r (Fig. 4). An $r = .983$ was measured for the line described by this plot. This type of corre-

lation should be expected, since the process measured consists of the moving of polymer chains through a cured matrix. Thus, an increase in the ν_e would be expected to reduce the mobility of all the macromolecular units (reduce the shift factor) as they are pulled out of the network that has become more cross-linked.

The values of β, γ, s, and t all showed a steady increase for those samples that had no tributyltin
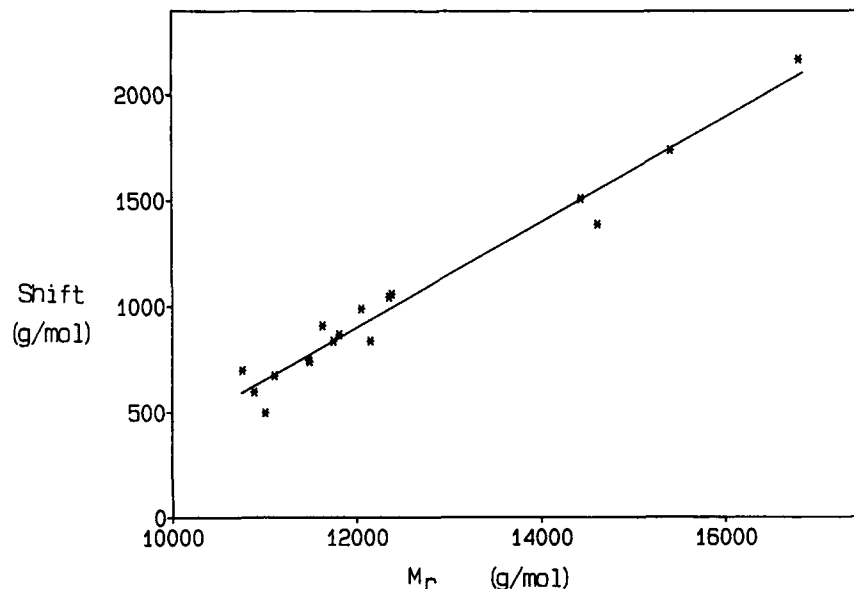

Figure 4 Shift factor that was used per decade of change in the testing rate vs. M_r for polymers **1–17**.

(TBT) end groups (**1–5**). The introduction of one TBT end group, polymers **6–12,** generally showed the same trend. When two TBT end groups were introduced into the polymers, significant changes were seen in the tensile retraction parameters determined for polymers **13–17.** The changes in these parameters for the polymers containing a different number of TBT ends per molecule are important. The number of TBT end groups now has the predominate influence on the values of the tensile retraction parameters measured. The effect of the molecular weight of the polymer on these parameters only has a secondary influence because of the reactions that the TBT groups can undergo. This will be further discussed in the following section.

Dynamic Mechanical Properties

A summary of some of the important values measured during strain sweeps on cured polymer samples **A–J** is shown in Table IX. At the two temperatures studied, the values of the tan δ, $\Delta G'$, and G'' all increased with increasing reinforcing nature of the carbon black. Lower values, of course, were obtained at the higher test temperature. Good linear least-squared relationships of the rheological properties to the surface area of the carbon black were obtained with $r \geq .96$.

Interesting plots were obtained when tan δ, $\Delta G'$, or G'' were plotted against the tensile retraction parameters required to fit eq. (4). Thus t, n, and $1/\gamma$ all gave excellent straight-line relationships when they were plotted against the results obtained from the dynamic measurements listed in Table IX. The values for r varied from $> .96$ with n to $> .92$ with t or $1/\gamma$.

The dynamic elastic modulus (G'), which is related to the filler level and cross-link density, was followed over the 0.25–15% strain range. The $\Delta G'$, which is the difference between the maximum and the minimum values of G', has been used to give a measure of the interaction of the carbon black with itself (the Payne effect[10]). These data show that the more reinforcing a carbon black becomes, the more difficult it is to disperse into rubber.

The dynamic loss modulus (G'') is related to the

Table IX   Significant Parameters Measured by Dynamic Testing of Elastomers Containing Different Carbon Blacks

| Polymer No. | Dynes/cm^2 | | | | | tan δ at 7% E |
| | at 14.6% E | | | $\Delta G''$ | | |
	$G' \times 10^{-7}$	$G'' \times 10^{-6}$	$\Delta G' \times 10^{-7}$	$\times 10^{-6}$	% E_{max}	
			Measured at 24°C			
A	1.474	1.238	0.359	0.150	3.98	0.0848
B	1.520	1.419	0.539	0.260	4.48	0.0963
C	2.018	2.000	0.774	0.421	2.98	0.1013
D	2.814	3.474	1.445	1.171	1.49	0.1293
E	2.831	4.252	2.196	2.085	1.25	0.1618
F	3.268	5.460	3.266	3.455	1.49	0.1808
G	2.956	4.961	2.812	2.965	1.25	0.1793
H	3.025	5.129	3.045	3.064	1.25	0.1808
I	3.168	5.682	4.135	4.378	1.25	0.1940
J	2.932	5.313	3.828	3.552	1.49	0.1925
			Measured at 65°C			
A	1.426	0.895	0.296	0.121	4.73	0.0657
B	1.496	1.065	0.425	0.230	4.73	0.0777
C	1.927	1.379	0.488	0.318	3.23	0.0780
D	2.644	2.484	0.885	0.717	1.49	0.1031
E	2.548	2.838	1.404	1.471	1.74	0.1276
F	2.577	3.381	1.830	1.893	1.25	0.1474
G	2.526	3.071	1.609	1.667	1.25	0.1373
H	2.460	3.235	1.785	1.867	1.49	0.1495
I	2.571	3.433	2.278	2.653	1.00	0.1537
J	2.471	3.488	2.336	2.431	1.00	0.1607

frictional forces between polymer chains and the concentration of end groups. The difference between the maximum and minimum value, $\Delta G''$, is also listed and represents a measure of the microdispersion of the carbon black. The correlation analysis performed with these data show similar responses for G'' and $\Delta G''$. As a result, only the relationships with G'' will be discussed. As the reinforcing nature of the black increased, a steady decrease in the microdispersion can be seen. The $\% E_{max}$ associated with the $\Delta G''$ also showed a steady decrease with the increased reinforcing nature of the filler.

The tan δ or G''/G' was evaluated at 7% E as a convenient point to measure the hysteresis of the vulcanizate. Of course, the lower the value of tan δ, the less energy the network would lose upon being deformed. Poor microdispersion of the carbon black accounts for a large part of the increase in tan δ with the decreasing N value of the carbon blacks.

Similar measurements were also made on the stocks of different molecular weight containing varying levels of TBT end groups, samples **1–17**, and these are summarized in Table X. Plotting the listed values of tan δ, and G'' vs. the shift factor, ν_e, and S showed the presence of different responses for the polymers dependent on the number of TBT attached to the chain. The best linear least-squared

straight lines were obtained only if the polymers were grouped according to the number of TBT end groups present. Figures 5–7 showed the data and the linear least-squares line drawn for the relationship of tan δ to the parameters listed above. Similar plots were also obtained with G'' and $\Delta G'$, with slightly poorer r values. These plots indicate that the tensile retraction measurements are responding to the number of unreacted ends present in the cured stock. Thus, the more complete the reaction with carbon black, then the fewer number of imperfections (lose chain ends) that are present. The data in each of these plots are best-fitted by using three straight lines, depending upon whether the polymer had 0, 1, or 2 TBT end groups. These three lines show that, as the number of TBT ends increase on a copolymer, the number of loose ends has a corresponding decrease. Since TBT end groups are known to react with carbon black and reduce the hysteresis of the vulcanizate,[9] the measurement of these polymer–filler interactions show the utility of tensile retraction measurements.

As previously seen in Figures 5–7, the presence of TBT end groups has a profound influence on the interactions of the parameters measured. The values of tan δ, $\Delta G'$, and G'' are all greatly dependent upon the presence of the number of TBT end groups on

Table X   Dynamic Properties Measured at 24°C on Elastomers Containing Varying Levels of TBT and N-351 Carbon Black

| Polymer No.	Dynes/cm²					tan δ at 7% E
	at 14.6% E			$\Delta G''$		
	$G' \times 10^{-7}$	$G'' \times 10^{-6}$	$\Delta G' \times 10^{-7}$	$\times 10^{-6}$	$\% E_{max}$	
1	2.470	6.326	5.775	8.334	0.85	0.2875
2	2.552	5.777	5.464	6.093	1.44	0.2533
3	2.467	4.848	3.623	4.284	1.24	0.2190
4	2.070	2.589	1.362	1.063	1.45	0.1318
5	2.110	2.574	1.442	1.181	1.25	0.1305
6	1.793	3.277	0.766	0.804	0.45	0.1824
7	1.774	2.788	0.770	0.687	1.05	0.1575
8	1.885	2.317	0.798	0.733	1.05	0.1263
9	1.924	2.187	0.892	0.705	0.85	0.1183
10	1.894	2.144	0.999	0.736	1.45	0.1187
11	1.949	2.158	1.277	0.916	1.25	0.1181
12	2.081	2.667	1.750	1.182	2.04	0.1367
13	1.796	2.535	0.697	0.698	0.65	0.1419
14	1.785	2.129	0.709	0.573	0.85	0.1205
15	1.861	1.964	0.765	0.706	0.25	0.1079
16	1.905	1.827	0.710	0.650	0.45	0.0993
17	1.853	1.808	0.759	0.661	0.85	0.1020
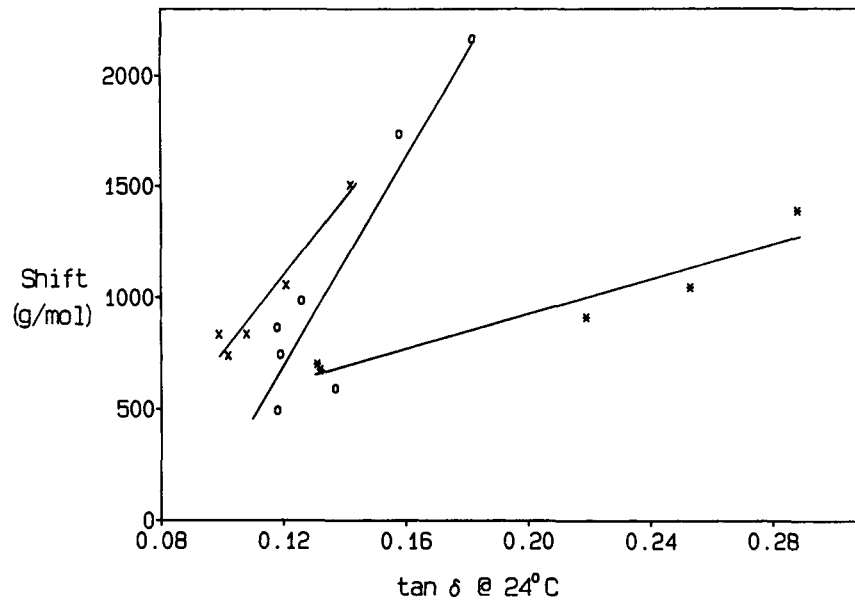
Figure 5 Shift factor vs. tan δ at 24°C for polymers **1–17** with (*) no TBT, (O) 1 TBT, and (x) 2 TBT end groups. The lines drawn have an r of .95, .92, and .97, respectively.

the polymer. This suggests that not only immobilization of some of the ends of the polymer has occurred but also better dispersion of the carbon black on a microscale has been obtained by the presence of the TBT end group.

A plot of $\Delta G'$ vs. n, the intercept from the lowest-strain region of the tensile retraction measurements for samples **1–17,** can be seen in Figure 8. This also

shows that the addition of one and two TBT groups to the end of the SBR greatly improves the interaction of the carbon black with the polymer. The fact that three separate lines are needed to fit the data, in contrast to the response seen with the series prepared with different structure blacks, indicates the strong influence that the number of TBT groups has on this parameter and on this strain range. The
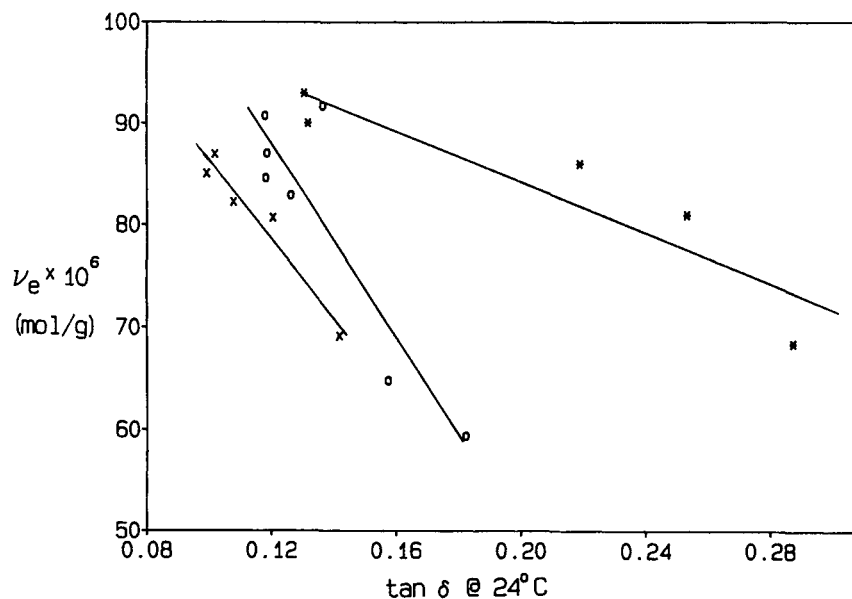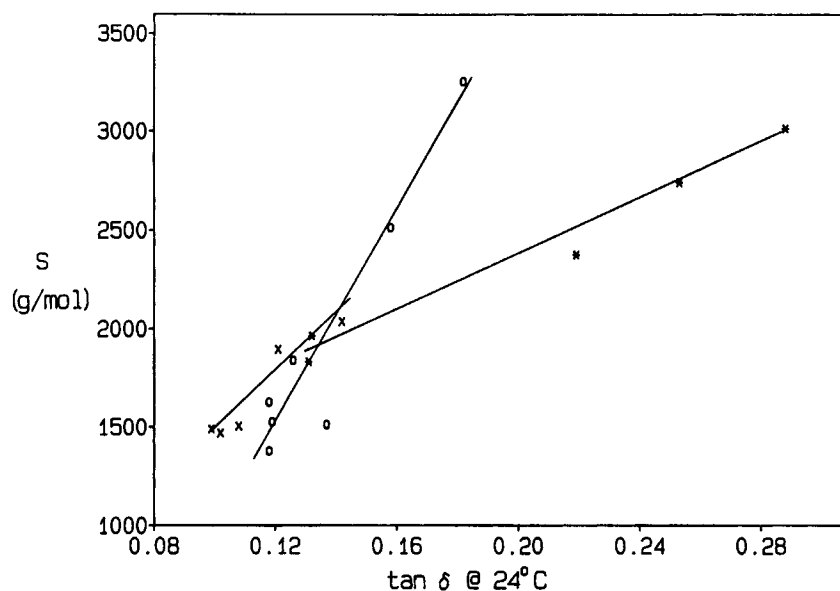

Figure 6 ν_e vs. tan δ at 24°C for polymers **1–17** with (*) no TBT, (O) 1 TBT, and (x) 2 TBT end groups. The lines drawn have an r of $-.92$, $-.90$, and $-.97$, respectively.

Figure 7 S from eq. (2) vs. tan δ at 24°C for polymers **1–17** with (∗) no TBT, (○) 1 TBT, and (x) 2 TBT end groups. The lines drawn have an r of .99, .96, and .93, respectively.

polymers without any TBT end groups showed the expected effect of increasing polymer M_n, giving a reduced value of $\Delta G'$. However, this effect was not as dramatic once at least one TBT group was introduced into the polymer.

In addition, a plot of tan δ vs. the reciprocal of mixing energy times M_n (Fig. 9) also showed the effect of the three types of polymer used for this study. This plot shows three separate linear regions depending on whether the polymer had 0, 1, or 2

TBT groups. The largest change per increment of M_n increase was inversely proportional to the number of TBT groups present on the SBRs.

The two highest M_n polymers prepared with one TBT group (**11** and **12**) were included since they had an unusually low mix energy that was brought about by their crumbling during processing.

These two samples gave data points that were observed not to give as good of fit to the line for one TBT end group when plotted against $1/M_n$. How-
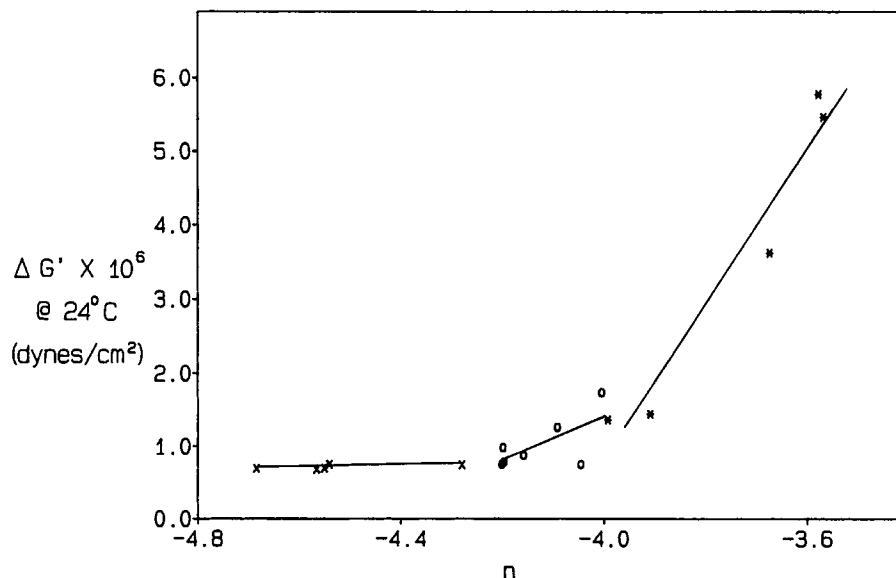

Figure 8 $\Delta G'$ at 24°C from dynamic mechanical testing vs. n from eq. (4) for polymers **1–17** with (∗) no TBT, (○) 1 TBT, and (x) 2 TBT end groups.
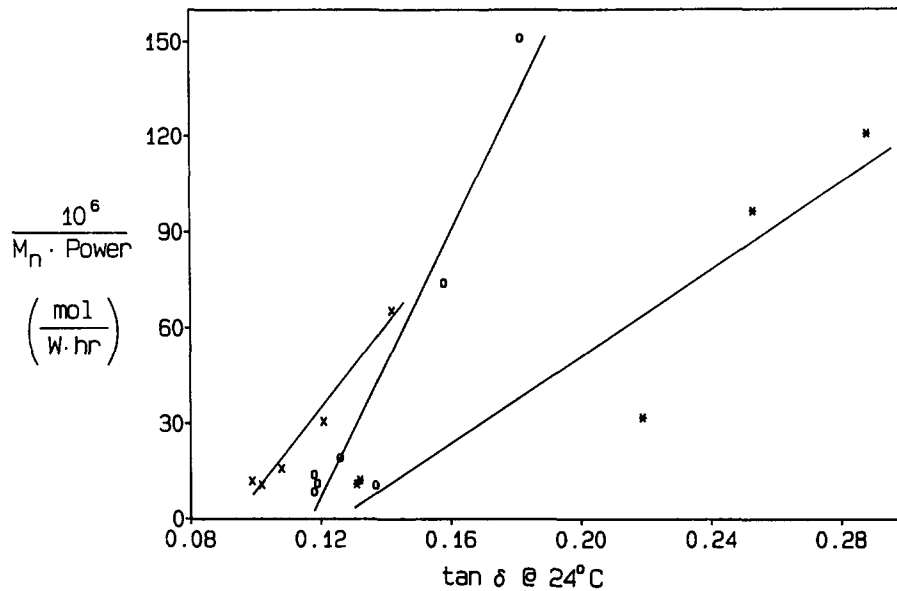
Figure 9   The reciprocal of the product of the mixing power times the M_n vs. tan δ at 24°C of polymers **1-17** with (*) no TBT, (O) 1 TBT, and (x) 2 TBT end groups. The lines drawn have an r of .93, .96, and .99, respectively.

ever, if these data were corrected by plotting the reciprocal of the product of M_n and the power level recorded for mixing each batch, then results seen in Figure 9 could be obtained. The data with one TBT showed an improvement in r from .85 to .96 by this treatment. The improved fit of this line shows the importance that mixing has in reducing hysteresis.

surement. The reaction of TBT end groups with the filler had the effect removing the loose end of the polymer and thus reducing the type of interaction that could be determined by tensile retraction and by dynamic measurements. The expected relationship between tan δ and G'' also showed the effect of the presence of end groups that react with carbon black.

CONCLUSIONS

The slopes and intercepts, determined by tensile retraction measurements on filled SBRs that were cured under the same conditions, were found to be dependent upon the type of carbon black used. The variations in structure and surface area of the carbon black greatly influenced the parameters determined by tensile retraction. These changes were seen in all three strain regions measured and gave a linear correlation to the structure and the surface area of the filler, with a good value of r.

In addition, the introduction of one or two TBT caused changes in all of the parameters determined by tensile retraction. The dependency upon the polymer M_n was still seen, but the number of TBT end groups in the copolymer had the greater influence on the responses measured. The intercept, n, which measures the effective number of cross-links at the lowest-strain region, was shown to have a linear relationship to the $\Delta G'$ from dynamic mea-

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