

Determination of the Molecular Weight Between Cross-links of Elastomeric Stocks by Tensile Retraction Measurements I. SBR Vulcanizates

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Synopsis

Tensile retraction measurements were used to determine the effective molecular weight between cross-links of vulcanized SBR rubbers. The procedure has proven to be a rapid, precise, and reproducible method of obtaining the total number of effective cross-links present in an unperturbed elastomer. Since the only data needed besides stress-strain curves were the sample density and the volume fraction of filler present, questionable evaluation of unknown constants was avoided. In addition, an indication of the interactions between the polymer and filler can be studied. Such a relationship with hydrocarbon rubbers appears to give information that will directly relate to end use applications.

INTRODUCTION

The determination of the cross-link density ν_e of hydrocarbon rubbers has been most conveniently done by the swelling of the vulcanized rubber to determine the volume fraction of rubber in the swollen sample ν_r . The ν_r can then be used along with the Flory-Rehner equation¹ to allow the calculation of ν_e . This procedure does require that equilibrium swelling be obtained and that the polymer-solvent interaction constant χ be properly evaluated. The molecular weight between cross-links M_c determined by this procedure has allowed the ordering of samples cured to different levels quite successfully. However, an accurate determination of M_c has only been accomplished over a narrow range of ν_r where χ is truly a constant. Unfortunately χ has been shown to vary with concentration, molecular weight, and temperature.² The latter two variations are readily controlled, but the first required the use of a different χ for each different range of values of ν_r measured.

During swelling, the sample is often subjected to a three-dimensional extension ratio λ ranging from 1.2 to 2.0 or greater. In addition oils, plasticizers, and soluble portions of the polymer are extracted such that the M_c determined is not representative of the effective M_c of the originally prepared sample but is that of an extracted and partially elongated polymer. It is known that polymer-filler interactions, weak polymer-polymer interactions, and contributions due to entanglements are lost upon straining of an elastomer.³ Thus, at best only a poor representation of the original state of the rubbery sample is obtained by swelling.

Recently, a way to avoid these problems has become available by proper application of rubber elasticity theory to the retraction curve of tensile testing.⁴ By using tensile retraction (TR) data it is now possible to calculate the effective M_c for an unswollen and unextracted rubber at $\lambda = 1.0$ by knowing only the volume fraction of filler v_f and the density of the sample. Both of these values are easily determined by simple procedures. These measurements have been made on SBR containing various fillers or no filler and cured with sulfur or peroxide.

Recently, Fedors⁴ published a procedure for the determination of the cross-link density of elastomers by application of the kinetic theory of elasticity. For this, the retraction curve from tensile measurements was used and calculated as

$$\sigma = v_e RT (\lambda - \lambda^{-2}) \quad (1)$$

where σ is the stress based on the undeformed dimensions, v_e is the concentration of effective network chains, R and T are the gas constant and absolute temperature, respectively, and λ is the extension ratio.

The Mooney-Rivlin⁵ equation for tensile extension has a similar form of

$$\frac{\sigma}{2(\lambda - \lambda^{-2})} = C_1 + \frac{C_2}{\lambda} \quad (2)$$

where C_1 and C_2 are empirical constants. In retraction it was shown and verified by this work that $C_2 = 0$. Thus the expression

$$2C_1 = v_e RT \quad (3)$$

holds true for TR measurements.

EXPERIMENTAL

Test Procedure

A 0.25-in. strip 6 in. long was cut out of a 0.040–0.080 in. thick plaque of the desired stock. A span of 2 in. was clamped in the Instron, and successive maximum elongations of 10, 25, 50, 100, 200, 300, 400, and 500% were run while adjusting the chart speed and crosshead speed to give from 6 to 30 in. chart travel at a speed of 0.50 to 5 in./min. The load cell range was selected to allow the maximum travel on the chart to be between 30 and 90% of full scale.

Testing was done on a fresh strip for each desired maximum strain in the initial work. Alternatively, each test was run in succession without reclamping; however, the original length, width, and thickness of the sample were used in all subsequent calculations. Identical results were obtained by both procedures.

The test was run by elongating the sample at a constant rate to a desired maximum extension (λ_{\max} for unfilled or Λ_{\max} for the filled samples) and

then immediately retracting this sample at the same rate until the stress reached zero. The percentage set was taken as the percentage elongation at which the return curve reached zero stress. This point is taken as the origin for all subsequent measurements of stress and strain on the retraction curve.

Data points were measured most readily with a digitizer, which then calculated the C_1 , percentage set, Λ_{\max} , and M_c for the sample. Generally, standard deviations of less than 10% and more typically of about 5% were measured.

POLYMERS TESTED

The formulation of the tested samples is summarized in Table I.

RESULTS AND DISCUSSION

A typical stress-strain curve suitable for tensile retraction measurements is shown in Fig. 1. Here SBR sample 2 was tested at 25°C by first subjecting the test specimen to 50% elongation and then immediately allowing retraction to occur at the same rate as used for the tensile portion of the test. The point at which the stress returned to zero was chosen as the point of

TABLE I
Formulation of SBR Stocks

Sample number	A. Dicumyl peroxide cured at 160°C for 45 min				d (g/ml)	v_f
	Dicup (phr)	Rubber ML ₄	HAF (phr)			
1	0.10	50	50		1.12	0.207
2	0.20	50	50		1.12	0.207
3	0.41	50	50		1.12	0.207
4	0.10	50	—		0.94	0
5	0.20	50	—		0.94	0
6	0.15	52	—		0.94	0
7	0.40	52	—		0.94	0
Sample number	B. Sulfur cured ^a at 160°C for 30 min			d (g/ml)	v_f	
	Filler type	Filler (phr)				
8 ^b	HAF	60		1.16	0.242	
9	HAF	60		1.17	0.259	
10	HAF	60		1.17	0.259	
11	MT	60		1.17	0.259	
12	CaCO ₃	60		1.28	0.191	
13	CaCO ₃	80		1.36	0.232	
14	CaCO ₃	40		1.19	0.145	
15	—	—		0.995	0.047	
16 ^c	—	—		0.967	0.029	

^a SBR, ML₄ = 52 used with 3.0 phr zinc oxide, 2.0 phr stearic acid, 1.0 phr Santocure NS, and 2.0 phr sulfur.

^b 10 phr aromatic oil added.

^c Santocure NS and sulfur both reduced to 0.5 phr.

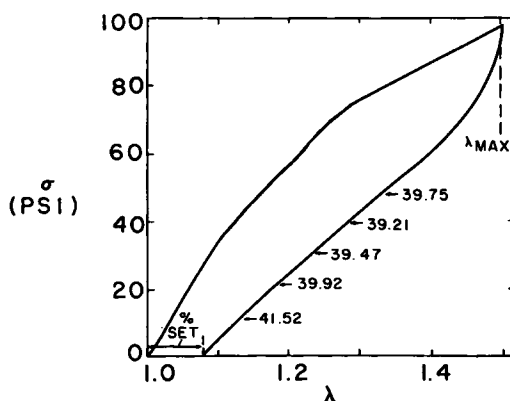


Fig. 1. Stress-strain tensile retraction curve of sample 2 at 25°C. The arrows on the retraction curve represent the values of C_1 calculate for the indicated points.

strain equal to 1. The calculations indicated in eq. (1) are then made at least on five points on the last 70% of the retraction curve and always give a constant value of C_1 . Usually this measurement is accompanied by a standard deviation of less than 5%. Repeated cycling to the same λ_{\max} always gave the same value of C_1 independent of the cycle on which the calculations were made. The value of C_1 measured did, however, decrease as the λ_{\max} increased. The test shown in Fig. 1 had a slight inflection in the extension curve at approximately 1.25λ . This was caused by the previous testing of this sample to that extension ratio, but in no way has it been seen to interfere with the retraction curve. Applying eq. (3) to all the vulcanized SBR that were studied provided insight as to how a rubbery network behaves on deformation. Thus total cross-link densities of these samples also can be shown to decrease as the λ_{\max} increases.

RATE OF TESTING

The equations above are dependent upon the sample being at equilibrium for the measurements to be meaningful. This was first established by testing at different extension rates from 25 to 1000% per minute. For this testing at 25°C, a λ_{\max} of 3.0 was chosen and the value of C_1 was calculated for a black-loaded, sulfur-cured SBR, sample 9. The results are listed in Table II. As can be seen, no apparent trend can be established in the fluctuation of the value of C_1 with increasing speed of the test. The average value of C_1 appears constant throughout the test speed range employed. Thus for this sample under the conditions used it must be concluded that the value of C_1 is independent of the speed of testing. As a result, all subsequent tests were run at strain rates to produce the best curves for data retrieval.

It is interesting to note that the percentage set, that is, the percentage elongation at which the retraction curve returned to zero stress, showed an increase with increasing strain rate for black-loaded SBR. Figure 2 shows these changes as a linear function of the logarithm of the testing speed. This relationship is that which would be expected from the relaxation time

TABLE II
Determination of Variation of C_1 with Speed of Testing for a 60-phr HAF Black-Loaded SBR Sample 9

Strain rate (%/min)	C_1 (psi)	% Set
25	34.34 ± 1.44	26.6
50	34.21 ± 1.15	28.8
100	34.60 ± 1.31	29.3
250	33.63 ± 1.21	31.3
500	33.03 ± 0.95	32.5
1000	33.12 ± 1.03	34.0
Average	33.82 ± 0.67	

involved in the movement of a cross-linked rubber chain through a filled system.⁶

The work reported by Fedors⁴ suggests that a specific elongation be used in order to determine a M_c of the system. This, however, is very arbitrary and introduces considerable error, particularly when going from one system to another. It has been determined by this work that if $1/C_1$ is plotted versus λ_{\max} , a good straight line is always obtained over the entire range of λ_{\max} measured.

Most conveniently, the molecular weight between cross-links at a given strain M_c can be plotted versus λ_{\max} . Equation (4) shows the relation of M_c and C_1 :

$$M_c = \frac{dRT}{C_1} \quad (4)$$

Where d is the density of the sample, T is the absolute temperature, and R is the gas constant (1206 psi cm³/K/mol). Using λ_{\max} measured from 1.1 to 6 almost always gave a linear correlation coefficient with M_c of 0.98 or better.

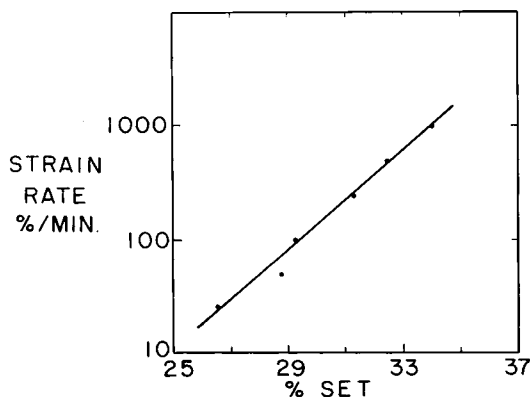


Fig. 2. Tensile retraction percentage set versus strain rate for a rubber stock, sample 9.

The $\lambda_{\max} = 1$ intercept was designated as M_c^1 ; this is the M_c characteristic of the unstressed rubber and would represent the sum total of the chemical and effective physical cross-links present in the elastomer. In general, this should be similar to the M_c^s calculated from swelling data using the Flory-Rehner equation. Some slight differences would be expected since a swollen sample is actually under a three-dimensional elongation of up to 100% or more. This, of course, would give a value of M_c^s larger than M_c^1 since there is a definite slope obtained from tensile retraction M_c versus λ_{\max} measurements. This M_c^1 is believed to be the effective total M_c of the vulcanizate. The value obtained by extrapolation represents the unperturbed state that the elastomer is in after curing. To a large extent this total M_c is not changed greatly during the total useful life of many rubbery products. No corrections must be made in the data for extraction of oils or plasticizers or even the sol fraction. Thus the M_c^1 obtained by TR measurements can be used with greater confidence that it is a good measure of the total effective M_c of the rubber.

FILLER EFFECTS

In the case of filled rubber stocks, λ must be replaced by the strain amplification factor Λ .⁷ This was necessary to account for the increased strain that the soft segments must bear because of the reduced cross section produced by an inelastic rigid filler. The volume fraction of this filler v_f was used for the calculation of eqs. (5) and (6).

$$\Lambda = \epsilon X + 1 \quad (5)$$

where

$$X = 1 + 2.5v_f + 14.1v_f^2 \quad (6)$$

and ϵ is the elongation applied. This equation was first applied to viscosity enhancement of a liquid by the addition of fillers and was later applied in the same fashion to filled polymers^{7,8} with much success.

With this correction a plot of Λ_{\max} versus M_c also gave excellent straight-line plots for all filled systems. In this, all the solids or solid-forming materials are used to calculate v_f . Thus in rubber stocks all the solid additives are considered fillers. Of course, in order to measure the total M_c in the sample tested the M_c^1 intercept value must be also corrected for the filler present. Such a correction, of course, is readily applied by multiplying the intercept by the filler factor X of eq. (5). This was first derived by Guth and Gold⁹ and has been used frequently in swelling of filled systems. The characteristic molecular weight between polymer chain restrictions determined by tensile retraction M_r can thus be calculated by eq. (7):

$$M_r = XM_c^1 \quad (7)$$

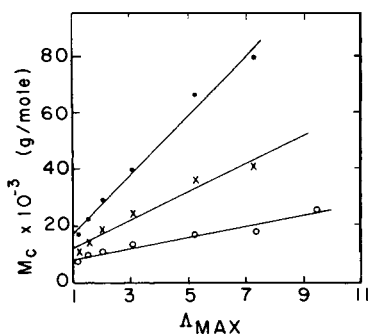


Fig. 3. Tensile retraction data of SBR-50 phr HAF cured with dicumyl peroxide, 0.10 phr (●), 0.20 phr (x), 0.41 phr (○), samples 1, 2, and 3.

PEROXIDE CURE

The validity of this approach can be evaluated in a number of ways to show that it indeed gives reasonable values consistent with known relationships in polymer science. One such approach was the peroxide cure of emulsion SBR containing 50 phr HAF black at three different peroxide levels, samples 1, 2, and 3 (Fig. 3). Such a plot shows an increasing cross-link density as the peroxide concentration $[I_2]$ increases with a concurrent decrease in the slope. Plotting the M_r versus $[I_2]^{1/2}$ (Fig. 4) gave the expected straight-line relationship.

The decrease in slope with increasing state of cure is quite apparent in Fig. 3. The slope itself must represent the reduction of cross-link density by progressively larger strain such that entanglements, end-group effects, flaws, and poor filler-polymer interactions can be destroyed. The dewetting of the filler should be the main cause for the increased slope in the filled samples and has been described by Mullins and Tobin⁸ and explained by Bueche³ as "Mullins softening."

As would be predicted, the slope should have a dependency on the level of chemical cross-linking. The tighter network will have fewer loose ends that can be pulled out and thus more entanglements are trapped that can

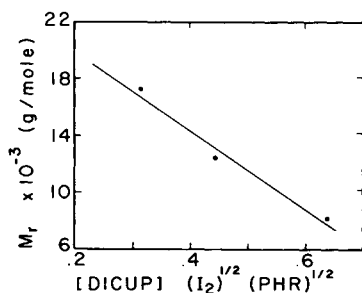


Fig. 4. The $\Lambda_{max} = 1$ intercept (M_r) of peroxide cured SBR-50 HAF versus dicumyl peroxide concentration.

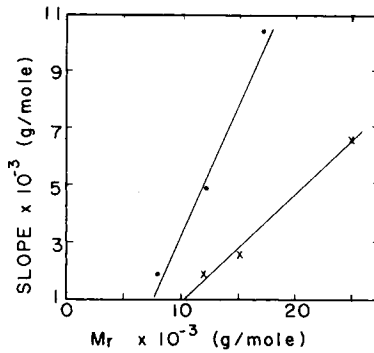


Fig. 5. The M_r versus slope of the tensile retraction plots of peroxide cured SBR, 50 phr HAF black (●) and gum (x).

act as effective cross-links. A plot of the slope versus the intercept for these peroxide-cured samples (Fig. 5) shows this type of behavior for both the filled and unfilled SBR. The difference in the lines produced with the filled and unfilled stocks gives an indication of the interaction of the HAF black filler with the SBR.

SULFUR CURE

Curing of rubber stocks with sulfur also gave typical TR plots with well-characterized slopes and intercepts. Plots made from tests performed on a stock containing added processing oil, sample 8, compared with one not containing oil, sample 9, can be seen in Fig. 6. Here a slight increase in the M_r was observed by the presence of the oil but the slopes are very similar. The higher M_r would be expected since, in fact, this is a slightly swollen network that would have fewer cross-links per unit area when cured to the same extent.

The use of calcium carbonate, a nonreinforcing filler (Fig. 7), also showed similar slopes and a slightly shifted intercept for the use of filler at 40 phr, sample 12, and 80 phr, sample 13. Here the higher level of filler gave the lower M_r , which would be consistent with a physical dilution of the cross-linked sites by the presence of the filler.

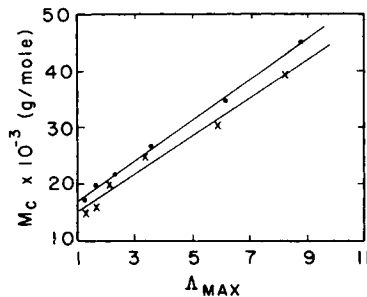


Fig. 6. Tensile retraction data from sulfur-cured SBR-60 HAF, sample 9 (●), and sample 8 (x) with 10 phr added oil.

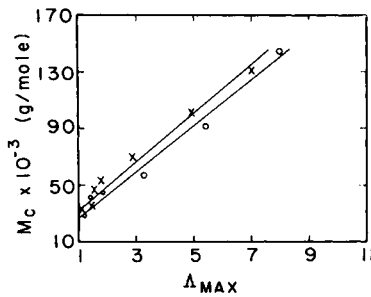


Fig. 7. Tensile retraction data from sulfur-cured SBR, sample 12, filled with 60 phr CaCO_3 (x), and sample 13, filled with 80 phr CaCO_3 (O).

SWELLING

Using the M_r determined by this work and the equilibrium swelling values of v_r , determined in heptane at 25°C listed in Table III, the value of χ was calculated. For this the Flory-Rehner equation¹ was solved for χ in eq. (8):

$$\chi = \frac{dV_0(0.5v_r - v_r^{1/3})}{M_r v_r^2} - \frac{\ln(1 - v_r) + v_r}{v_r^2} \quad (8)$$

where d is the density of the sample and V_0 is the molar volume of the solvent.

TABLE III
Calculation of χ from M_r to Fit Heptane Swelling of SBR Vulcanizates

Sample number	M_r ($\times 10^{-3}$)	v_r	% Soluble	χ
Sulfur-cured SBR-HAF				
8	15.2	0.439	4.7	0.690
9	16.9	0.458	4.3	0.710
10	13.1	0.466	5.1	0.710
Sulfur-cured SBR-MT				
11	34.3	0.397	4.9	0.674
Sulfur-cured SBR- CaCO_3				
12	32.5	0.136	17.7	0.411
13	27.7	0.271	7.1	0.564
14	16.4	0.392	5.1	0.650
Peroxide-cured SBR-HAF				
1	17.1	0.245	12.2	0.520
2	12.3	0.316	8.8	0.569
3	8.14	0.393	6.3	0.618
Sulfur-cured gum SBR				
16	27.5	0.083	54.4	0.234
15	11.7	0.383	7.7	0.636
Peroxide-cured gum SBR				
4	24.9	0.214	14.3	0.526
5	15.1	0.313	9.7	0.589
6	12.4	0.333	10.1	0.596
7	9.43	0.390	8.3	0.634

The volume fraction of rubber in the swollen sample v_r was corrected for the weight fraction of filler f_{fil} present and the weight fraction of soluble polymer f_{sol} by using eq. (9):

$$v_r = \frac{1}{1 + \frac{d_r}{d_s} \left(\frac{1 - f_{\text{sol}}}{1 - f_{\text{sol}} - f_{\text{fil}}} \right) \left(\frac{W_s}{W_0} - 1 \right)} \quad (9)$$

where the densities of the rubber and of the solvent are expressed by d_r and d_s , respectively, and W_0 and W_s represent the corresponding dry weight and swollen weight of the sample.

A plot of χ versus v_r (Fig. 8) for all of these data shows a smooth curve that initially has χ rapidly increasing with increasing v_r . Then at high values of v_r , a plateau value of χ is reached. This corresponds to the predicted relationship calculated by Yamakawa,¹⁰ except that the initial rapid drop of χ with the first cross-links cannot be seen with these samples.

Since this curve was generated from a variety of samples containing different types and levels of filler with both peroxide and sulfur cures and even with gum vulcanization, it must be concluded that the M_r generated by TR must be characteristic of the effective network produced. It is of interest to note that no such curve containing all the points can be generated by using M_c^1 .

The values of χ determined by this technique appear to be most reasonable. Previous workers¹¹ have shown χ values of about 0.59 for SBR gum vulcanizates that contained 12.5–28.5% styrene. These samples had measured values of v_r in heptane of 0.349 and 0.371, respectively. In comparison, this work with a 23% styrene SBR shows a v_r of about 0.32 to correspond to this same χ value.

Using the values of M_r generated in this work as a true effective network present in these samples, some of the variations within the series tested can now be better explained. Sample 5 was prepared with a higher level of peroxide than 6, but the TR data indicate 5 to have the higher M_c . Since

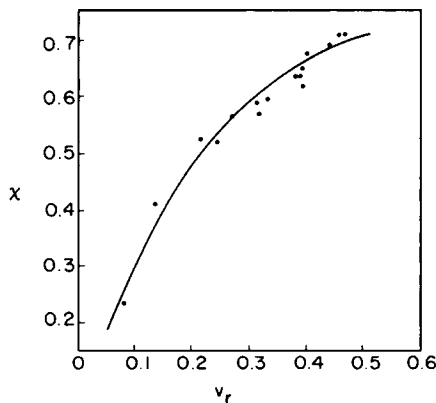


Fig. 8. Change in χ calculated from M_r with v_r in SBR swollen in heptane at 25°C (●).

both the v_r and M_r measurements agree in the trend observed, that two different rubber sources were used to prepare these stocks suggests that the unpurified rubbers used contained slightly different levels of impurities that could cause the observed reduction in the cure of sample 5.

Likewise, the high cross-link density associated with sample 14 when compared to 12, 13, or 16 suggests that the observed M_r is correct but not at the value what would be expected from the indicated series, probably a result of an inadvertent overcure.

Polymer-filler interactions obviously are the cause of the much lower M_r observed with the reinforcing HAF blacks. The partial or complete absence of these interactions can be seen when samples 9–13 and 15 are compared, not only in the value of M_r obtained but also the slope of the plot from which the M_r was obtained (see Table IV). Further work in the determination of the extent of the polymer-filler interaction and even filler-filler interactions from this type of data should prove valuable.

A summary of the slope, intercept, correlation coefficient, and X values determined for all these vulcanizates is in Table IV.

CONCLUSIONS

The use of tensile retraction measurements with vulcanized SBR has shown a simplified procedure for the determination of the effective molecular weight between cross-links for systems that are unfilled or filled with either reinforcing or nonreinforcing pigments. The data obtained are unique to the vulcanizate tested since all of the effective cross-links (e.g., chemical, polymer-polymer, polymer-filler, and filler-filler interactions) are measured. In addition, this value of M_r can be determined with a high degree of reproducibility. These measurements are independent of the type of cure em-

TABLE IV
Summary of Tensile Retraction Data on SBR

Sample number	M_r ($\times 10^{-3}$)	Slope ($\times 10^{-3}$)	Correlation coefficient	X
1	17.2	10.4	0.9937	2.12
2	12.3	4.93	0.9882	2.12
3	8.14	1.92	0.9801	2.12
4	24.9	6.56	0.9972	1.00
5	15.1	2.66	0.9850	1.00
6	12.4	1.82	0.9920	1.00
7	9.43	2.05	0.9502	1.00
8	15.2	3.33	0.9961	2.43
9	16.9	3.58	0.9984	2.59
10	13.1	2.79	0.9760	2.59
11	34.2	5.18	0.9871	2.59
12	32.5	17.2	0.9980	1.99
13	27.7	15.9	0.9882	2.34
14	16.4	4.28	0.9943	1.66
15	11.7	1.90	0.9934	1.11
16	27.5	30.8	0.9910	1.08

ployed but are highly sensitive to the state of cure. In addition, this presents a good means of evaluation of the polymer-solvent interaction constant at any volume fraction of rubber. The relationship of the slope of the Λ_{\max} versus M_c plots to filler type was suggested. The exact relationship will be further studied to clarify the polymer-filler interactions suggested. A third relationship of the relaxation time of these cured rubbers with filler and state of cure also appears possible from the data collected, and this will also be the subject of further study. This technique should be applicable to any elastomeric system, whether they are blends or copolymers or even polyurethanes.

The author would like to express his thanks to Mr. D. Graves for preparation and curing of the SBR vulcanizates and Mr. J. Doshak for running the Instron and collecting much of the data using the digitizer. Valuable discussions with Dr. S. L. Cooper of the University of Wisconsin and Dr. T. Ward of VPI were appreciated. In addition thanks is given to the Firestone Tire & Rubber Company for permission to publish this work.

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Received April 26, 1985

Accepted December 9, 1985