Tensile Retraction Measurements. IV. Determination of Loose End Pullout in Gum Vulcanizates

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SYNOPSIS

Tensile retraction measurements have been made on unfilled rubbers cured with either sulfur or dicumyl peroxide to different levels of crosslink density. The rubbers chosen were emulsion and solution polymerized anionic SBRs, cis-polybutadiene, natural rubber, and anionic 1,4-polybutadienes of different molecular weight. The measured molecular weight between crosslinks (M_c) at each extension gave a smooth curve when plotted against the maximum extension (Λ_{max}) used for the measurement. This curve was separated into three linear regions that characterize the cured rubber. The first region, above about 30% elongation, gave a $\Lambda_{max} = 1$ intercept that decreased with either increased polymer M_n or increased level of curatives. Subtracting this calculated crosslink density from the measured crosslink density below about 30% elongation gave another smooth curve when plotted against Λ_{max}. A second linear relationship was described in the general range of 5–30% elongation. Below about 5% elongation, a third linear relationship was found. This line was determined from the differences between the calculated and the observed crosslink densities in the lowest strain region of the intermediate strain plot. Possible explanations of these three linear regions have been made. Supporting evidence was gained from temperature-dependent experiments as well as from correlation of experimental results with polymers of different values of T_g.

INTRODUCTION

The retraction portion of the stress–strain tensile elongation curve of elastomers has been investigated over the years as a means to determine the effective crosslink density (ν_e) of the rubbers.[1,2] The very early work of Flory et al.[1] was done at equilibrium using a triple-beam balance to measure the stress. They reported that as the test specimen increased in thickness to about 7 mil a deviation from a constant response was noted. A particular interesting deviation from theory was also noted for those samples prepared at the lowest level of crosslink density. These samples appeared to have a much higher value of ν_e than what would be predicted from the level of curative used. This was partially attributed to the contribution of entanglements.

Later, Fedors[2] used an Instron stress–strain tester to determine the value of ν_e in a nonequilibrium method. This work was based on the retraction from $\lambda = 2.6$, which was similar to the extension used in the work of Flory et al. ($\lambda = 2.0$). Fedors showed that the C_2 of the Mooney–Rivlin equation had a value of zero under these conditions of testing, and as a result the data appeared to be equivalent to that collected under equilibrium conditions.

In a more recent paper, Hergenrother and Doshak[3] have demonstrated that tensile retraction (TR) can be used to determine the entanglement molecular weight (M_e) of the rubbery center block of a thermoplastic elastomer. Here, the plot of the observed molecular weight between crosslinks (M_c) vs. maximum extension (Λ_{max}) showed an excellent linear relationship that gave the M_e when extrapolated to $\Lambda_{max} = 1$. However, at very low extensions, a curvature was seen. This was attributed to the presence of a competing process that was only seen in the lowest range of deformation that was used. A plot of the logarithm of the difference in crosslink

Table I   Characterization of the Polymers Used

Polymer	Type	Preparation	1, 2 (%)	$M_n \times 10^{-3}$	Disp M_w/M_n
A	SBR[a]	Li$^+$ in soln	12	94.9	2.72
B	SBR[b]	Emulsion	15.2	84.3	4.94
C	NR	Tree latex	—	120	3.41
D	PBD	Ziegler pzn	0.9	83.5	3.21
E	PBD	Li$^+$ in soln	11	75.9	1.10
F	PBD	Li$^+$ in soln	11	129	1.14
G	PBD	Li$^+$ in soln	11	169	1.16
H	PBD	Li$^+$ in soln	11	355	1.33

[a] Contains 23.5% styrene of which 0.3% is blocks with DP > 4.
[b] Contains 23.9% styrene of which 2.2% is blocks with DP > 4.

density ($\Delta\nu_e$) between the observed crosslink density (ν_0) and the calculated crosslink density (ν_c) vs. Λ_{max} in this low extension range gave a straight line. This low-strain phenomenon was attributed to the pullout of the rubbery portion of an AB diblock impurity in the ABA triblock that was tested.

Gum vulcanizates can be pictured as having a similar structure as the AB impurity in an ABA, that is, the chain from the last crosslink site to the end of the polymeric chain will behave as a loose end. The TR technique should show whether a similar type of short-range processes are present in such gum vulcanizates. This paper presents the results of TR experiments performed on several types of cured polymer systems.

EXPERIMENTAL

The characterization and type of the polymers used in these TR experiments are listed in Table I.

Gum vulcanizates, cured to various crosslink densities, which were prepared by varying the amounts of sulfur and accelerator (Accel) added to the polymers, are shown in Table II. The standard formulation used contained 3 parts per hundred of

rubber (phr) of zinc oxide, 2 phr of stearic acid, and 1 phr of an alkylated para-phenylenediamine antioxidant.

In addition, different levels of dicumyl peroxide were milled into some of the PBDs. Polymer H, because of the high molecular weight, could only be compounded in solution followed by evaporation of the solvent and vacuum drying. These polymers were cured with dicumyl peroxide (DICUP) as described in Table III. Although the polymers did contain small amounts of antioxidants as stabilizers, no attempts were made to remove them or to add excessive amounts of peroxide to compensate for their presence.

TESTING PROCEDURE

The best geometry for the test specimen was obtained by molding in a 5.75 $\times$ 2.60 $\times$ 0.060 in. closed cavity mold. This mold has two cylindrical ribs of 0.27 in. diameter on each of the sides such that a 2.06 in.-wide flat plaque of the desired thickness would be formed at the cure temperature. This width was chosen so that the majority of the cured rubber stocks would have exactly a 2.00 in. span between the cylindrical ribs at ambient test temperatures.

Table II   Formulation and Cure of Gum Rubbers

	Sample No.						
	1	2	3	4	5	6	7
Polymer	B	B	B	A	A	C	D
Sulfur (phr)	1.8	1.3	0.9	1.8	0.9	1.8	1.8
Accel (phr)	1.0	0.7	0.5	1.0	0.5	1.0	1.0
d (g/cc)	0.982	0.979	0.966	0.982	0.966	0.944	1.040

All stocks were cured 40 min at 150°C.

Table III   Rubbers Cured with Dicumyl Peroxide

	Sample No.					
	8	**9**	**10**	**11**	**12**	**13**
Polymer	B	E	F	G	G	H
DICUP (phr)	0.2	0.1	0.1	0.1	0.025	0.025
d (g/cc)	0.95	0.913	0.913	0.913	0.913	0.913

All stocks were cured 30 min at 160°C.

Strips were cut from the molded plaques to be either 0.25 or 0.50 in. in width. Both width and thickness were accurately measured before each test. Density and the volume fraction of filler (v_f) were also determined for each sample tested. As previously considered, the v_f was determined by calculation of any additive that was not liquid or soluble in the rubber at ambient temperature.[4]

Sample clamping was accomplished by modifying a flex life fixture so that the cylindrical rubber rib at each end of the test piece would slide snugly into the slotted hole of the clamp. Such an arrangement eliminates most of the slippage at high extensions while not causing detectable compression of the sample at the beginning of the test. Thus, any distortion of the low-extension measurements was avoided.

At 25°C, 2.00 in. was the initial length of the test specimens. When testing was to be done at temperatures other than 25°C, the thermal expansion of the rubber test piece must be taken into account by increasing the above dimensions by 0.01 in. for each 25°C increase in the test temperature. Thus, a sample length of 2.02 in. was used when testing was done at 75°C.

When testing was done at any temperature other than 25°C, it was necessary to condition the specimen at the test temperature for at least 1 h prior to mounting in the fixture and testing. Failure to do this resulted in the first few pulls showing an increase in crosslink density as the Λ_{max} was increased. This was due to not having the correct length of sample for the initial small strain testing and thereby incorrectly determining an abnormally high value for the associated set measurement. This problem was readily detected during the test since it gave a large standard deviation associated with the M_c calculated for the first few pulls.

For each test specimen, 10 evenly spaced elongations were measured in each particular set of pulls. Seven sets were collected during each test. In each set, the maximum extension was steadily increased.

It was not necessary that the same sample be used for the entire test, but doing so eliminates any errors associated with measurement of the dimensions and allowed for faster testing. To shorten the time needed for the test, the speed was increased when a new set of pulls were used. When a speed change was made, the last elongation of the previous set was repeated as the first pull of the new set. The difference in the M_c calculated on these pulls in which the speed of testing was varied was used to correct all the data collected to a uniform test speed of 0.1 in./min (5%/min). The magnitude of this shift factor was found to vary directly with the M_c of the sample being tested. The amount of shift[3] that was applied per decade of speed change has been included in the data summary. Table IV gives a summary of the test procedure used for this study.

An Instron 1122 tester controlled by a Hewlett Packard 9836 computer was used for the testing, data acquisition, and calculations. The program was written so that a short pre-pull cycle to 0.3% was initially made before the zeroload was measured. This zeroload was then used as the baseline throughout the test and was used as a means of detecting the endpoint of each elongation cycle. This set point that was rate dependent was the most im-

Table IV   Test Conditions Used for Tensile Retraction Measurements of Gum Vulcanizates

Cross Head Speed (in./min)	% Elongation of Set		Full-scale Load (lbs)
	Min	Max	
0.05	0.5	2.3	1
0.1	2.3	5.0	1
0.1	5.4	9.0	1
0.5	9	18	1
1.0	18	45	2
2.0	45	99	5
5.0	99	207	5

portant point needed for all calculations of M_c and subsequent travel time for the next pull. Generally, a standard deviation of the average M_c calculated from the 25 points collected on each pull was less than 1%.

The M_c and the Λ_{max} at which it was measured were then entered into a 20/20 spread sheet program in a VAX data processing system. All shifting for speed, plotting, statistical calculations, and subsequent data fitting were done in the spread sheet.

RESULTS AND DISCUSSION

The TR data that were collected was plotted as described previously.[3-5] A typical plot can be seen in Figure 1 using sample **7**. The previously described linear relationship between M_c and maximum extension was observed above about 1.2% elongation and can be fit by Eq. (1):

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

Here M_c is the molecular weight between cross-links in g/mol, M_r is the molecular weight between chain restrictions in g/mol, S is the slope in g/mol, Λ_{max} is the maximum strain, ν_e is the effective cross-link density in mol/cc, and d is the density of the stock in g/cc. For **7**, the $M_r = 5,650$ g/mol and $S = 619$ g/mol.

The new clamping procedure employed here allows the use of thicker samples (0.060 in.), without the accompanying problems associated with

compression of the sample by the tightening of the fixture. This, no doubt, was the same sort of distortion that was previously mentioned as restricting Flory et al. to work with thin sections.[1] Using Eq. (1), the gum vulcanizates described in Tables II and III were evaluated to give the results listed in Table V.

The M_r showed the expected increase with decreasing amounts of curative for both the sulfur-cured and peroxide-cured elastomers. The two SBR elastomers, stocks A and B, both gave an increase in M_r as the level of sulfur used for the cure decreased (**1–5**). With the polybutadiene rubbers, the M_r decreased as the number average molecular weight of the polymer increased (**9–13**). In fact, the peroxide level had to be reduced to one-quarter for samples **12** and **13** in order to obtain samples that were not too highly cured. The shift factor also showed the same sort of increase with the changes of the polymer as did M_r.

Generally, the data collected at elongations below 10% show a marked deviation from this calculated line. This deviation can be seen better with a sample of lower M_n, that is, a sample that contains more end groups. Sample **9** in Figure 2, which has a lower M_n than sample **7**, clearly shows this effect. Here, the drawn line was calculated from Eq. (1) using an $S = 1,560$ g/mol and an $M_r = 5,360$ g/mol. This is the same sort of deviation that we reported previously at low extensions with ABA-type thermoplastic elastomers.[3]

Each data point in Figure 2 that deviated from the calculated line was measured as a difference in cross-link density ($\Delta\nu_e$), by subtracting the calcu-
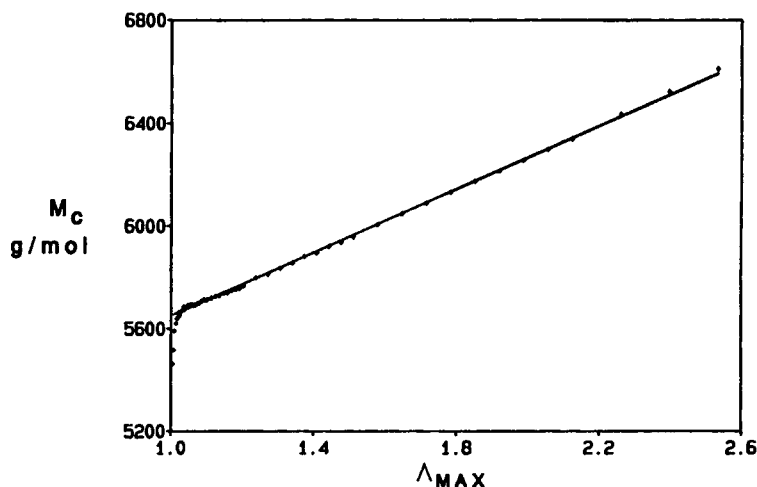

Figure 1 M_c vs. Λ_{max} of a sulfur-cured cis-polybutadiene, **7**. The solid line was calculated using Eq. (1) with a slope = 619 g/mol and an intercept = 5650 g/mol.

Table V   Constants Determined by Tensile Retraction of Gum Vulcanizates

Polymer No.	M_r (g/mol)	S (g/mol)	r	Λ_{max} (range)	Shift (g/mol)
		Sulfur-cured Elastomer			
1	5,490	1080	.9978	> 1.20	212
2	6,850	1260	.9958	> 1.20	434
3	10,200	3140	.9884	> 1.20	1535
4	5,900	1440	.9960	> 1.20	372
5	7,620	4080	.9973	> 1.20	1348
6	6,130	550	.9983	> 1.014	10
7	5,650	619	.9994	> 1.012	116
		Peroxide-cured Elastomer			
8	8,860	2190	.9933	> 1.24	1132
9	5,360	1560	.9979	> 1.18	440
10	3,590	685	.9994	> 1.14	168
11	2,730	183	.9779	> 1.082	45
12	10,200	8790	.9987	> 1.18	3071
13	4,910	2610	.9971	> 1.18	1235

lated crosslink density (ν_c) from Eq. (1) from the observed crosslink density (ν_0) Eq. (2):

$$\Delta\nu_e = \nu_0 - \nu_c \qquad (2)$$

The logarithm of this $\Delta\nu_e$ was then plotted against Λ_{max} to give Figure 3. The high-extension region of this plot gave a good straight line that was fitted by Eq. (3):

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

For sample **9**, the slope (s) is -6.635 and the intercept (m) is -4.615. This would represent a M_c at unit strain (β) = 10^{-m} of 41,200 g/mol.

Increasing the molecular weight of the base polymer from 75,900 g/mol (sample **9**) to 129,000 g/mol (sample **10**) and again to 169,000 g/mol (sample **11**) gave cured stocks that showed progressively lower values of M_c, S, β, and s.

In Figure 3 it can be seen that, at very low extensions, the experimental data deviate from the straight-line relationship of Eq. (3). By subtracting
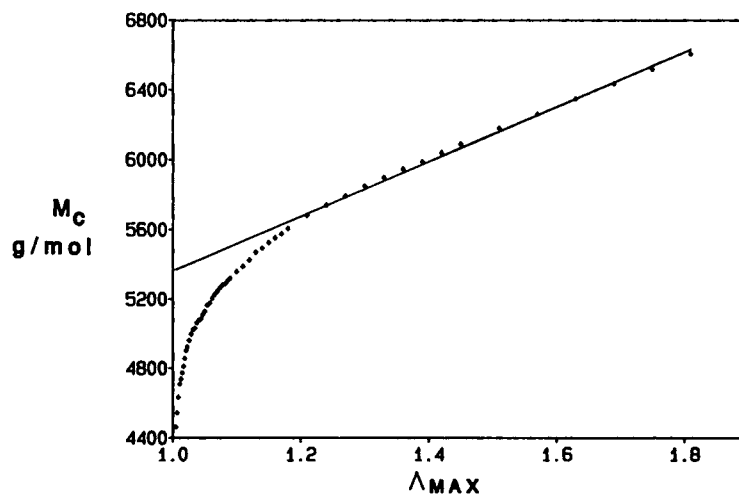

Figure 2 M_c vs. Λ_{max} of a peroxide-cured 75,900 g/mol 1,4-polybutadiene, **9**. The solid line was calculated using Eq. (1) with a slope = 1560 g/mol and an intercept = 5360 g/mol.
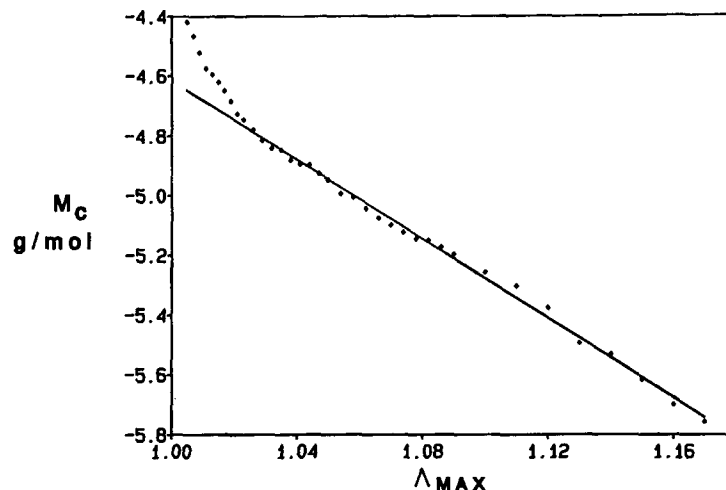
Figure 3   Logarithm $\Delta\nu_e$ of **9** from Eq. (2) vs. Λ_{max}. The solid line was calculated using Eq. (3) with a slope = -6.635 and intercept = -4.615.

this calculated $\Delta\nu_e$ from the value determined in Eq. (2), a $\Delta\Delta\nu_e$ was obtained that also showed a linear first-order plot vs. the maximum extension (Fig. 4). The straight line drawn through the points was calculated from Eq. (4):

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

The slope (t) is -66.60 and the intercept (n) is -4.430 for this low-strain region. This would represent a M_c at unit strain $(\gamma) = 10^{-n}$ of 26,900 g/mol.

By combining Eqs. (1), (3), and (4), a general equation can be obtained [Eq. (5)] that completely

describes the experimental data for these vulcanizates, over the entire strain region:

$$M_c = \cfrac{1}{\Delta\nu_e + \Delta\Delta\nu_e + \cfrac{1}{M_r + S(\Lambda_{max} - 1)}} \qquad (5)$$

A relationship of this type would account for the high values of ν_e that were reported in the work of Flory et al.[1] when lightly cured samples were tested.

Using the values of the slopes and intercepts measured by the above procedures, Eq. (5) was used to calculate the M_c over the entire Λ_{max} range for **7**. A plot of the calculated M_c vs. the measured M_c
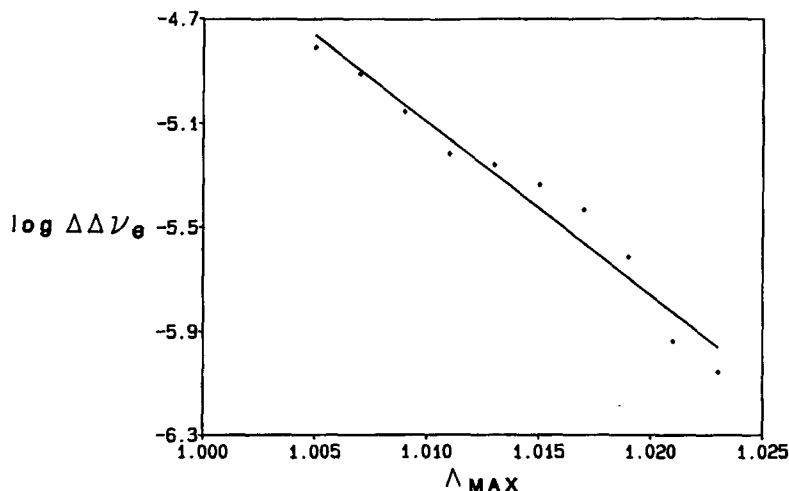

Figure 4   Logarithm $\Delta\Delta\nu_e$ of **9** vs. Λ_{max}. The solid line was calculated using Eq. (4) with a slope = -66.603 and intercept = -4.430.

showed an excellent straight line with a value of the linear least-squares correlation coefficient (r) of .9997.

The curved portion of the M_c vs. Λ_{max} TR plots were separated into the appropriate first-order linear plots [Eqs. (3) and (4)] to give the results summarized in Table VI.

The appearance of two low-extension linear first-order regions in many of these gum stocks was totally unexpected. The above data suggest that this second region is also associated with the interactions of the free chain ends. These ends, or more specifically, the portion after the last effective crosslink, must be trapped in the matrix sufficiently such that the pullout can be seen by TR. The highest molecular weight polymers, natural rubber **6**, and the high *cis* polybutadiene **7**, both have broad molecular weight distributions and only show a slight indication of one such linear first-order region.

The cure of the solution polymerized polybutadiene samples **9**, **10**, and **11** showed an increase in crosslink density with increasing M_n. Only the data for sample **9**, which was the lowest M_n polymer, could be fitted with Eq. (5). In fact, the data of **10** and **11** showed a distinct break when Λ_{max} was plotted against Eq. (2). Figure 5 shows the data for sample **10** in this region. The M_r determined for this polymer was about one-third of the M_e of polybutadiene.[3] Because of this extremely high level of crosslinking in sample **10**, it is not surprising that an interaction between the loose ends would be de-

tected. The data requires that a kinetic second-order plot of the change in crosslinks would be needed to explain this observation. This is shown in Figure 6 with the plot of $1/\Delta\nu_e$ or ΔM_c vs. extension. Here it can be pictured that the chain ends are locked so tightly into the rubber matrix that they are forced to interact strongly with each other during pullout. Once these ends are free of each other, then the regular interactions with the crosslinked matrix would adequately describe the changes observed in ν_e with extension. This can be seen in the linear portion of Figure 5 or by looking at the difference between the crosslinks measured and the straight-line portion of Figure 6. This difference can best be fitted with a first-order relationship to give Figure 7. Here the slope is positive because of the way in which the data were processed. The important feature of this plot is the fact that these data can be separated into two rate processes, one of second order and the other of first order.

Although it has been recently suggested that the previously published TR data[4,5] was only a result of fortuitous circumstances,[6] the underlying thought for such a statement must be addressed. The proposed argument[6] was that on extension the free chain ends that were pulled out generated a compressive force that would resist retraction. This force arises from the inability of the free end to reinsert itself into the crosslinked rubber matrix, at a speed comparable to the speed of retraction. This compression should have a measurable effect on the

Table VI   Low-strain Constants Evaluated from the First-order Region of the Tensile Retraction Curves

| Polymer No.	β (g/mol)	s	$-r$	γ (g/mol)	t	$-r$
			Sulfur-cured Elastomers			
1	124,000	−6.950	.9960	61,800	−50.81	.9779
2	47,800	−4.802	.9980	17,200	−68.30	.9922
3	41,000	−3.650	.9965	17,600	−44.79	.9739
4	42,300	−6.607	.9966	95,200	−38.85	.9361
5	34,500	−5.351	.9976	15,500	−68.01	.9867
6	—	—	—	45,400	−118.3	.9409
7	—	—	—	37,000	−107.9	.9740
			Peroxide-cured Elastomers			
8	33,700	−4.206	.9902	25,400	−51.24	.9974
9	41,200	−6.635	.9981	26,900	−66.60	.9801
10	24,900	−11.39	.9847	—	—	—
11	22,900	−16.29	.9700	—	—	—
12	25,900	−7.49	.9987	13,400	−53.94	.9937
13	14,800	−5.619	.9905	7,440	−46.83	.9933
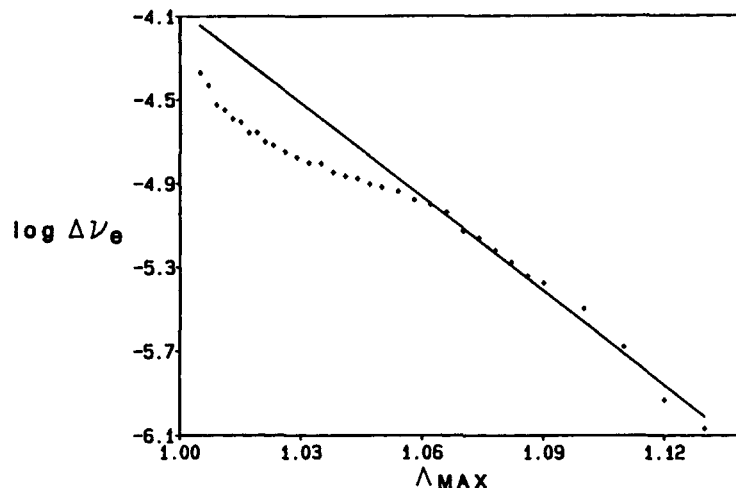
Figure 5   Logarithm $\Delta\nu_e$ of a peroxide-cured 129,000 g/mol 1,4-polybutadiene, **10** vs. Λ_{max}. The solid line was calculated using Eq. (3) with a slope = -14.934, intercept = -4.070, and $r = -.9928$ for the last 12 points.

data collected. We have in the interim demonstrated[3] that there is a rate dependency of the M_c measured on test speed. This dependency can be related to the percent set associated with the measurement. Since the percent set has been shown to be critical to the calculations, it would appear that the treatment of the data resulted in an empirical correction of this compressive force in the calculation of the ν_e at each of the speeds considered. Thus, although equilibrium measurements are not made, the data from TR appear to be an accurate, fast, and reproducible measurement of ν_e and gives a good evaluation of the level of cross-linking present in those rubber stocks thus far considered.

NONAMBIENT TEMPERATURE TESTING

Certain stocks were run at temperatures other than ambient in order to determine whether the experimental data were dependent on the difference between the test temperature and the polymer T_g. These results are summarized in Table VII.

At 75°C, the solution SBR (polymer A) used in samples **1**, **2**, and **3** showed a loss of the linear region described by Eq. (3) only with the most highly crosslinked sample: **1**. Samples **4**, **5**, and **8**, which were based on an emulsion prepared SBR (polymer B), all still showed a low-strain region that could be fit by Eq. (3) when tested at 100°C or lower. At
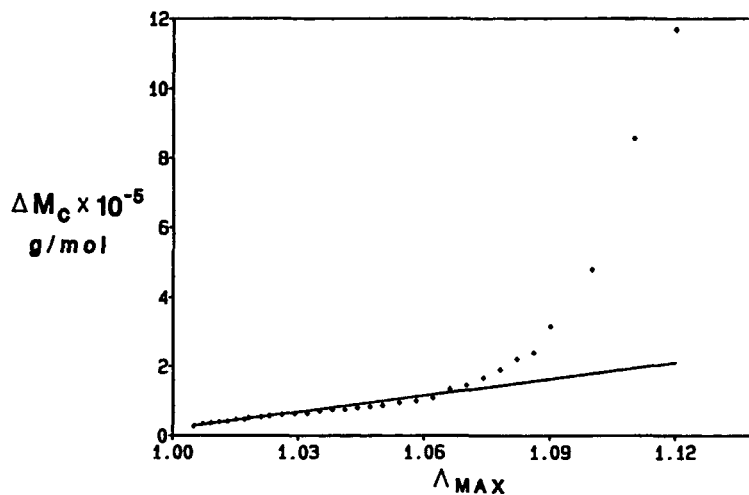

Figure 6   Reciprocal $\Delta\nu_e$ of **10** vs. Λ_{max}. The solid line was calculated using Eq. (1) with a slope of 1,480,000 g/mol, intercept of 18,000 g/mol, and $r = .9922$ for the first 22 points.
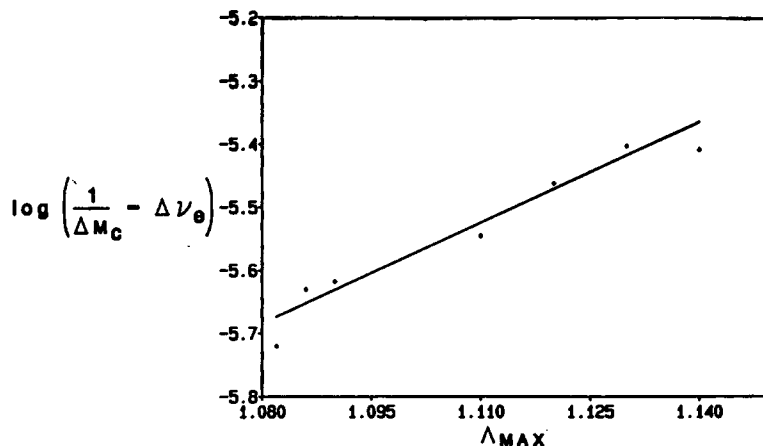
Figure 7 Logarithm $[(1/\Delta M_c) - \Delta \nu_e]$ vs. Λ_{max} for **10**. The solid line was calculated with a slope = 6.436, intercept = −6.201, and r = .9664.

125°C, the most lightly cured sample, **5**, also showed the loss of the middle linear region. Since the T_g's of these polymers are −65.7 and −50°C for polymers A and B, respectively, the change in T_g does not appear to be adequate for explaining the presence or absence of this low-strain linear region.

When **5** was tested at a variety of temperatures, a plot of the logarithm of the slopes and intercepts obtained vs. the reciprocal of the absolute temperature gave a reasonable Arrhenius plot for the intercepts (Fig. 8) and the slopes (Fig. 9) for most of these constants. These plots show that the lowest-strain region can be effectively frozen out by lowering the test temperature. As the temperature is

increased, the intermediate strain region gradually merges into the high-strain region, and in the case of sample **5**, this contribution is no longer observed above approximately 100°C.

To make a fair comparison of the constants measured as a function of temperature, all the TR curves for a given sample were compared at the same number of pulls; that is, for **5**, all the data collected was restricted to the first 60 pulls that corresponded to the elongation needed to break the sample at 100°C. Because of this, and the poor temperature control (±2°C) typical in such testing, a larger than desired scatter was seen in the Arrhenius plot, but it was considered acceptable at this point in the develop-

Table VII Constants Determined by Tensile Retraction Measurements on Cured Gum Rubbers at Temperatures Other Than Ambient

Sample No.	Temp. (°C)	M_r (g/mol)	S (g/mol)	β (g/mol)	s	γ (g/mol)	t
1	75	5,760	670	—[a]	—	52,600	−59.37
2	75	7,800	1100	167,000	−2.600	ND[b]	ND
3	75	11,000	2070	118,000	−2.412	8,750	−168.2
4	75	6,760	888	198,000	−3.405	29,900	−69.67
5	125	11,300	1890	—	—	75,000	−18.41
5	100	12,100	2600	189,000	−3.165	ND	ND
5	75	10,300	1810	114,000	−3.398	49,000	−52.59
5	50	9,480	4350	51,000	−4.989	9,870	−122
5	−26	3,870	1890	8,790	−9.550	—	—
8	100	10,730	1780	82,700	−3.106	52,500	−28.64
8	75	10,600	1800	70,800	−3.747	34,400	−43.52
12	−50	2,510	561	38,100	−9.850	30,400	−38.02

[a] —, indicates that the equation needed to utilize these constants could not be fit to the data in this range.

[b] ND, indicates that this value could not be determined because of the excessive vibrations that prevented the accurate reading of the load cell.

Table VIII   Slopes of the Arrhenius Plots for Various Cured Elastomers

Sample No.	Value of the Slope $(1/K)$					
	M_r	m	n	S	s	t
1	−41	—	13	417	—	−137
2	−115	−97	—	116	540	—
3	−68	−84	65	368	365	−1170
4	−121	−119	94	425	584	−515
5	−320	−91	−94	423[a]	355	764
8	−129	−54	−40	138	423	944
12	−544	15	32	−1070	106	136

[a] The value listed was determined from the 24 and 125°C data only. If the data from −25 to 50°C were used, this slope would be −402 deg⁻¹.

ment of the TR test. Table VIII summarizes the slopes obtained from Figure 8 and 9. Also included were those slope values calculated from the two or three temperature data listed on Table VII.

It is interesting that M_r and m increase with increasing temperature for all of the SBR samples considered. The value of n had a much smaller temperature dependence, and any trend could well be hidden in the errors associated with such a measurement. The Arrhenius plot of slopes S and s showed a decrease with increasing temperature. As can be seen in Figure 9, the value of S increases with decreasing temperature down to 25°C and then rapidly drops at the lowest test temperature. This same sort of decrease in the slope S was also seen with sample **12**, where the only temperature range considered was 25 to −50°C. This change in slope in

the Arrhenius plot can best be explained by the approach of the glass transition temperature of these polymers, which would account for an increase in chain stiffness. All the other polymers listed in Table VIII were calculated well above this transition, since data for them were collected only at 25 and 75°C. The accuracy of such plots were greatly reduced because of the lack of data determined at other temperatures.

These data indicate that the intercepts, from the three equations that were used to describe the TR curve, for the most part give a negative slope of the Arrhenius plot. The values, listed in Table VII, which were in the −544 to −40 deg⁻¹ range, corresponded to an activation energy for the processes of 2.5 to 0.2 kcal/mol, respectively. These activation energies from the change of the intercepts with tem-
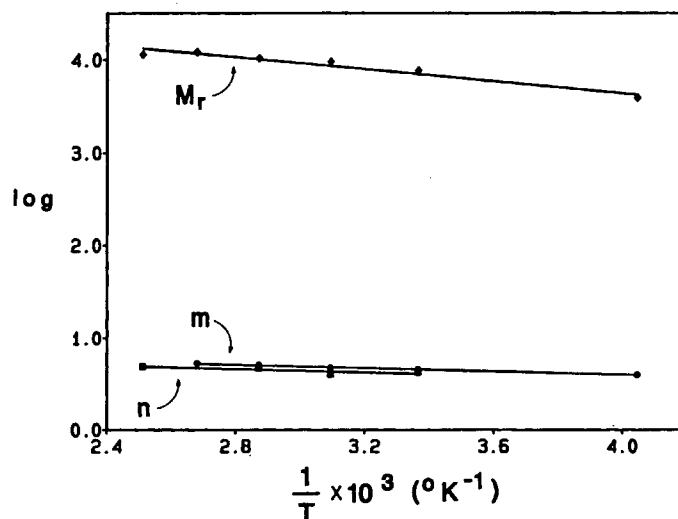

Figure 8   Arrhenius plot of the intercepts for the equations used to describe 5, where M_r is (◆), m is (●), and n is (■).
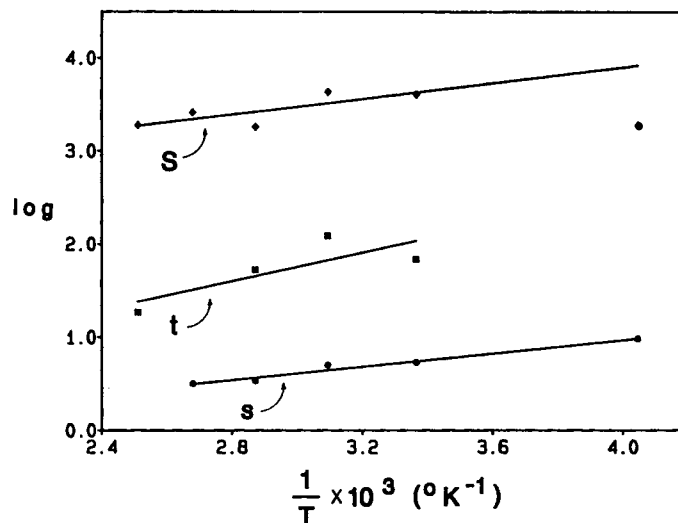
Figure 9   Arrhenius plot of the slopes for the equations used to describe 5, where S is ($\blacklozenge$), s is ($\bullet$), and t is ($\blacksquare$).

perature indicates the presence of a low-energy interaction; that is, the process measured was only the result of rearrangement of the polymer chains and not from the breakage of chemical bonds. The data from the slopes also gave good Arrhenius plots that generally had a positive slope. The exceptions to the above were those values evaluated at temperatures near the T_g and those constants n and t from Eq. (4) where only two test temperatures were used in their evaluation.

When it is considered that these plots, which have been shifted to a strain rate of 5%/min, are all actually a representation of a function of ν_e vs. time, then the kinetic interpretation that was used would appear most reasonable. The results obtained here are somewhat similar to those obtained from the stress relaxation studies reported by Bartenev and Lyalina[7] on SBR polymers. The explanation that they proposed for the three linear first-order relaxation regions that they obtained can also be applied to this work. This consists of the following: (1) The first region (those with relaxation times of 10^{-4}–10^{-6} s) corresponded to orientation of the free chain segments. (2) The second region (this was for the portion of the curve with relaxation times of 10^2–10^4 s) resulted from the rearrangement and friction of the segments making up the macromolecular structure. (3) The third region (this required relaxation times of 10^7–10^9 s) was attributed to rearrangement and rupture of transverse chemical bonds in the chain.

In the work of Bartenev and Lyalina,[7] the data constituting the first two regions were calculated in

the same manner as were the first two regions of the present work. The explanation proposed by Bartenev and Lyalina seems very reasonable, with the faster of these two processes being due to the orientation or pullout of the loose ends. This first-order process becomes a more complicated kinetic second-order interaction when the samples are chemically crosslinked so tightly that the molecular weight between crosslinks is less than the entanglement molecular weight (M_e) of the polymer. For polybutadiene, the value of M_e was determined[3] to be 7580 g/mol by TR at the same 5%/min test rate that was used in this study.

The second region is another kinetic first-order process where the loose end is characterized by rearrangement and friction with the macromolecular segments. Such an interaction would be highly dependent on both the short- and long-chain branching of the polymer and may disappear when testing at elevated temperatures.

It has already been established[3-5] that the region of highest strain can best be described by a kinetic second-order process where the highly crosslinked chains interact with each other as the stress is applied. This type of interaction probably were not seen by Bartenev and Lyalina because of the long times needed for their measurements. During their experiment, the test strip was reported as showing cracks due to the attack of ozone on the rubber. Such a degradation would give a pseudo first-order rate, which they correctly associated with breakage of chemical bonds. This would, of course, mask any underlying second-order rate process.

The effect of the different cure systems and the types of polymers that were used should also have a major effect on these Arrhenius plots. Further examples will be needed to reduce the data scatter obtained by testing at elevated temperatures before any such assignment can be made. These studies are in progress and will be the subject of further publications.

SUMMARY

A rapid nondestructive determination of the molecular weight between crosslinks of a gum vulcanizate by tensile retraction been described that is both accurate and reproducible. In addition, the measurement has been used to measure the physical interaction of a variety of gum vulcanizates with themselves. Three distinct regions have been identified that give information regarding the ν_e of the sample and the interaction of polymer chains with each other during extension. These include the pullout of loose chain ends during small deformations, the interaction of these loose chain ends with the crosslinked matrix at intermediate extensions, and the covalent crosslink density of the polymer at the highest levels of elongation. Temperature-dependent studies on certain polymers show promise as a means of determining the differences in the behavior of the elastomer as a function of temperature and polymer type. Although a firm theoretical base for these observations is still uncertain, it does appear that the experimental data are not the result of a fortuitous set of circumstances.

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