

Glass Formation in Polymers: II. The System Rubber-Sulfur

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Volume versus temperature relations encompassing a wide range in temperature and composition have been determined for a series of natural rubber-sulfur vulcanizates and mixtures. The characteristic temperature of glass formation is deduced from these studies. The glass temperature is found to increase continuously from -69° to $+90^{\circ}$ C in the vulcanizates as the amount of bound sulfur is increased and to be invariant with the composition in the mixtures. A qualitative interpretation of these results is given in terms of the free-volume theory of glass formation.

1. Introduction

The physical and mechanical properties of bulk amorphous polymers depend to a large extent on the relationship between the temperature of study and the temperature at which glass formation occurs. Thus at temperatures above that for glass formation amorphous polymers exhibit rubberlike elastic behavior, while at temperatures below the transformation temperature brittle inelastic behavior is observed. This phenomenon is exemplified in a remarkable fashion by sulfur vulcanizates of natural rubber. For this system, at room temperature, normal rubberlike behavior is observed when relatively small amounts of sulfur have reacted. On the other hand, as the amount of bound sulfur increases the polymer becomes hard and inelastic. It is, of course, well known that with the increase in the amount of combined sulfur the glass temperature, T_g , increases from -69° to temperatures which are well above room temperature [1]¹ and it is this fact that causes the observed changes in physical properties.

Glass formation occurs as a consequence of the fact that as the temperature or pressure is varied the time necessary for molecules or segments of molecules to rearrange from one local liquid equilibrium structure to another becomes comparable with, or greater than, the time scale of the experimental observations [2, 3]. One important problem has been that of being able to quantitatively describe the variation of T_g of a given polymer with structural or compositional changes that are introduced. A great deal of success has been achieved in solving this general problem by considering the changes that occur in the free volume of the system as a result of the alteration of the structure or composition [3 to 7]. Based on the theory of activated processes, the free volume can be considered to be a measure of the ease with which the necessary molecular rearrangements occur. Furthermore, the variation of the free volume should be intimately related to the changes that occur in the specific volume of the system.

The earlier work of McPherson [8] and Scott [9] indicates that one consequence of the reaction of sulfur and natural rubber is a significant and systematic change in the density of the system. These results give indication that the change that occurs in T_g might be explicable by considering the variation of the specific volume of the system with temperature and composition. The data reported, however, do not cover a sufficiently wide range in temperature to be suited for this purpose. Thus there is no complete set of data available which describe the variation of T_g with composition and give the specific volume-temperature relations for the same series of compounds over a wide composition range.

The present work was undertaken to investigate this problem more thoroughly. Detailed studies of the volume-temperature relations of purified natural rubber, natural rubber-sulfur mixtures, and of vulcanizates of these two substances, encompassing the completely accessible composition range and covering a very wide range in temperatures, were made. The present paper discusses the variation of T_g with composition in both the mixtures and vulcanizates and interprets it in terms of the changes that occur in the specific volume of the system.

2. Experimental Procedures

2.1. Materials

The natural rubber used in this study was a sample of smoked sheet, technically classified yellow. This sample was purified by extracting with acetone for 8 days; it was then dried in vacuum, and 1.25 percent of phenyl- β -naphthylamine was added as an antioxidant. Two master samples containing 30 percent and 32 percent sulfur by weight were prepared by mixing the rubber and sulfur on a small mill. The other mixtures and samples for vulcanization were prepared on the mill by adding an appropriate amount of the purified rubber to one of the master samples.

The vulcanization was accomplished by curing in a conventional press for 20 hr at 150° C. Eighteen vulcanizates of varying compositions were prepared, and the order of preparation and measurement of

¹ Figures in brackets indicate the literature references at the end of this paper.

their respective physical properties was randomized so that any slow oxidative processes which might occur during storage would not bias the results. To further minimize oxidation and degradation all of the rubber samples were stored in a solid-carbon dioxide chest. The unreacted mixtures of the rubber and sulfur were prepared by pressing in a vacuum mold at 100° C prior to their physical examination. The percentage of sulfur chemically bound in the vulcanizates was determined by analysis after the removal of free sulfur by acetone extractions. The method of analysis was a micro Carius combustion followed by the gravimetric determination of the sulfur as barium sulfate.² It was found that the percentage of bound sulfur was usually less than the sulfur contained in the mixtures prior to vulcanization.

2.2. Methods

The linear thermal expansion of the mixtures and of the vulcanizates was determined by using a photoelectric recording interferometer. The design and operation of this instrument have been described by Work [10]. He concluded that T_g can be measured with a precision of $\pm 1.0^\circ$ C with this instrument and that the coefficients of linear expansions are reproducible within ± 5 percent.

In making these measurements three specimens about 5 by 5 by 3 mm were cut from each sample and used as spacers between the two quartz optical flats. The specimens were first heated in the interferometer to the maximum temperature to be used, then several runs on both heating and cooling cycles were made. The heating was done electrically and the cooling by liquid nitrogen. The rate of temperature change was about 1° C per minute and a temperature interval from -180° to $+140^\circ$ C was studied.

The record from the photoelectric recording interferometer gives thermocouple emf horizontally as a measure of temperature and a vertical step for each fringe or half wavelength change in thickness of the specimens. The linear expansion at any temperature T can be found from this record by means of the equation:

$$\Delta L/L_0 = N\lambda/2L_0 + C \quad (1)$$

The temperature T is determined from the thermocouple emf; ΔL is the change in length between the reference temperature T_0 and T ; L_0 is the average thickness of the specimens at T_0 (25° C in the present work); N is the number of fringes between T_0 and T ; λ is the wavelength of the light used in air at temperature T_0 ; and C is a factor correcting for the change in wavelength in air with temperature. The values of C at various temperatures for the helium yellow light ($\lambda = 5876$ Å) used are given by Merritt [11].

In interpreting the experimental results, it is more convenient to consider the specific volume and its changes with temperature rather than the change in length. To accomplish this conversion the specific

volume v at temperature T was calculated from the linear expansion by the relation

$$v = v_0(1 + \Delta L/L_0)^3 \quad (2)$$

where v_0 is the specific volume at a reference temperature T_0 . This relation is exact when the expansion is isotropic. This assumption appears to be well founded for amorphous polymers, and the volume expansion calculated from interferometric data compares well with the direct determination of this quantity by dilatometric means [12]. The specific volumes of the samples were determined at 25° C by the method of hydrostatic weighing [13].

3. Results

The volume-temperature relations, determined in the described manner, for the series of rubber-sulfur vulcanizates encompassing a composition range of 0 to 30 percent bound sulfur are plotted in figure 1. The curve pertinent to a specific vulcanizate is designated by a number corresponding to the percent bound sulfur. The glass temperature T_g is taken at the point of intersection of the two straight lines which represent the volume-temperature coefficient in the liquid and in the glassy state. Above T_g the volume-temperature data are well represented by a linear relation. However, below T_g the linear region covers only a very small temperature interval and the data are best represented by a curve of decreasing slope with decreasing temperature, as has been observed in other polymeric systems [7, 12]. Although for this reason a precise determination of T_g is difficult, values which are reliable on a comparative basis can be easily obtained.

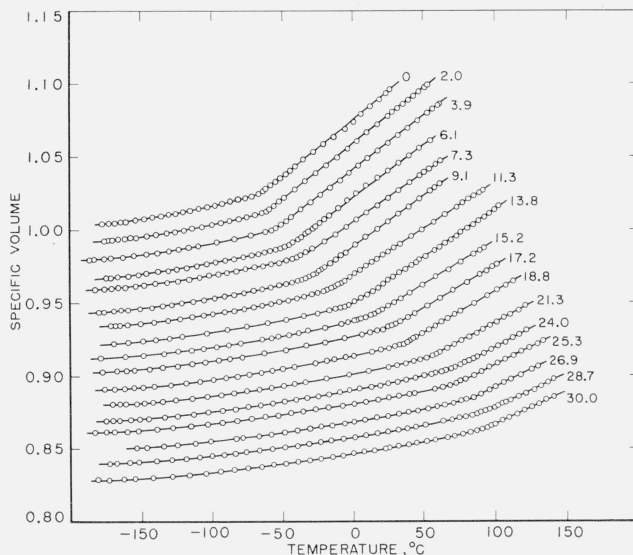


FIGURE 1. Plot of specific volume as function of temperature for each of the rubber-sulfur vulcanizates.

Number on right indicates percent bound sulfur.

² The chemical analysis was performed by R. A. Paulson and Miss L. J. Tregoning of the National Bureau of Standards.

Values of T_g for the various rubber-sulfur vulcanizates are listed in the fifth column of table 1. For this series of compounds T_g continuously increases as the combined sulfur content is increased, ranging from -69°C for the pure natural rubber to $+90^\circ\text{C}$ for the sample containing 30 percent sulfur. Thus a very wide range in glass temperatures can be achieved merely by reacting an appropriate quantity of sulfur with natural rubber. The manner in which T_g changes with sulfur composition is illustrated in figure 2. The curve in this figure is distinctly S-shaped since the initial amounts of bound sulfur cause only a relatively slight rise in T_g . However, when about 4 percent sulfur has been combined the rate of increase accelerates and finally levels off at the higher sulfur contents. The general shape of the curve in figure 2 is similar to that given by Boyer and Spencer [1] where values of T_g as a function of sulfur content, determined by a wide variety of methods, were collected from the then existing literature. A similar plot is also given by Schmieder and Wolf [14] where the values of T_g were determined by dynamical mechanical methods. In the latter work the values of T_g are significantly higher over the complete composition range than those reported here, while the compilation of Boyer and Spencer appears to be in good agreement with the present work except at the very highest sulfur contents where the literature values appear to be about 10° lower.

In figure 1 the volume-temperature curves depicting each of the compounds are displaced to lower values as the sulfur content is increased. Thus at a reference temperature either in the liquid state or in the glassy state the specific volume decreases with increasing sulfur content. This decrease in specific volume and the concomitant increase in T_g is similar to that which is observed in many other polymeric systems [3, 7]. Taking 25°C as a reference tempera-

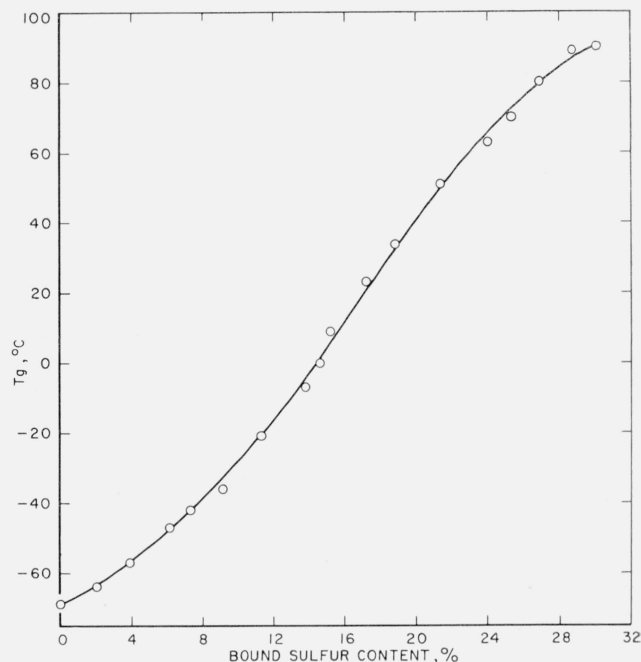


FIGURE 2. Plot of glass temperature, T_g , as function of bound sulfur content for rubber-sulfur vulcanizates.

ture in the liquid state, the specific volumes corresponding to this temperature are given in table 1 and are also plotted in figure 3. For those systems which are actually in the glassy state at the reference temperature the appropriate values of the specific volume were obtained by a linear extrapolation of the liquidus. From figure 3 it can be seen that the specific volumes of the vulcanizates at the reference temperature decrease linearly with composition until about 19 percent sulfur at which point the rate of decrease of the specific volume becomes appreciably

TABLE 1. Thermal expansion data and glass transition temperatures for natural rubber-sulfur vulcanizates

Nominal sulfur content	Bound sulfur content	V_{25} Measured specific volume at 25°C	(V_{25}) Specific volume ^a in liquid state at 25°C	T_g Glass transition temperature	α_1 Slope volume-temperature curve above T_g	α_g Slope volume-temperature curve immediately below T_g
%	%	cm^3/g	cm^3/g	$^\circ\text{C}$	$\text{cm}^3/\text{g}^\circ\text{C}$	$\text{cm}^3/\text{g}^\circ\text{C}$
0	0.0	1.095	1.095	-69	775×10^{-6}	223×10^{-6}
2	2.0	1.078	1.078	-64	762	219
4	3.9	1.059	1.060	-57	748	202
6	6.1	1.040	1.040	-47	727	211
8	7.3	1.021	1.025	-42	688	188
10	9.1	1.005	1.010	-36	708	197
12	11.3	0.985	0.988	-21	638	198
14	13.8	.965	.966	-7	645	188
15	14.6	.958	.960	0	616	165
16	15.2	.948	.951	+9	599	212
18	17.2	.933	.935	23	581	199
20	18.8	.919	.920	34	566	188
22	21.3	.905	.900	51	527	201
24	24.0	.894	.881	63	518	210
25	25.3	.884	.873	70	491	208
28	26.9	.872	.861	80	475	212
30	28.7	.861	.846	89	485	202
32	30.0	.850	.841	90	471	178

^a The specific volumes are corrected for the amount of free sulfur present.

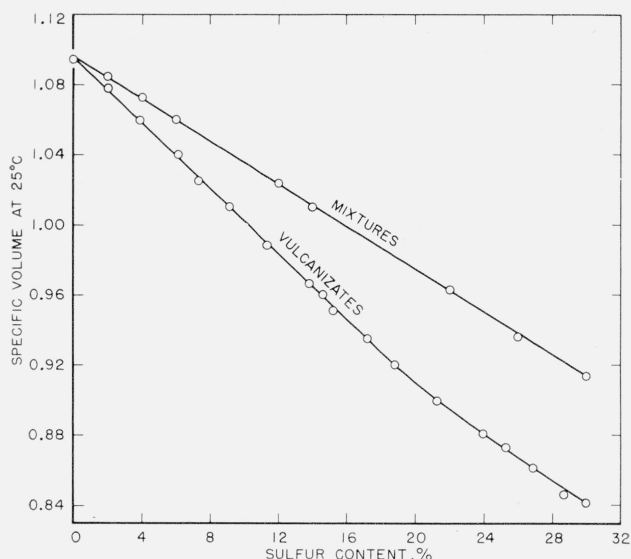


FIGURE 3. Plot of specific volume in liquid state at reference temperature (25°C) against percent sulfur.

Upper curve for mixture, lower curve for vulcanizate.

less. If actual specific volumes had been plotted, this change in slope would have been even larger [8] because of the fact that at compositions of 19 percent or more sulfur the glass transition is above 25°C . In addition to the decrease in specific volume that is observed, there is also a significant continuous decrease in the volume-temperature coefficient above T_g , while a definite but smaller decrease occurs in the linear portion below T_g . The appropriate values of the volume-temperature coefficients are also given in table 1.

The volume-temperature relations for some typical natural rubber-sulfur mixtures, as contrasted to the chemically combined systems, are illustrated in figure 4. For each of the mixtures the data can again be well represented by a straight line in the liquid region and by a curved line in the glassy state. The glass temperatures, as determined from the data of figure 4, are remarkably constant and can be assigned a value of $-68^{\circ}\text{C} \pm 1^{\circ}$ for all the mixtures. The dependence of the specific volume of the mixtures at 25°C on the sulfur content is also shown in figure 3; the data are well represented by a straight line. The values of the specific volume observed and those calculated by the additive mixing law agree very well and indicate that no net change in volume occurs on mixing. A similar observation was made some years ago by McPherson [8]. The pertinent physical constants for these mixtures are tabulated in table 2.

4. Discussion

The very large changes in the glass temperature of natural rubber that are induced by reaction with sulfur must be caused by the alteration of the liquid state structure. These changes in structure occur as a consequence of the chemical processes that have

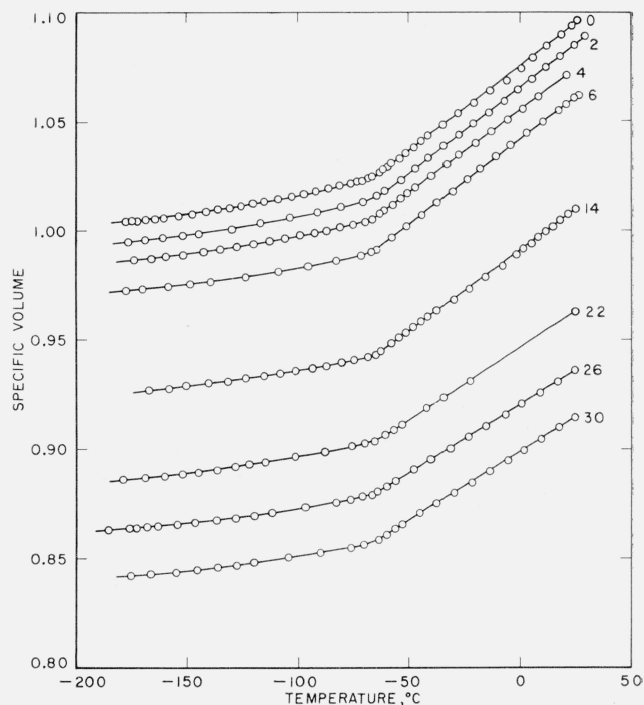


FIGURE 4. Plot of specific volume as function of temperature for the rubber-sulfur mixtures.

Number on right indicates percent sulfur.

taken place. The natural rubber-sulfur reaction, though well known and intensively studied, is quite complex. There are wide areas of disagreement among various investigators as to the mechanism of the reaction and the resulting structures that are formed [15, 16]. It is clear, however, that a portion of the combined sulfur is utilized to form intermolecular crosslinks. The complexity of the chemical process precludes at present the possibility of ascribing the changes in T_g to specific chemical alteration, and somewhat more general considerations must be given to explain the drastic changes in the physical and mechanical properties that occur.

The variation of the glass temperature in other polymeric systems with the systematic alteration of structure or the composition has been satisfactorily

TABLE 2. Thermal expansion data and glass transition temperatures for natural rubber-sulfur mixtures

Nominal sulfur content	v_{25} Specific volume at 25°C	T_g Glass transition temperature	α_l Slope volume-temperature curve above T_g	α_g Slope volume-temperature curve immediately below T_g
%	cm^3/g	$^{\circ}\text{C}$	$\text{cm}^3/\text{g}^{\circ}\text{C}$	$\text{cm}^3/\text{g}^{\circ}\text{C}$
0	1.095	-69	775×10^{-6}	223×10^{-6}
2	1.085	-68	789	224
4	1.073	-68	756	196
6	1.060	-68	783	181
12	1.024	-67	553	198
14	1.010	-67	739	180
22	0.963	-67	651	180
26	.936	-68	619	168
30	.914	-68	630	157

explained on the basis of free volume considerations [3-7]. The problems treated, using this concept, have been those where the free volume itself need not be specified but the changes in the free volume, as manifested by the changes in the specific volume, are determined, and the change in T_g relative to that for a reference polymer can be calculated. This procedure is limited to cases where the changes that are occurring do not drastically alter the chemical or molecular structure of the polymer and has been successful in treating the molecular weight dependence of T_g [3], the effect of crosslinking [4], dilution with low-molecular-weight materials [5], copolymerization [5, 6], and the effect of increasing the number of groups in a polymer side chain [7]. It is of interest to apply the aforementioned ideas to vulcanizates of rubber-sulfur.

In utilizing this method the specific volume in the liquid state is assumed to consist of two parts; that volume which would be occupied by a closely packed liquid structure and the remaining volume which is termed the free volume. The net change in the specific volume of a given system, when subject to an external change, may reflect changes in the occupied volume, in the free volume, or in both. One consequence of the reaction of natural rubber with sulfur is that at a reference temperature in the liquid state the specific volume is reduced. Following procedures used in describing T_g for the poly(*n*-alkyl methacrylate) series of polymers, a certain fraction *f* of this volume change is attributed to a decrease in the free volume of the system, so that the relative change in free volume that occurs at temperature *T* can be expressed as

$$\phi^s(T) = \phi^0(T) - f[\bar{v}^0(T) - \bar{v}^s(T)] \quad (3)$$

where $\phi^s(T)$ and $\phi^0(T)$ are the specific free volumes of the vulcanizate and pure rubber, respectively, and $\bar{v}^s(T)$ and $\bar{v}^0(T)$ are the corresponding values of the specific volumes at a temperature *T* in the liquid state. It is further assumed that the free volume varies linearly with temperature so that

$$\phi(T) = \phi_g + \Delta\alpha(T - T_g) \quad (4)$$

where ϕ_g is the free volume at the glass temperature T_g , and $\Delta\alpha$ represents the rate of change of the free volume with temperature. By writing equation (4) for the vulcanizate and for pure rubber at a temperature T_R and substituting these results in equation (3), the following expression is obtained relating the glass temperature of the vulcanizate T_g^s to that of the pure polymer and to the volumes of the system:

$$T_g^s = T_R - (\Delta\alpha^0/\Delta\alpha^s)(T_R - T_g^0) + (f/\Delta\alpha^s)[\bar{v}^0(T_R) - \bar{v}^s(T_R)] + (\phi_g^s - \phi_g^0)/\Delta\alpha^s \quad (5)$$

where T_R is a reference temperature taken to be 298° K and the superscript 0 refers to pure rubber while the superscript *s* refers to the vulcanizate.

In order for equation (5) to be converted into a form that can be useful in interpreting the experimental results, it is necessary that the appropriate criterion for glass formation be specified. The simplest condition to take is that glass formation represents a state of isofree volume. This criterion was originally applied by Fox and Flory [3] in explaining the effect of molecular weight on the glass temperature of polystyrene and has been applied in explaining the effect of composition in copolymers and polymer-diluent mixtures and the effect of structural changes on the glass temperature of the poly(alkyl methacrylates). When the aforementioned criterion is applied, equation (5) simplifies to

$$T_g^s = 298 - 94\Delta\alpha^0/\Delta\alpha^s + f/\Delta\alpha^s[\bar{v}^0(298) - \bar{v}^s(298)] \quad (6)$$

It has been suggested [17, 18] that the condition ϕ_g/\bar{v}_g is a constant at T_g is a more satisfactory specification of glass formation. When this condition is introduced into equation (5) an additional term results in equation (6). However, it has been found that this slight correction does not sensibly alter the results [7].

Utilizing equation (6), values of *f* for each of the vulcanizates can be computed by using smoothed data derived from table 1 and assuming that the volume-temperature coefficient for the free volume can be identified with the difference in the corresponding coefficients in the liquid and glassy state. The quantities used in the calculation and the resulting values of *f* that are computed from equation (6) are given in table 3. It can be seen from these results that a reasonable value for the magnitude of the quantity *f* is obtained; it being less than unity and comparable to that obtained for other systems. As contrasted to the results for other systems, however, these deduced values of *f*

TABLE 3. Calculation of *f*, the fraction of the specific volume change upon vulcanization which occurs in the free volume^a

Bound sulfur content	$\Delta\alpha^s$	$\bar{v}^0(298) - \bar{v}^s(298)$	<i>f</i>
%	$cm^3/g \text{ } ^\circ K$	cm^3/g	
0.0	5.57×10^{-4}	0.000	-----
2.0	5.48	.017	0.226
3.9	5.38	.035	.230
6.1	5.22	.056	.261
7.3	5.12	.068	.263
9.1	4.93	.085	.261
11.3	4.68	.107	.289
13.8	4.38	.129	.299
14.6	4.27	.137	.305
15.2	4.19	.143	.319
17.2	3.91	.160	.322
18.8	3.68	.175	.318
21.3	3.35	.195	.313
24.0	3.03	.214	.296
25.3	2.90	.223	.294
26.9	2.81	.234	.289
28.7	2.72	.246	.283
30.0	2.72	.254	.274

^a The values in the second and third columns are taken from smoothed curves, $\Delta\alpha^0 = 5.57 \times 10^{-4}$.

remain only approximately constant with increasing amounts of bound sulfur. They gradually increase from a value of 0.23 at 2 percent combined sulfur to a maximum value of 0.32 at 17 percent sulfur and then slowly decrease once again. Though the deviation of each value of f from the mean is not very large, the lack of constancy in this quantity is such that using the mean value of f in equation (6) does not adequately represent the data of figure 2.

From free volume considerations it would be expected that the glass transition temperature for the rubber-sulfur vulcanizates should increase as the amount of combined sulfur increases since a concomitant decrease in specific volume occurs. Though this effect is observed, the simple relation that has been derived in equation (6), though known to be applicable to other systems [7], is only qualitatively correct for the system discussed in the present work. The reason for the lack of quantitative agreement in this instance, when compared to other systems, can be due to complications caused by structural alterations induced by the chemical processes. Even at the lower levels of bound sulfur only a portion of the sulfur is involved in intermolecular crosslinks, the fate of the remainder of the sulfur being still a matter of argument [16]. The structure of the compounds containing the higher amounts of bound sulfur is still obscure. With the distinct possibility existing of major structural changes on reaction with sulfur it is not surprising that the relatively simple consideration set forth above yields only qualitative agreement with experiment. It must also be remembered that 32 percent bound sulfur corresponds to one sulfur atom bound per isoprene unit. On this basis a relatively large amount of sulfur is incorporated into the compounds and could thus be treated as a second component, similar to a copolymeric ingredient or low molecular weight diluent. Although, in a formal fashion, the problem can be treated from this point of view by methods previously described [5, 6],

several arbitrarily selected parameters are required which can not be evaluated independently. Thus, the physical significance of the results is open to question.

On the other hand, in the case of the natural rubber-sulfur mixtures the concepts outlined above appear to apply very well. In this instance there is no net change in the specific volume of the system on mixing over the complete composition range. Thus the free volume available to the polymer is neither increased nor decreased and consequently T_g remains invariant with composition.

5. References

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