Effect of Cross-Links on the Glass Transition Temperature of End-Linked Elastomers

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ABSTRACT: Changes in the glass transition temperature of end-linked networks as a result of the cure process have been studied by examination of a series of stoichiometrically imbalanced PDMS networks covering a wide range of stoichiometric ratio values. The data were compared to existing theories in an effort to resolve the question of cross-link contribution to T_g. The results support the notion based on the Gibbs–DiMarzio theory that elastically effective junctions rather than any branch point dominate the contribution of cross-links to T_g. It has also been shown that existing theories are capable of predicting cure-related changes in T_g for a variety of cross-linked systems.

Introduction

The change in the glass transition temperature (T_g) of polymers undergoing curing reactions is a problem of practical and fundamental interest. A considerable amount of work on a variety of cross-linked systems has been published over the years and summarized in two recent publications.[1,2] Generally speaking, cross-linked systems are formed by four types of reactions.

(I) Reactions between two or more chemically different functional groups attached to *small molecular weight* multifunctional species and usually placed at the *molecule ends* result in the formation of a highly cross-linked thermoset system with relatively short strands between cross-link points. Ideally, each type of functional group (or species) is capable of reacting only with the other type of functional group (species). Almost every reaction results in the formation of nonlinear structures with only very limited chain extension at the onset of the reaction. Epoxies are most prominent in this category.

(II) *End-linking* of *high molecular weight prepolymers* by means of low molecular weight cross-linkers leads to the formation of sparsely cross-linked elastomers. Cross-link density is determined by the molecular weight of the prepolymer (M_o). The transition from type I to type II networks is arbitrarily defined around $M_o = 1000$.

(III) *Networks formed by the copolymerization* of di- and multifunctional *monomers*. The styrene–divinylbenzene system may serve as an example. The monomers react primarily with other difunctional monomers and occasionally with the multifunctional comonomer. In the course of the reaction long linear chains are formed through the primary polymerization reaction. Branching and eventually cross-linking are the result of the less frequent reaction with the multifunctional species. Cross-link density is controlled by the relative amounts of the two types of monomers. Relatively very small amounts of the multifunctional monomer are sufficient for gelation.

(IV) Vulcanization of *polymer chains* occurs by cross-linking of functional groups distributed *along the chain backbone*. Cross-linking is effected either by small molecular weight curing agents (e.g. sulfur or peroxide in natural rubber) or by irradiation. Type IV reactions are similar to type II reactions except for the position of the reactive groups and, thus, the regularity of the molecular weight between cross-links. Also, the gel point in type IV systems occurs at a very early stage of the reaction relative to type II reactions.[17,18]

Although changes in T_g are observed for all four types of curing reactions the mechanisms responsible for these changes and their relative magnitude differ from one network type to the other. The vast majority of research in this area has focused on type I reactions and only limited attention has been given to the other three types of networks.[1,2]

The increase in T_g of a polymeric system undergoing cure is believed to be the result of several processes: (i) reduction in the concentration of chain ends[3,4] up to their complete disappearance at full conversion in a perfect (defect free) network (This effect is expected to contribute the most in the formation of thermosets and end-linked networks. Its relative importance decreases with the increase of M_o.); (ii) disappearance of small molecular weight molecules[5] ("plasticizer effect") (With the exception of radiation-cured systems, this effect may influence all types of curing reactions); (iii) formation of branch points and cross-links;[6–8] (iv) non-Gaussian chain statistics[2] (The last will only affect systems with relatively short chains between branch points (high cross-link density) such as thermosets). Recently, it has also been shown[9] that the formation of cyclic structures may increase the T_g of polymers.

Some or all of these processes take place simultaneously during cure, with its magnitude and relative importance changing continuously in the course of the reaction depending on the reaction type (I–IV) and on the starting materials (cf. Table I). As a result, it is difficult to separate experimentally their individual contributions. Most of the experimental work has been carried out on epoxy and urethane systems typically with molecular weights between cross-links below 1000. However, limited data on other systems are available as well.[1,2] In type I systems the disappearance of chain ends, formation of branches, formation of elastically effective cross-links, and non-Gaussian effects are all expected to contribute to the shift in T_g.

Two theories capable of dealing with this combination of factors are available. The theory proposed by Hale, Macosko, and Bair[2] (HMB theory) makes use of the earlier works of Gibbs and DiMarzio[7,10] on the effect of cross-links and branch points. A term accounting for non-Gaussian distribution of chain configurations has also been incorporated into the model. According to this theory T_g

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Table I
Factors Affecting the Change in Glass Transition Temperature as a Result of Cross-Linking in the Four Types of Networks[a]

reaction type	chain ends	monomer depletion	branch points	cross-links	non-Gaussian
I	+++	+++	+++	+++	+
II	+/0	+/0[c]	+++	+++	0
III	0[b]	+++	+	+++	0
IV	0	+/0[c]	0	+++	0

[a] Key: +++, very important; +, moderate importance; 0, negligible effect. [b] Excluding considerable amounts of either chain propagation or termination by combination. [c] Important only in the case of high initial cross-linker concentrations.

of a cross-linked system is given by

$$T_g = T_{g,u}/[1 - K_2X_e/(1 - YX_e^2)] \qquad (1)$$

where X_e is the *elastically effective* cross-link density (defined as the moles of chains per mole of segments), Y is a parameter that accounts for non-Gaussian behavior, and K_2, the only adjustable parameter in the model, is the DiMarzio constant which depends on the chemical nature of the polymer and has been argued to be universal.[7] The effect of chain ends is accounted for by $T_{g,u}$ which is defined as the T_g of an un-cross-linked system identical to the cross-linked one in every respect except that the cross-links are missing. It is obtained from the Ueberreiter–Kanig[4] expression for the molecular weight dependence of T_g for a linear polymer:

$$1/T_{g,u} = 1/T_{g,\infty} + K_1/M_n \qquad (2)$$

where $T_{g,\infty}$ is the T_g of an infinitely long polymer and M_n is the number average molecular weight. In some cases it is more convenient to modify eq 2 so that $T_{g,u}$ is given in terms of the conversion of functional end groups rather than molecular weight. According to the HMB theory, any T_g increase in the pregel region is only due to changes in $T_{g,u}$. In the postgel region T_g increases as a result of the combined effect of cross-link formation and chain-end disappearance.

The theory presented by Stutz, Illers, and Mertes[1] (the SIM theory) is a modification of the DiBenedetto equation:[5,8]

$$T_g = T_{g,u}\,[1 + K_2X_c/(1 - X_c)] \qquad (3)$$

where X_c is the cross-link density expressed as the mole fraction of *all cross-links* present in the system weighed by functionality. The parameter K_2 is related to DiBenedetto's[8] lattice energy ratio. In the SIM model their is no distinction between the pre- and postgel regions since all junctions connecting three chains or more, whether branching points or cross-links, are included in X_c. But, in the computation of X_c the factor $(i - 2)/2$ is used to weigh higher functionality (i value) junctions more heavily.

The Fox–Flory[3] equation is used to account for the disappearance of chain ends:

$$T_{g,u} = T_{g,\infty} - K_1/M_n \qquad (4)$$

For a more complete discussion of this and the previous model the reader is referred to the original papers.

The effect of cross-linker consumption (plasticizer effect) although not specifically discussed in these two models is readily incorporated into both theories by means of the $T_{g,u}$ term, as will be demonstrated in the Discussion.

The glass transition temperature may be discussed either in terms of free volume, hard core volume, and localized segmental mobility[5,6,11] or in terms of reduced configurational entropy.[10] This constitutes the main point of disagreement between the SIM and HMB models. Using the first approach, glass transition is a short-range phenomenon and any cross-link whether elastically effective or not should contribute the same to T_g. Furthermore, a branch point is identical in this context to a three-functional cross-link, and a four-functional junction being more rigid than a three-functional one should have a bigger effect on T_g. If, on the other hand, the Gibbs–DiMarzio approach is accepted as in the HMG model, glass transition is a long-range phenomenon and only elastically effective junctions should be considered. Contradictory experimental data are available concerning the contribution of branches. Some data based on either well-characterized stars or branched polymers may be interpreted as supporting the Gibbs–DiMarzio approach whereas other data seem to support the free-volume approach.[2] As to the contribution of cross-links, Hale et al. have tried to resolve the disagreement by comparing their carefully taken experimental data on epoxy–novolac systems as well as data from the literature to the predictions of the HMB and the SIM models. The only major difference they reported between the agreement of the two models with the data is attributed to the onset of non-Gaussian effects at very high conversions.

The difficulty in determining whether all junction points or only elastically effective cross-links contribute to the increase in T_g is due to the simultaneous contribution from several processes in the chemical systems studied. In addition, the good agreement between the theoretical models and the data is partially accomplished by the need to obtain the value of K_2 in eq 1 or 3 (and in many cases also K_1 in eq 2 or 4 due to the lack of appropriate model linear systems) by data fitting. In this work we have tried to circumvent these problems in order to reach a conclusion concerning the appropriate approach to the contribution of junctions in cross-linked elastomers.

The approach taken in this work was to use a type II network forming reaction. By selection of a relatively long prepolymer, the difference between eqs 2 and 4 for $T_{g,u}$ vanishes. The values of the parameters in these equations ($T_{g,\infty}$ and K_1) are readily obtained independently. Due to the large distance between junction points, non-Gaussian effects may be entirely neglected. In place of quenching the reaction to obtain data at intermediate conversions, imbalanced stoichiometry has been employed. Mixtures with various degrees of stoichiometric imbalance r, were prepared and allowed to react till completion eliminating any uncertainties involved in determination of conversion and in the measurement of T_g on partially reacted systems. As opposed to thermally quenched reactions which are commonly used in this type of studies, T_g measurements may be repeated and factors such as thermal history and rate of heating carefully examined, increasing the accuracy of T_g determination. In addition, since for $r < 1$ the cross-linker has been completely reacted and incorporated into the system, the plasticizer effect is eliminated in the systems used for parameter evaluation. The change in T_g is obtained by direct comparison of the T_g for the primary chain and that of the cross-linked system at full conversion. Finally, the system allows a test of the models which is not biased by the fit of K_2 to the data. The concentration of elastically effective junction points in cross-linker lean ($r < 1$) and cross-linker rich ($r > 1$) systems is not symmetric about the $r = 1$ point. The structure of the networks at equal distances from the point of stoichiometric balance is quite different. Also, at $r < 1$ all junctions are four functional whereas for $r > 1$ a mixture of functionalities from zero to four is present, enabling a test of the weighing scheme suggested by Stutz and co-workers.[1] Hence, it is possible to determine the value of the adjustable parameter by means of the data for $r < 1$ and since the chemistry of the system is unchanged, to use the same value to predict the behavior of T_g for $r > 1$. This will allow us to examine directly the HMB vs the SIM hypotheses. The main drawback of the approach used here is the small change in T_g observed in type II systems relative to that for type I systems.

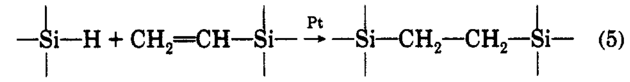
Experimental Section

Materials. The networks used in this study were prepared by a reaction between vinyl-terminated linear poly(dimethylsiloxane) (PDMS) and a four-functional silane cross-linker. The prepolymer and cross-linker were obtained from Petrarch Systems (Bristol, PA). Oligomers and low molecular weight contaminants were removed from the polymer by vacuum stripping. The molecular weight of the polymer $M_n = M_0 = 3500$, was determined by SEC and by NMR end-group analysis. The cross-linker (tetrakis(dimethylsiloxy)silane ($\mathrm{(HSiMe_2O)_4Si}$, $M_a = 328.7$, $T_g = 129$ K) was found by GC/MS to be at least 99% pure and was used as received.

Sample Preparation. The cross-linked samples were prepared by mixing the appropriate amounts of the prepolymer and cross-linker required to achieve the desired value of r, the stoichiometric ratio of reactants defined as the ratio of initial molar concentration of silane groups to that of vinyl groups:

$$r = [\mathrm{SiH}]_0/[\mathrm{Vi}]_0$$

It was followed by the addition of the platinum-based catalyst.[12] The error in the value of r was estimated at 0.02. The network was formed in bulk at 298 K by the hydrosilation reaction:



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{H} + \mathrm{CH_2{=}CH}-\overset{|}{\underset{|}{\mathrm{Si}}}- \xrightarrow{\mathrm{Pt}} -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{|}{\underset{|}{\mathrm{Si}}}- \qquad (5)$$

The evolution of structure in this system is well characterized, and the chemistry of its cure has been studied extensively.[12,13] The extent of side reactions of the cross-linker hydride silane groups was found to be negligible under the conditions used here.[14]

Thermal Analysis. All the samples prepared in this work were subjected to thermal analysis by differential scanning calorimetry (DSC). A Mettler 3000 series thermal analyzer system incorporating a Mettler DSC 30 instrument was employed. The temperature scale of the instrument was calibrated with n-hexane. In order to ensure an identical thermal history for all samples the following conditions were employed: The DSC cell containing the sample was rapidly cooled to 123 K and then heated to 273 K at a rate of 5 K/min, during which the change in specific heat as a function of temperature was recorded. The midpoint of the endothermal change associated with the glass transition was used for T_g since it was found here and by others[9] to be the most reproducible temperature. The reproducibility of the T_g measurements was within 0.5 K.

The DSC traces for four representative samples are shown in Figure 1. The trace corresponding to the unreacted prepolymer ($r = 0$) shows clearly the glass transition endotherm at 149.3 K followed by a pronounced cold crystallization exotherm at 186 K and finally two distinguishable endotherms for the melting of two crystalline forms at 227 and 235 K. This trace is in agreement with earlier extensive studies on thermal transitions in linear and cyclic PDMS.[9] The remaining traces correspond to three samples beyond the gel point at increasing degrees of cure. The most noticeable feature is the dramatic decrease in the cold crystallization exothermic peak and the corresponding endotherms until its practical disappearance, indicating the loss of crystallinity in the cross-linked system. There is no detectable shift in the cold crystallization or melting points with extent of cure.

Results and Discussion

The measured changes in T_g are depicted in Figure 2 as function of r, the stoichiometric ratio of the reactants.

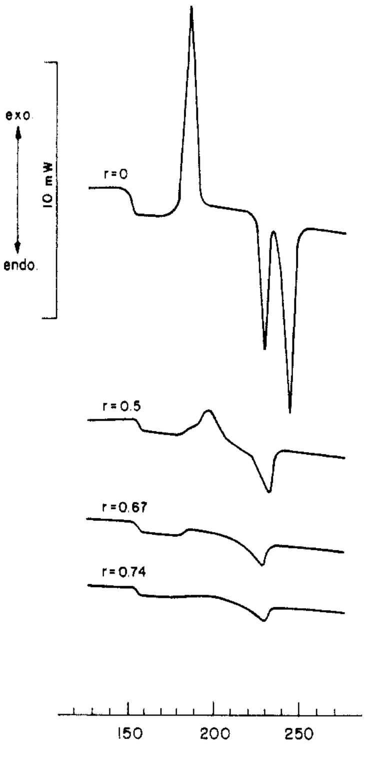


Figure 1. DSC traces for endlinked PDMS at different degrees of cross-linking. The trace corresponding to the prepolymer is labeled $r = 0$.

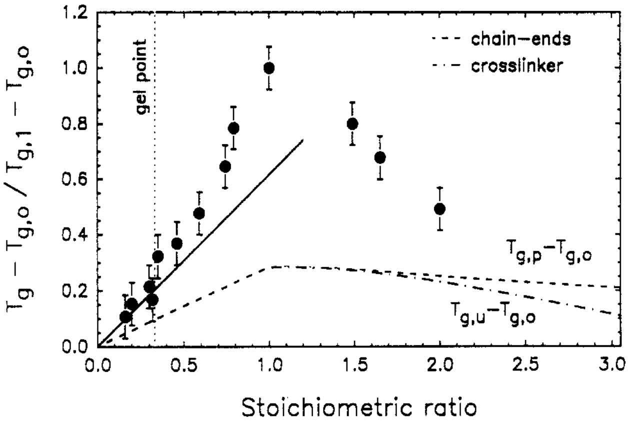


Figure 2. Change in T_g with degree of cross-linking. The experimental points correspond to data taken on end-linked PDMS. The solid line is the best fit linear regression line through the pregel points. The dashed line is the predicted change in T_g due to decrease in chain ends (eq 16). The dash-dot line represents the additional plasticizing effect of the cross-linker molecules (eq 8).

At low values of r, up to approximately the gel point, T_g is found to increase linearly with the degree of cure. The solid line in Figure 2 shows the linear fit of the pregel points. A somewhat stronger dependence on r is found beyond the gel point, as indicated by the departure from the solid line. The largest change in T_g is observed at the point of stoichiometric balance ($r = 1$) in which, theoretically, all primary chain ends are tied together by four-functional elastically effective junctions. It also corresponds to the highest cross-link density attainable in this system. For $r > 1$ there is a drop in T_g with increasing r although this decrease is at a smaller rate than the corresponding increase on the other side of the maximum. The values of the heat capacity differences at T_g, dC_p, as function of r are shown in Figure 3. Here too it is possible, despite the experimental scatter, to detect different

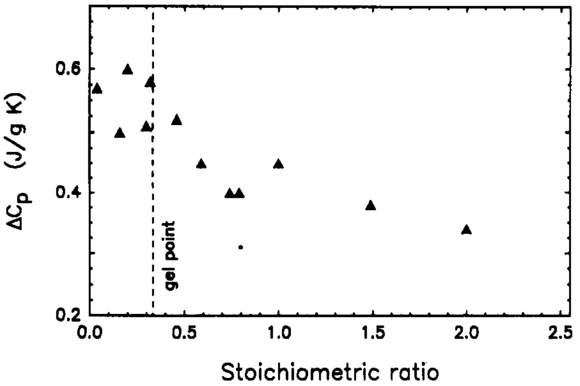


Figure 3. Change in C_p at the glass transition for end-linked PDMS networks.

behavior before and after the gel point. Up to the gel point the values of dC_p seem to scatter around a constant value of approximately 0.55 J/(g K). Past the gel point a steady decrease is observed in agreement with data on other systems.[2]

It has been suggested[15] that for thermosets

$$dC_{p,1}/dC_{p,o} = T_{g,o}/T_{g,1} \tag{6}$$

where the subscripts o and 1 indicate $r = 0$ and $r = 1$ (or $p = 0$ and full conversion $p = 1$) respectively. For the PDMS system examined here $dC_{p,1}/dC_{p,o} = 0.73$ and $T_{g,o}/T_{g,1} = 0.96$. These values are quite different from those reported for epoxy systems.[15] We have also examined the width of the glass transition temperature, but no consistent change with r has been found.[16]

Chain Ends and Diluents. The most obvious reason for an increase in T_g is the loss of chain ends similar to the situation in the case of linear polymers of increasing molecular weight. Since both models suggested for T_g dependence on M_n[3,4] are suitable for the relatively high molecular weights used in this work, we shall use the Fox–Flory relation (eq 4) in the foregoing discussion.

Let us consider the case of B_2, a linear polymer with a reactive end-group B at each chain end and molecular weight M_0 reacting till completion with a monomeric cross-linker A_f of functionality f and molecular weight M_A. The stoichiometric ratio r is defined as the initial ratio of A groups to B groups:

$$\begin{aligned} r &= [A]_o/[B]_o = f[A_f]_o/2[B_2]_o \\ &= fW_A M_o/2W_B M_A \end{aligned} \tag{7}$$

The square brackets $[\,]_o$ indicate an initial molar concentration, and W_A and W_B are the mass of A_f and B_2, respectively, in the reaction mixture. The reaction between a cross-linker and a chain may result in the formation of an end-capped chain (if only one arm of the cross-linker has reacted), a point of extension (if two of the f arms have reacted), and either branch point or junction point (if at least three arms have reacted). The difference between the last two is whether the chains emanating from this point are dangling chains (branch point) or connected to the network by its other ends (junction point). By the standard definition[17,18] a junction point is considered elastically effective if at least three strands emanating from it lead to the gel. For the case of $r < 1$, at the end of the reaction all cross-linker units have reacted and are part of f-functional branch points or junctions. Thus, $T_{g,u}$ is determined by the reduction in chain ends only. The situation is somewhat more complicated in the case of $r > 1$. Here, at the end of the reaction a mixture of A_f molecules with 0, 1, 2, ..., f reacted arms is present. If two or more arms of a cross-linker molecule have reacted, each reacted arm results in the consumption of one chain end and the situation is similar to that discussed previously. If only one arm has reacted we will assume that no change in T_g has occurred. This is not strictly true since an end-capped chain may have a somewhat higher T_g as a result of the new bulky chain termination. But, in view of all other effects on T_g this is a minor correction which may be neglected with little effect on the results. If none of the arms have reacted the cross-linker will act as diluent resulting in a reduction of T_g.

Let's denote by $T_{g,u}$ the value of T_g of an un-cross-linked system identical to the cross-linked one in every respect except that the cross-links are missing. $T_{g,p}$ represents T_g of the reacted polymer molecules after the effect of chain-end disappearance has been accounted for, and $T_{g,m}$ is the T_g of the cross-linker monomer. Following DiBenedetto[5] we may write an expression for $T_{g,u}$ taking into account the plasticizing effect of the cross-linker:

$$T_{g,u} = \left[\frac{1-s}{T_{g,p}} + \frac{s}{T_{g,m}}\right]^{-1} \tag{8}$$

where s is the segment fraction of diluent (i.e. unreacted A_f) in the system. Since the ratio of polymer to cross-linker segment size is proportional to the ratio of molar volumes,[5] it is not difficult to show that

$$s = \frac{(1-p)^f}{1 + (f/g)(M_o/M_a)(\rho_A/\rho_B)(1/r)} \tag{9}$$

Here ρ_A and ρ_B are the densities of the cross-linker and polymer respectively, p is the conversion of A, the reactive groups on the cross-linker, and g is the functionality of the polymer (2 in the case discussed here). The numerator in eq 9 represents the fraction of cross-linker molecules which have not reacted at all.[1,17] For $r < 1$, $p = 1$ which by eq 9 leads to $s = 0$ or $T_{g,u} = T_{g,p}$. For $r > 1$, $p = 1/r$ and as r approaches infinity $s \rightarrow 1$ and $T_{g,u} \rightarrow T_{g,m}$. In general, for type II reactions M_o/M_a is a large number, $f/g > 1$, and the density ratio is of the order of unity. Hence, only for large values of r or in the case that $T_{g,p}$ and $T_{g,m}$ are very different the diluent effect will play any role.

We will now turn our attention to the derivation of an expression for $T_{g,p}$. Our hypothesis is that eqs 2 and 4 are manifestations of the dependence of T_g on the concentration of chain ends in the system rather than molecular weights. Thus, we wish to recast the Fox–Flory[3] equation (eq 4) in terms of chain ends:

$$T_g = T_{g,\infty} - K_1[\mathrm{ce}]/2W \tag{4'}$$

$$T_{g,p} = T_{g,o} + (K_1/M_o) - K_1[\mathrm{ce}]/[2W_B(1 + 2rM_A/fM_o)] \tag{10}$$

Equations 7 and 4 for M_0 have been used in eq 4′ to obtain eq 10. Here [ce] is the molar concentration of chain ends, and W the total weight is just the sum of W_A and W_B. The initial concentration of chain ends is simply

$$[\mathrm{ce}]_o = 2[B_2]_o = 2W_B/M_o \tag{11}$$

Inserting eq 11 into eq 10 and rearranging

$$T_{g,p} = T_{g,o} + (K_1/M_o)\{1 - [\mathrm{ce}]/[\mathrm{ce}]_o(1 + 2rM_A/fM_o)\} \tag{12}$$

The concentration of chain ends after the reaction has

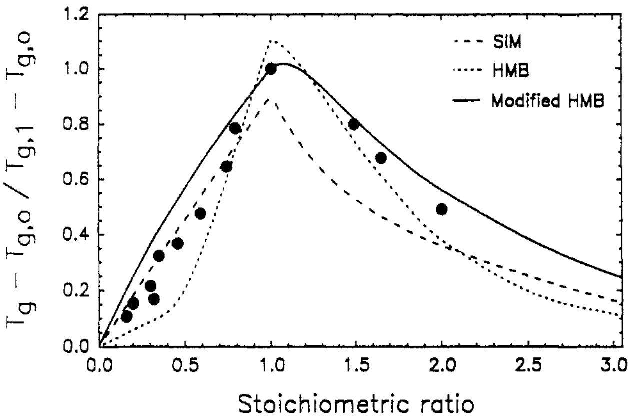


Figure 4. Comparison of the fit of three glass transition theories (SIM[1], HMB[2], and modified HMB) to the PDMS data. The theoretical lines were fit to the $r < 1$ data. The same parameters were used to compute the lines for $r > 1$. The parameter values used to compute the theoretical lines are listed in Table III.

been completed is obtained from the remaining number of unreacted A groups:[1,17]

$$[\mathrm{ce}] = [\mathrm{ce}]_o - [\mathrm{A}_f]_o \sum_{i=2}^{f} i X_i \qquad (13)$$

Here X_i is the fraction of A_f molecules with i reacted arms. It is given by

$$X_i = \binom{f}{i} p^i (1-p)^{f-i} \qquad (14)$$

Making use of eqs 7, 11, and 14, we may rewrite eq 13

$$[\mathrm{ce}]/[\mathrm{ce}]_o = \left\{1 - (r/f) \sum_{i=2}^{f} i \binom{f}{i} p^i (1-p)^{f-i}\right\} \qquad (15)$$

The value of $T_{g,p}$ may now be calculated from eqs 12 and 14. It may then be used in eq 8 to get the combined effect of diluent and chain-end consumption on T_g. For the special case of $f = 4$ and complete reaction it is easy to show that

$$T_{g,p} = T_{g,o} + (K_1/M_o)\{1 - (1-r)/(1 + rM_A/2M_o)\} \qquad r < 1 \quad (16a)$$

$$T_{g,p} = T_{g,o} + (K_1/M_o)\{1 - (1-1/r)^3/(1 + rM_A/2M_o)\} \qquad r > 1 \quad (16b)$$

The computed change in T_g as a result of chain-end disappearance ($T_{g,p}$) is shown in Figure 2 by the dashed line and the combined effect of chain ends and diluent ($T_{g,u}$) by the dash–dotted line. The value of $K_1 = 6500$ K/(g mol) used in eq 16 was obtained from the work of Clarson and co-workers.[9] The experimental values are higher than the computed ones for the entire range of r values tested including the pregel region. It is quite obvious from Figure 2 that the increase in T_g in cross-linked systems cannot be explained by chain ends alone.

Cross-Links and Junction Points. The predictions of the SIM and HMB models are compared in Figure 4. In both models $T_{g,u}$ has been computed by means of eqs 8 and 16 as described above. In the SIM model[1] depicted by the dashed line, the weighed total number of cross-links and junctions X_c (eq 3) is given by

$$X_c = a_f \sum_{i=3}^{f} (i - 2/2) X_i \qquad (17)$$

where X_i, the fraction of i-functional A_f molecules, is given by eq 14 and a_f, the mole fraction of cross-linker in the system, is $a_f = [1 + ((f/g)r)]^{-1}$. For $f = 4$ and $g = 2$

$$X_c = r/(r + 2) \qquad r < 1 \qquad (18a)$$

$$X_c = (2r - 1)/(r + 2)r^3 \qquad r > 1 \qquad (18b)$$

The best fit of eq 3 to the data for the range $0 < r < 1$ was obtained with $K_2 = 0.053 \pm 0.003$. This value was used to compute the curve shown by the dashed line in Figure 4. The value obtained here for K_2 is one order of magnitude lower than the values reported for other systems.[1]

In fitting the HMB model (eq 1) to the data the non-Guassian parameter Y was set equal to zero. The number of elastically effective junctions X_e, was computed by the Miller–Macosko[17,18] method. The best fit value for K_2 over the range $r_{\mathrm{gel}} < r < 1$ is 0.103 ± 0.016. The dotted line in Figure 4 corresponds to the prediction of the HMB model. Hale et al.[2] reported $K_2 = 0.117$ for their epoxy-novolac system and values ranging from 0.1 to 2.11 for data gathered from the literature on other type I systems.

The SIM model is in very good agreement with the experimental data for values of r below 1. It underestimates considerably the stoichiometrically balanced system and the data for $r > 1$. Since at $r < 1$ all junctions are four functional whereas at $r > 1$ there is a large number of three-functional junctions, it seems that the weighing scheme used in the SIM model by which a reduced weight is assigned to three-functional junctions is responsible for the discrepancy between the model and the data at $r \geq 1$.

The HMB model on the other hand, underestimates the effect of cross-links formed in the pregel region. For higher values of r ($r > 0.6$) and especially for $r > 1$ the HMB model is in very good agreement with the data and considerably better than the SIM model. The basic premise of the HMB model is that branch points or elastically ineffective junctions do not contribute to T_g. In the case of the systems evaluated by Hale and co-workers (type I) the distance between junction points and the length of the branches was considerably smaller than that existing in our system. Thus, it is conceivable that for short network strands (as in type I networks) the differences between elastically effective and ineffective junctions has an effect on T_g. But, as the distance between junction points increases, the difference between the effect of a junction and that of an elastically effective cross-link on T_g decreases. An alternative explanation to the larger change in T_g at the pregel region may be attributed to the formation of one chain long cyclics. The latter have been found to have a higher T_g when compared to equivalent linear chains.[9] Cyclic structures composed of more than one chain will have practically the same T_g as their linear counterparts. Presently, we have no way to quantify this effect although indirect evidence to the formation of such cyclics at $r < 1$ is available in the form of delayed gel point.[19]

In an attempt to improve the agreement between the data and the HMB model, we have modified the latter by replacing in eq 1 X_e (the concentration of elastically effective cross-links) by X_t the total number of junctions with $i > 2$ reacted arms. Contrary to the SIM model, all junctions are weighed equally irrespective of their functionality. Hence, $X_t = r/(r + 2)$ for $r < 1$ and $X_t = (4r - 3)/(r + 2)r^3$ for $r > 1$. The solid line in Figure 4 corresponds to the modified HMB (m-HMB) model with $K_2 = 0.09 \pm 0.01$. From the three models presented here and depicted in Figure 4 the m-HMB model gives the best fit for type II systems over the entire range of r values tested.

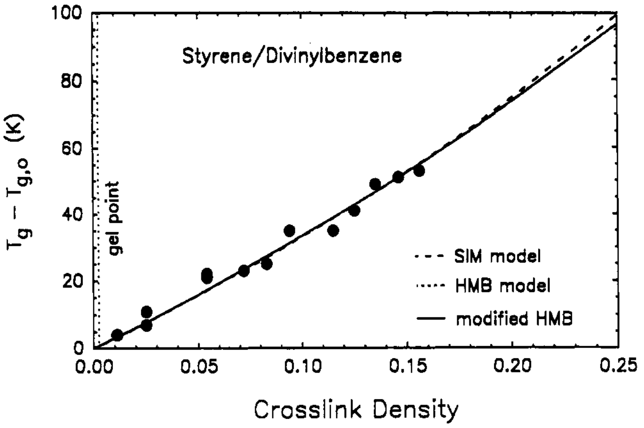


Figure 5. Type III network. Experimental data are for styrene–divinylbenzene (Kanig[20]). Theoretical lines were computed with the parameter values listed in Table II.

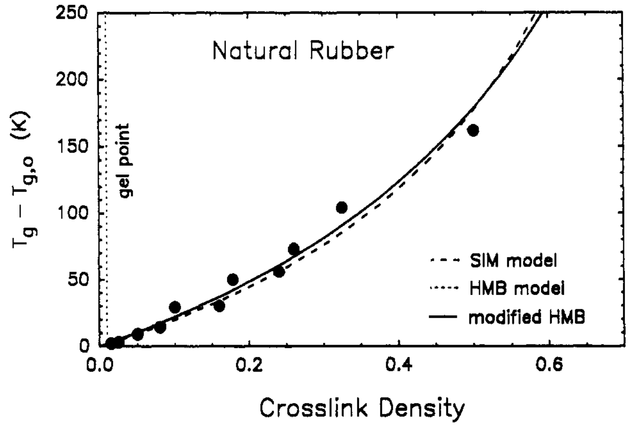


Figure 6. Type IV network. Experimental data are for peroxide and irradiation-cured natural rubber (Heinze et al.[21]). Theoretical lines were computed with the parameter values listed in Table II.

For a limited range of r values a better agreement with the data may be obtained by using one of the two other models. It should be stressed that in all three models only one adjustable parameter, namely K_2, has been employed to fit the data.

Type III and Type IV Systems. The comparison between the HMB and SIM models by means of experimental data on type I systems was inconclusive, partially due to the lack of independent data on model systems necessary for the evaluation of $T_{g,u}$. The results presented above on type II systems are in disagreement in some respects with both models. For this reason we wish to contrast the predictions of the SIM, HMB, and m-HMB models for selected type III (styrene–divinylbenzene copolymer[20]) and type IV (natural rubber cross-linked by irradiation or peroxide vulcanization[21]) systems. Plasticizer effects may be neglected for both systems since the T_g data have been obtained on completely reacted samples. The variation in the degree of cure was achieved by modification of the relative amounts of divinyl, peroxide, or radiation dose. Chain ends do not contribute at all in these reaction types, as shown in Table I. In addition, it is safe to assume that all cross-links are four functional and that non-Gaussian effects do not play any role due to the relatively high molecular weight between cross-links. The SIM model has been shown to be in good agreement with these data.[1]

In Figures 5 and 6 the three models are compared with experimental data. The values of K_2 used to fit the data for the four types of curing reactions are summarized in Table II. For the computation of the HMB model it is necessary to determine the cross-link density threshold value for gelation. In the styrene–divinylbenzene copolymerization the gel point value of the cross-link density is (ref 17a, eq 80)

$$X_{\text{gel}} = (1 - q')/(5q' - 1) \qquad (19)$$

where $q' = (R_p + R_{tc})/(R_p + R_t)$ and is typically greater than 0.99. Here R_p is the rate of the propagation reaction, R_{tc} is the rate of termination by combination, R_t is the global rate of all termination reactions. No data are available[20] for the evaluation of q' and it has been assigned the minimal value of $q' = 0.99$ which leads to gelation at a cross-link density of 0.0025. This value is marked in Figure 5 by the dotted line. The actual gel point is probably at a lower cross-link density. Due to the very low gel point value the difference between the HMB and modified HMB models is very small and the two curves coincide in Figure 5.

Table II
Value of K_2, the Cross-Link Contribution Constant for the Four Different Types of Systems

chem syst	syst type	SIM[1]	HMB[2]	m-HMB
epoxy–novolac[2]	I	2.37	0.117	
PDMS (this work)	II	0.053	0.103	0.090
styrene/DVB[20]	III	0.82	0.84	0.84
natural rubber[21]	IV	0.79	0.89	0.89

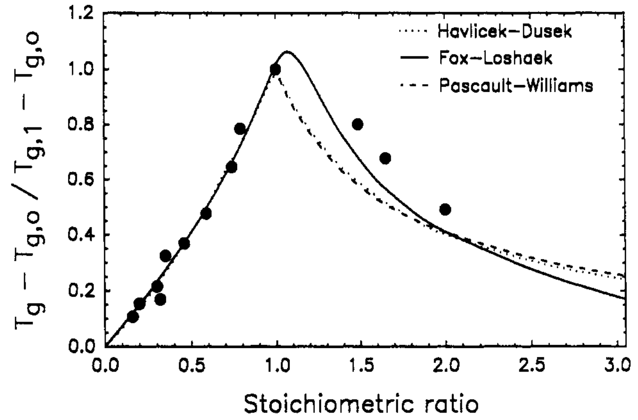


Figure 7. Fit of two-parameter relations to our PDMS data: solid line, Fox and Loshaek[6] (eq 20); dashed line, Pascault and Williams[15] (eq 21); dotted line, Havlicek and Dusek[22] (eq 22). Parameter values used to compute the lines by best fit to the $r < 1$ data are listed in Table III.

Similar difficulty exists in the determination of the gel point for the vulcanized natural rubber.[21] Here too, no data are available on x_{wo}, the degree of polymerization of the original NR chains. For a minimal weight average degree of polymerization of 100, the cross-link density at gelation is[17a] $X_{\text{gel}} = (x_{wo} - 1)^{-1} = 0.01$, as indicated by the dotted line in Figure 6. Due to the early onset of gelation, the difference between the number of elastically effective junctions and the total number of junctions is negligible and leads again to the complete overlap of the HMB and m-HMB models. Thus, for type III and IV reactions the three models discussed here are indistinguishable. All three models show excellent agreement with the data using practically the same parameter value $K_2 = 0.8$–0.9 (Table II).

Additional Models. For the sake of completeness we also compare in Figure 7 our data to the free-volume theory of Fox and Loshaek[6] (solid line in Figure 7), the Pascault–Williams[15] modification of the DiBenedetto theory (dashed line), and the empirical relation of Havlicek and Dusek[22] (dotted line):

Table III
Summary of the Parameter Values Used To Fit the Models Examined in This Work to the End-Linked PDMS Data (at $r < 1$)

model	eq	params
Stutz, Illers, Mertes[1]	3	$K_2 = 0.053$
Hale, Macosko, Bair[2]	1	$K_2 = 0.103$
modified HMB	1	$K_2 = 0.090$
Fox and Loshaek[6]	20	$a = 5.25$ K, $b = 1.90$
Pascault and Williams[15]	21	$T_{g,1} = 156$ K, $\beta = 0.68$
Havlicek and Dusek[22]	22	$T_{g,1} = 156$ K, $C = 9.4 \times 10^{-5}$ K^{-1}

Fox and Loshaek[6]

$$T_g = T_{g,u} + aX_t/(1 - bX_t) \tag{20}$$

a and b are two adjustable parameters which fit our data with $a = 5.25$ K and $b = 1.90$ ($a = 2.26$ K, $b = 1.23$ in ref 2).

Pascault and Williams[15]

$$(T_g - T_{g,o})/(T_{g,1} - T_{g,o}) = \beta p/[1 - (1 - \beta)p] \tag{21}$$

with $\beta = dC_{p,1}/dC_{p,o} = T_{g,o}/T_{g,1}$. The equality between the T_g and heat capacity ratios has been found here as well as in many other instances[15] to be incorrect. A good fit of eq 21 is obtained only if β is used as an adjustable parameter $\beta = 0.68$ ($dC_{p,1}/dC_{p,o} = 0.73$, $T_{g,o}/T_{g,1} = 0.96$) relatively close to the heat capacity ratio. The second parameter used in the model is $T_{g,1} = 156$ K.

Havlicek and Dusek[22]

$$1/T_g = (1 - p)/T_{g,o} + p/T_{g,1} + Cp(1 - p) \tag{22}$$

For best fit $C = 9.4 \times 10^{-5}$ K^{-1} and $T_{g,1} = 156$ K.

The fit of all three models is excellent for $r < 1$; the three models are practically indistinguishable in this range. Of the three models depicted in Figure 7, the best agreement with the data at $r > 1$ is demonstrated by the Fox–Loshaek model at the expense of a poorer fit at $r = 1$. The good fit of the models in Figure 7 is due to the additional adjustable parameter used in these equations allowing for larger mathematical flexibility rather than a more accurate physical model. The need to have an a priori knowledge of $T_{g,1}$, which is unavailable in most cases, limits the predictive usefulness of these models. The parameter values used to fit the different models discussed in this paper to the PDMS data are summarized in Table III.

Conclusions

The data on stoichiometry imbalanced end-linked elastomeric networks support the hypothesis of Hale et al.[2] (HMB theory) that changes in T_g are larger after the gel point due to the contribution of elastically effective junctions not present in the pregel region. Yet, it was not possible to account for the change in T_g in the pregel region using the HMB theory. This may be the result of formation of cyclic structures or be due to the contribution of branch points ignored by this theory. The weighing scheme of junction functionality used in the SIM theory[1] underestimates the $r > 1$ data. The good fit to these data when all junctions are counted equally (modified HMB theory) further supports this conclusion. Finally, either the HMB or the m-HMB models may be used for prediction of T_g changes in networks. An approximate value of $K_2 = 0.1$ may be used for end-linked systems (type I or II) and $K_2 = 0.85$ for random cross-linking (type III or IV). The generality of these values needs further testing on additional systems.[1,5]

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