

Polyurethane Elastomers Studied by the Mooney–Rivlin Equation for Rubbers

G. D. SPATHIS

National Technical University of Athens, Section of Mechanics, 5 Heroes of Polytechnion Avenue, GR-157 73 Athens, Greece

SYNOPSIS

A series of poly(ester–urethane) block copolymers were prepared via a two-step polymerization process. The prepolymer composition was kept constant in all the samples, while the NCO/OH ratio during extension was varied from 0.9 up to 1.2. By this way, chemical and physical cross-links were constructed into the materials. Equilibrium stress–strain measurements have been carried out for the examination of the elastomeric behavior of the materials tested. Calculation of an extra entropy term resulting from the network deformation is based on a first-principles derivation of the distribution function, taking into account a new type of network constraints. The process yields the Mooney–Rivlin equation and the constant C_2 as a function of physical cross-links.

INTRODUCTION

An important class of thermoplastic elastomers are the segmented polyurethanes. These polymers have the general structure ($A-B$), where B (the soft segment) is usually formed from a polyester or polyether macroglycol of molecular weight up to 2000. The hard segment A is formed by extending an aromatic diisocyanate with a low molecular weight diol such as 1,4-butanediol. The soft and hard segments are relatively short blocks that alternate n times to give a polymer of high molecular weight.^{1,2}

The segmented structure of polyurethanes is characterized mainly by hydrogen bonding between adjacent urethane groups. Hydrogen bonding causes relatively strong interactions even when the hard segments are very short. The polar nature of the hard urethane segments results in their strong mutual attraction, leading to domain formation. When the diisocyanate content is in excess, chemical cross-linking through allophanate linkages is also introduced into the copolymer.³ Both the existence of hard domains through hydrogen bonding, namely, the physical cross-linking and the chemical cross-linking, are responsible for the elastic behavior of polyurethanes.

In this study, by keeping the molar ratio of OH of polyester to NCO of aromatic diisocyanate constant, prepolymer of same chain length is obtained. By using different values of the NCO/OH ratio below and above the stoichiometric one, linear thermoplastic and cross-linked polyurethane block copolymers have been prepared.

The purpose of this work is to study the elastic behavior of all the above types of materials for the determination of the influence of physical and chemical cross-links as well as the contribution of the amount and type of hard domains.

From the stress–strain data, the Mooney–Rivlin curves are plotted and the values of constants C_1 and C_2 are obtained from these plots.

The second term of the Mooney–Rivlin equation has not been predicted by the classical theory of rubber elasticity or the more contemporary theoretical approaches.^{4–6} Therefore, the molecular origin of constant C_2 is still not known. It should be stressed here that this term is not just a small correction term to the classical rubber elasticity term since it has a substantial value because it is found from the material tested.

In a recent work, Flory⁷ attempted to calculate C_2 by introducing an entropic term resulting from the imposed constraints on the phantom network junctions. This term is controlled by a ratio k of the mean square fluctuation of a junction about its mean

position in the phantom network to the mean-square fluctuation allowed by the domain of constraint in the state of reference. This analysis led to an extra term that accounted approximately for C_2 but did not give the Mooney–Rivlin strain dependence.

In the present work, the calculation of the entropic term resulting from the network deformation is based on a first-principles derivation of the distribution function, taking into account a new type of network constraints. This process led exactly to the Mooney–Rivlin equation and to the constant C_2 strongly connected with the number of physical cross-links. The amount of physical cross-links that are constructed out of hydrogen bonding may be studied by infrared spectroscopy, primarily in the N—H stretching region. The N—H stretching region contains separate infrared bands attributed to “free” and hydrogen-bonded N—H groups. The hydrogen-bonded N—H stretching mode displays characteristic spectral perturbations such as frequency shift and changes in intensity and bandwidth.⁸ These changes are indicative of the effect of the introduced chemical cross-links on the physical network.

THEORY

The constitutive theory of an incompressible elastic body is based on the concept of the strain energy density function, W . The problem of determining the form of this stored energy function for rubberlike materials has been examined from both the theoretical and experimental point of view by a large body of research starting with the original work of Rivlin and Saunders.^{9,10}

Many representations of W have been proposed. Among these, the Mooney–Rivlin equation has probably received the most attention. The form of W as a function of the three principal extension ratios, λ_1 , λ_2 , and λ_3 , has not been chosen completely arbitrarily; but for a particular class of materials that are considered to be isotropic in the unstressed state and incompressible under whatever the stress, the stored energy function W , which has been found of particular interest, can be represented in terms of two strain invariants, I_1 and I_2 , by the following form¹¹:

$$W = C_1(I_1 - 3) + C_2(I_2 - 3) \quad (1)$$

where

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \quad (2)$$

$$I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 = \frac{1}{\lambda_1^2} + \frac{1}{\lambda_2^2} + \frac{1}{\lambda_3^2} \quad (3)$$

given that the third I_3 invariant satisfies the condition of incompressibility or constancy of volume:

$$I_3 = \lambda_1^2\lambda_2^2\lambda_3^2 = 1 \quad (4)$$

This expression, which represents the most general first-order relationship in I_1I_2 , was originally used by Mooney in 1940.¹¹ This form of stored energy function reduces to the equation furnished by the statistical theory for C_2 equal to zero, but gives a better fit to the experimental stress–strain curves. Apart from the fact that this approach has not yet been established theoretically,¹² a lot of fundamental objections exist about the way of attempting to assess the significance of constant C_2 . First of all, the Mooney–Rivlin constants obtained from uniaxial tension experiments do not agree with those determined in other modes of deformation.^{13,14} Subsequent literature is very rich in data indicating that C_2 depends on a lot of variables,^{15,16} such as the type and extent of deformation, the time scale of experiment, the temperature, the degree of swelling, the degree of cross-linkage, the physical entanglements, and the chemical nature of the polymer. However, despite of the above-mentioned objections, we believe that some of those could be removed if a theoretical work based on first principles attempts to calculate the entropy change of network deformation, taking into account the various constraints imposed on the network chains.

For obtaining the complete form of the strain energy function W , we will follow a similar process with the classical rubber elasticity theory based on the Gaussian distribution function for the free orienting chain. We start with an amorphous network containing cross-linked long-chain molecules. In the undeformed state, the network is assumed to occupy a unit cube, which consists of N chains each with n links and each link has an effective length b , and in the undeformed state, the ν th chain has an end-to-end distance given by a vector R , having components (x_ν, y_ν, z_ν) , connecting two junction points. Under homogeneous strain, the unit cube is transformed into a rectangular parallelepiped with edge lengths equal to the principal extension ratios λ_1 , λ_2 , and λ_3 . According to the affine deformation assumption, each chain of the network will be deformed into the state vector r , having components (x'_ν, y'_ν, z'_ν) given by

$$x'_\nu = \lambda_1 x_\nu, \quad y'_\nu = \lambda_2 y_\nu, \quad z'_\nu = \lambda_3 z_\nu \quad (5)$$

By calculating the total entropy of deformation for the whole assembly of chains, classical rubber elasticity theory yields finally the following result:

$$\Delta S = -1/2Nk(I_1 - 3) \quad (6)$$

Introducing further the usual assumption that there is no internal energy change of the system under deformation, the Helmholtz free energy of deformation is obtainable directly from the above equation. Hence, we have $W = -T\Delta S$, and, thus:

$$W = 1/2NkT(I_1 - 3) \quad (7)$$

In obtaining the above equation for the strain energy density function, a number of fundamental assumptions were made. Apart from the incompressibility of the rubber and the affine deformation of the network, these assumptions also include the fact that all the network chains are Gaussian with the same molecular weight and number of links in the unstrained state. Moreover, following carefully the elementary calculation of the entropy, we are compelled to accept that also in the deformed state each individual chain of the network obeys a Gaussian function for the end-to-end distance. The root mean square (rms) distance between cross-links is kept constant in both the deformed and undeformed state, given that the number of links n and the equivalent chain length b are constant. In the next step of the ΔS calculation, when a summation is carried out for the whole assembly of the network chains, the sum of the squares of the components ($\sum x'_\nu{}^2$, $\sum y'_\nu{}^2$, $\sum z'_\nu{}^2$) in the strain state of the network should be derived from the sum of the squares ($\sum x_\nu{}^2$, $\sum y_\nu{}^2$, $\sum z_\nu{}^2$) in the unstrained state by applying the affine transformation,

$$\begin{aligned} \sum_{\nu=1}^N x'_\nu{}^2 &= \lambda_1^2 \sum_{\nu=1}^N x_\nu{}^2, \\ \sum_{\nu=1}^N y'_\nu{}^2 &= \lambda_2^2 \sum_{\nu=1}^N y_\nu{}^2, \quad \sum_{\nu=1}^N z'_\nu{}^2 = \lambda_3^2 \sum_{\nu=1}^N z_\nu{}^2 \end{aligned} \quad (8)$$

so that for a random network in the unstrained state all directions of the R_ν vector are considered to be equally probable for the whole assembly. Hence,

$$\sum_{\nu=1}^N x_\nu{}^2 = \sum_{\nu=1}^N y_\nu{}^2 = \sum_{\nu=1}^N z_\nu{}^2 = 1/3 \sum_{\nu=1}^N R_\nu{}^2 \quad (9)$$

Furthermore, the summation over the whole assembly is given by

$$\begin{aligned} \sum_{\nu=1}^N R_\nu{}^2 &= N \langle R_\nu{}^2 \rangle, \\ \sum_{\nu=1}^N r_\nu{}^2 &= 1/3N(\lambda_1^2 + \lambda_2^2 + \lambda_3^2)R_\nu{}^2 \end{aligned} \quad (10)$$

The above-mentioned remarks can be summarized as follows: During deformation, the network junctions transform affinely, leading to a summation of squares [see eq. (10)], so that each individual chain has a mean square end-to-end distance equal to that of the undeformed state. These assumptions for the chemical cross-link network are plausible if the main body of each chain between junctions is free to orient without any constraint from the neighbor chains. Apart from the fact that many attempts have been directed in removing some of the above assumptions,¹⁷ the nonideal behavior of the rubberlike materials is still not predicted. This result is an indication that the above-mentioned simplification is not a possible source for a nonideal behavior. However, as many authors have previously suggested, there is still a fundamental assumption that introduces a source of perturbation in the ideal behavior of rubbers. This extra assumption concerns the fact that in the Gaussian statistical theory the network chains are free to choose configurations independently from the configurations of neighboring chains. However, the configuration available to any chain depends on the topological relationship with neighboring chains.¹⁸ Among the causes that constitute important steric obstructions resulting as topological constraints of the chains are physical entanglements.¹⁹ Starting from the above remark, many efforts have been made in the direction of quantitative conclusions for the deviations from the Gaussian statistical theory. However, before any attempt to improve the freely orienting Gaussian chain, we believe that there is still enough "room" inside the Gaussian statistical theory (for additional entropy change) if we take into account the nature of constraints imposed from the network itself. Therefore, instead of modifying the single-chain distribution function, we introduce a "pseudonetwork" to account for the topological constraints imposed on the chains of the ideal network.

Consequently, we will assume that the available configuration space around each individual chain will not remain unaffected under the imposed deformation. The way in which the above idea is introduced is the following: Each x -component of the freely orienting chain in the unstrained state oc-

copies a cubic volume with edges of length equal to the roots of the following expressions:

$$\langle x_\nu^2 \rangle = \langle y_\nu^2 \rangle = \langle z_\nu^2 \rangle = 1/3nb^2 \quad (11)$$

After the imposed affine deformation, because of topological constraints, this cubic volume is transformed into a rectangular parallelepiped having now three unequal edges. The new mean square length for each individual component of the chain in the deformed state is given by

$$\begin{aligned} \langle x_\nu'^2 \rangle &= \lambda_1^2 \langle x_\nu^2 \rangle, \\ \langle y_\nu'^2 \rangle &= \lambda_2^2 \langle y_\nu^2 \rangle, \quad \langle z_\nu'^2 \rangle = \lambda_3^2 \langle z_\nu^2 \rangle \end{aligned} \quad (12)$$

This new configuration space that is now available for each chain results in a change of entropy for a certain group of chains N' of the real network that is considered to be under topological constraint. The above-mentioned assumption modifies the calculation process of the elementary rubber elasticity in accepting that apart from the chemical cross-linked network formed by N chains there is another "pseudonetwork" consisting of N' topologically constrained chains. Under deformation, each individual chain of this "pseudonetwork" of N' chains is now oriented in each x -component with a non-equal root mean square value so that

$$\langle r_\nu^2 \rangle = 1/3(\lambda_1^2 + \lambda_2^2 + \lambda_3^2) \langle R_\nu^2 \rangle \quad (13)$$

The "pseudojunctions" of this "pseudonetwork" are considered to be rearranged in such a way so that the summation over the assembly of network chains N' is unaffected by the imposed affine transformation. This is a reasonable assumption because the nature of the "pseudonetwork" is transient, and at equilibrium, the "pseudojunctions" are no longer active. Therefore, after summation, we have

$$\sum_{\nu=1}^{N'} R_\nu^2 = \sum_{\nu=1}^{N'} r_\nu^2 = N' \langle R^2 \rangle \quad (14)$$

The total entropy change of the whole assembly is a result of adding two terms. One term is obtained from the transformation of the chemical cross-linked network, and another term is obtained from the transformation of the "pseudonetwork." This second additive term of entropy is very easy to calculate, keeping in mind the fact that the entropy of the free orienting chain is given by the following equation:

$$S_\nu = C - 1/2k \left(\frac{x_\nu^2}{\langle x_\nu^2 \rangle} + \frac{y_\nu^2}{\langle y_\nu^2 \rangle} + \frac{z_\nu^2}{\langle z_\nu^2 \rangle} \right) \quad (15)$$

where the size of the volume element is absorbed in the constant C . If the available space for each component is transformed according to eq. (12), the corresponding entropy after the imposed perturbation will be

$$S'_\nu = C' - 1/2k \left(\frac{x_\nu^2}{\lambda_1^2 \langle x_\nu^2 \rangle} + \frac{y_\nu^2}{\lambda_2^2 \langle y_\nu^2 \rangle} + \frac{z_\nu^2}{\lambda_3^2 \langle z_\nu^2 \rangle} \right) \quad (16)$$

Subtracting eqs. (16) and (15) and summing over N' chains that are under topological constraints, the total entropy change $\Delta S'$ for this group of chains is obtained:

$$\begin{aligned} \Delta S' &= \sum_{\nu=1}^{N'} \Delta S'_\nu \\ &= -1/2k \left[\left(\frac{1}{\lambda_1^2} - 1 \right) \sum_{\nu=1}^{N'} \frac{x_\nu^2}{\langle x_\nu^2 \rangle} + \left(\frac{1}{\lambda_2^2} - 1 \right) \right. \\ &\quad \left. \times \sum_{\nu=1}^{N'} \frac{y_\nu^2}{\langle y_\nu^2 \rangle} + \left(\frac{1}{\lambda_3^2} - 1 \right) \sum_{\nu=1}^{N'} \frac{z_\nu^2}{\langle z_\nu^2 \rangle} \right] \end{aligned} \quad (17)$$

$$\Delta S' = -1/2kN' \left(\frac{1}{\lambda_1^2} + \frac{1}{\lambda_2^2} + \frac{1}{\lambda_3^2} - 3 \right) \quad (18)$$

where in obtaining the above formula the following relations have been used:

$$\sum_{\nu=1}^{N'} x_\nu^2 = \sum_{\nu=1}^{N'} y_\nu^2 = \sum_{\nu=1}^{N'} z_\nu^2 = 1/3N' \langle R^2 \rangle \quad (19)$$

$$\langle x_\nu^2 \rangle = \langle y_\nu^2 \rangle = \langle z_\nu^2 \rangle = 1/3 \langle R^2 \rangle \quad (20)$$

and $(C - C')$, a small logarithmic contribution equal to zero for incompressible rubbers.

As follows from the preceding phenomenological approach, the form of stored energy function W for an incompressible isotropic elastic material is still well defined by the Mooney-Rivlin form as expressed by eq. (1). The second term of this equation corresponds to the additional free energy change due to a new kind of nonpermanent network called the "pseudonetwork." This network is considered to be formed from a number of chains N' that are imposed by a new type of constraints. The physical entities, which are responsible for such constraints, are

mainly the elastically effective trapped entanglements. Apart from the entanglements, however, steric obstructions imposed by neighboring chains or physical cross-links that are not permanent inside the network during deformation could be taking part in the formation of the so-called pseudonetwork.

In the segmented polyurethanes, the existing polar groups are free to align themselves and form physical bonds. The number of these physical cross-links that are made out of hydrogen bonds are controlled by altering the NCO/OH ratio.

The dependence of constant C_2 on the amount of physical bonds of polyurethane elastomers is a strong indication for the correctness of the above-mentioned assumptions.

MATERIALS

The materials tested were prepared in a two-step polymerization process by reacting the symmetric diphenylmethane diisocyanate (MDI) with a hydroxyterminated polyester to form a soft block segment. The polyester used was a polyethylene adipate (PEA) with an average molecular weight of 2000. The resultant polymer was then extended with a low molecular weight diol (1,4-butanediol, BDO) to form a hard block segment.

The whole polymerization process is as follows: The polyester has been dehydrated under vacuum at 130°C for 2 h. The dry polyester was then heated at 120°C with mechanical stirring, the MDI was added, and the stirring was continued for 30 min. Then, the dry butanediol was added to the mixture under vigorous agitation. This hot thickening mixture was stirred for 1 min and poured into hot plates. The final product was compression-molded into sheets and postcured in an oven for 24 h at 110°C.

The polyester urethane elastomers involved in this study were varied by altering the NCO/OH ratio, while the hard segment content was maintained at 30% and the prepolymer composition was kept constant with the ratio MDI/PEA equal to 2.8/1.0 (mol/L).

The values of the NCO/OH ratio are varied below and above the stoichiometric one, resulting in four different types of block copolymers with a varying number of physical and chemical cross-links. Moreover, the hard segment distribution, the domain morphology, and their contribution to the elastic behavior is different for all materials prepared.²⁰

EXPERIMENTAL

Stress–Strain Test

Equilibrium stress–strain measurements were made in simple extension on dumbbell specimens of an average cross-sectional area (2×3.75 mm²). Reference marks were made on each specimen about 27 mm apart and clamps applied to both ends.

The measurements were carried out with a conventional Instron, type 1121, tested at room temperature, at a crosshead speed of 20 mm/min. The distance between the reference marks was measured with a cathetometer 15 min after each application of load. In this period, the load achieved an approximately equilibrium value.

Infrared Spectroscopy

The IR spectra were obtained using a Perkin-Elmer 567 infrared spectrophotometer. Normal slit width and slow scanning speed were employed.

Thin films of the order of 10^{-4} m of the materials tested were prepared as follows: After each polymerization and while the material was still viscous, a small amount of capillary was compressed between two thin KBr plates. The samples were then placed in a vacuum over at 110°C for 24 h. The spectra were obtained under a dry nitrogen flow to avoid moisture condensation onto the KBr plates.

When analyzing characteristic infrared bands of the isocyanate group at 2265 cm⁻¹, no residual isocyanate groups were detected in any of the materials tested.

The frequency shift is defined as

$$\Delta\nu = \nu_b - \nu_f$$

where ν_f and ν_b are the frequencies of maximum absorption for the free and hydrogen-bonded N—H groups, respectively. The shift, $\Delta\nu$, in the stretching frequency of the hydrogen-bonded N—H group is considered as a measure of the strength of the hydrogen bond. As the hydrogen-bond strength increases, the (N—H···O=C) distance, measured in the solid state by X-ray crystallography, decreases, and this decrease is usually accompanied by an increase in the difference between the associated N—H stretching frequency and the nonassociated N—H stretching frequency.⁸

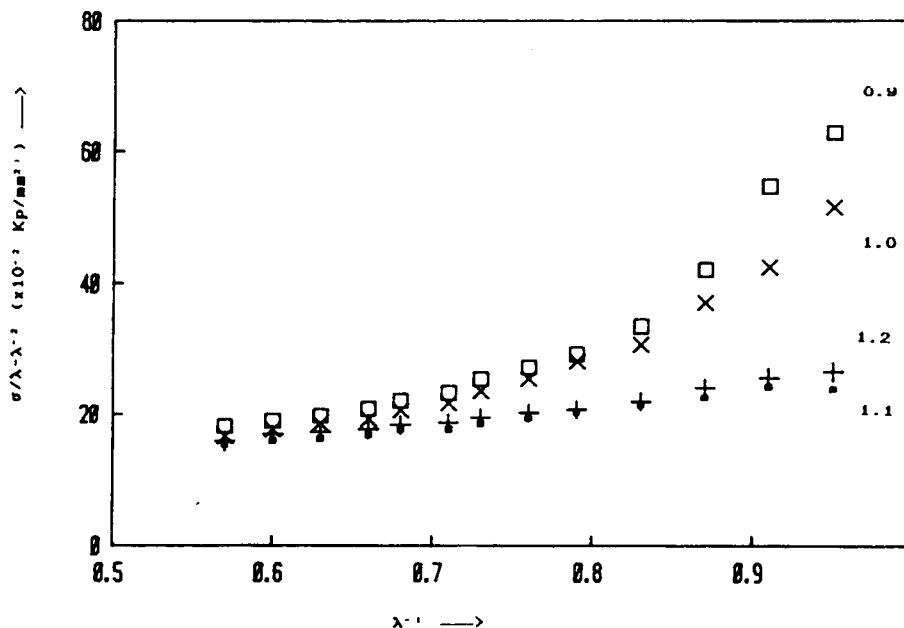


Figure 1 Mooney-Rivlin plots for polyurethanes with NCO/OH ratio values 0.9, 1.0, 1.1, and 1.2.

RESULTS AND DISCUSSION

From the stress-strain data, the Mooney-Rivlin curves are plotted in Figure 1. In this figure, the division of the materials into two different groups can be observed. In the first group with deficient stoichiometric MDI content, the hard segments probably are forming large domains irregularly distributed into the soft matrix, resulting to a reinforcing action on the material. Due to this fact, the Mooney-Rivlin curves appear to have a linear behavior in a narrow region of elongation, deviating at lower values of λ .

In the second group, because of the excess diisocyanate, chemical cross-links in terms of allophanate linkages are formed during the postcuring process. The diisocyanate links across the chains reduce their mobility, resulting in a morphology with less effective packing between macromolecules, looser hydrogen bonds, and, consequently, smaller hard domains. Therefore, a network with fewer defects is developed and the Mooney-Rivlin curves exhibit a linear behavior over a wide region of λ . This result reinforces the assumption that the second group of materials has stress-strain behavior close to that of an ideal rubber. These general conclusions are further supported by using infrared spectroscopy to study the shifting of the hydrogen-bonded N—H stretching peak.^{8,21}

The frequencies and frequency shifts of the hydrogen-bonded N—H stretching modes for the various values of the NCO/OH ratio are given in Table I.

The N—H stretching region contains mainly two infrared bands attributed to "free" and hydrogen-bonded N—H groups. The latter primarily reflects the distribution of the strength of the hydrogen bonds. The "free" N—H stretching band occurs at 3450 cm^{-1} in all the samples and appears as shoulder on the high-frequency side of the hydrogen-bonded band. The hydrogen-bonded N—H stretching mode shifts to higher frequency in going from a NCO/OH ratio value 0.9 to 1.2, respectively.

This result reinforces the assumption that the average strength of the hydrogen bonds decreased for the second group of materials tested. From this

Table I Changes of the N—H Stretching Mode as a Function of the NCO/OH Ratio

NCO/OH	ν_f (cm^{-1})	ν_b (cm^{-1})	$\Delta\nu$ (cm^{-1})
0.9	3450	3325	125
1.0	3450	3330	120
1.1	3450	3330	120
1.2	3450	3345	105

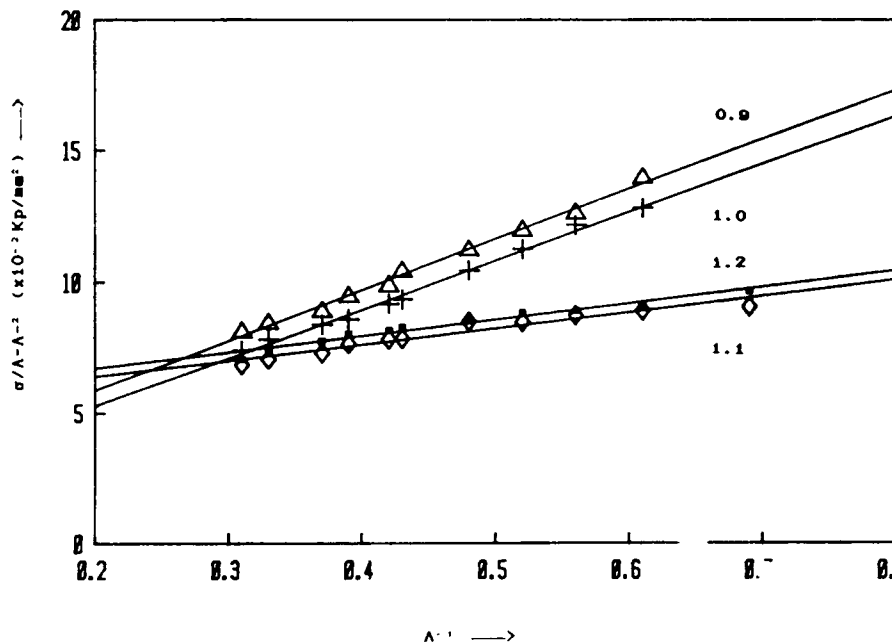


Figure 2 Mooney-Rivlin plots reduced with the use of the strain amplification factor X .

result, we conclude that physical cross-links are less effective for polyurethane elastomers.

We are coming now to the next step of calculating the Mooney-Rivlin constants C_1 and C_2 in order to test the validity of our original assumption. Before calculating constants C_1 and C_2 , however, we will try to deliver the stress-strain results from the influence of the hard domains that are distributed inside the soft matrix of the formed network.

The deviation from the Mooney-Rivlin equation of curves in Figure 1 is also due to the reinforcing effect of hard domains that is more intense in the case of NCO/OH ratio values 0.9 and 1.0. The presence of hard domains prevents the soft matrix to deform uniformly, resulting to an overall lower apparent strain than the strains occurring locally. The ratio of stress to strain is increased by a factor X that takes into account both this disturbance of the strain distribution and the absence of deformation in the fraction of hard domains at the initial elongations.

This factor has been shown^{22,23} to be

$$X = 1 + 2.5u_f + 14 \cdot 1u_f^2$$

where u_f , the filler (hard segment) content, is about 30% by weight of the total polymer for all the samples tested.

Although X was derived for unattached spheres, the use of this correction describes better the effect of the filler on the measured properties.

With the use of the strain amplification factor X , the Mooney-Rivlin plots have been replotted in terms of $\sigma/(\Lambda - 1/\Lambda^2)$ versus Λ^{-1} , where $\Lambda = 1 + X\epsilon$, σ is the applied stress, and ϵ is the strain. As is shown in Figure 2, the Mooney-Rivlin equations,

$$\sigma/(\Lambda - 1/\Lambda^2) = C_2\Lambda^{-1} + C_1$$

are reduced to linear forms for all types of specimens.

The values of constants C_1 and C_2 are obtained from these plots and are presented in Table II for all values of the NCO/OH ratio.

Table II Values of Constants C_1 and C_2 with Varying the NCO/OH Ratio

NCO/OH	C_1 ($10^{-2} K_p/mm^2$)	C_2 ($10^{-2} K_p/mm^2$)
0.9	1.97	9.59
1.0	1.72	9.17
1.1	3.68	2.99
1.2	3.89	3.06

The first group of materials, corresponding to physically cross-linked block copolymers, appears to have lower values of C_1 than does the second group, which is mainly chemically cross-linked. Inversely, the values of C_2 are higher for the first group.

All the materials prepared are characterized by the existence of physical and chemical cross-links. With the NCO/OH ratio values of 0.9 and 1.0, where the MDI content is below or equal to the stoichiometric one, the number of chemical cross-links is almost negligible and the rubber behavior is totally due to the physical cross-links.

The physical cross-links that are introduced by hydrogen bonding may be disrupted at higher elongations, resulting in lower values of C_1 for the first group of the materials tested.

For the second group with ratio NCO/OH values 1.1 and 1.2, where a sufficient number of chemical cross-links is expected to be formed in addition to the physical ones, higher values of C_1 have been observed.

Constant C_1 is explicitly related to the number of mechanically effective cross-links into the network. More specifically, C_1 is linearly related to the number of permanent cross-links following the equation

$$C_1 = V_{\text{eff}}RT$$

where V_{eff} is the effective cross-link density in mol/cc; R , the gas constant; and T , the absolute temperature.

Inversely, constant C_2 as it is extracted from the reduced Mooney–Rivlin equations is less than C_1 for the second group of materials tested.

This is a strong indication that constant C_2 is explicitly related with the nonpermanent physical cross-links of the formed network. This result reinforces the assumption mentioned at the beginning of this work, which integrates the process of the elementary rubber elasticity by accepting that apart from the chemical cross-linked network formed by N chains there is another “pseudonetwork” con-

sisting of the topological constraints on the body of a number of chains N' that follow a different kind of restriction under deformation.

REFERENCES

1. H. N. Ng, A. E. Allegrezza, R. W. Seymour, and S. L. Cooper, *Polymer*, **14**, 255–261 (1973).
2. L. H. Peebles, *Macromolecules*, **7**, 872–882 (1974).
3. D. A. Meyer, in *Vulcanization of Elastomers*, G. Alliger and I. J. Sjothun, Eds., Reinhold, New York, 1964, Chap. 10.
4. G. Ronca and G. Alegra, *J. Chem. Phys.*, **66**, 5720 (1977).
5. P. J. Flory and B. Erman, *Macromolecules*, **15**, 800 (1982).
6. S. F. Edwards and T. Viglis, *Polymer*, **27**, 483 (1986).
7. P. J. Flory, *Polymer*, **20**, 1317 (1979).
8. C. M. Brunette, S. L. Hsu, and W. J. Macknight, *Macromolecules*, **15**, 71–77 (1982).
9. R. S. Rivlin, *J. Appl. Phys.*, **18**, 444 (1947).
10. R. S. Rivlin, and D. W. Saunders, *Philos. Trans. R. Soc.*, **A243**, 251 (1951).
11. M. Mooney, *J. Appl. Phys.*, **11**, 582 (1940).
12. J. E. Mark, *Rubber Chem. Technol.*, **48**, 495 (1975).
13. N. W. Tschoegl, *J. Polym. Sci. A-1*, **9**, 1959 (1971).
14. L. R. G. Treloar, *Rep. Prog. Phys.*, **36**, 755 (1973).
15. A. Ciferri, *Rheol. Acta*, **12**, 276 (1973).
16. W. V. Chang, R. Bloch, and N. W. Tschoegl, *Chemistry and Properties of Crosslinked Polymers*, Academic Press, New York, 1977, p. 431.
17. K. Dusek and W. Prins, *Adv. Polym. Sci.*, **G1**, 43 (1969).
18. L. S. Priss, *J. Polym. Sci. Polym. Symp.*, **53**, 195 (1975).
19. S. F. Edwards, *Proc. Phys. Soc.*, **91**, 513 (1967).
20. W. Nierzwicki and E. Wysocka, *J. Appl. Polym. Sci.*, **25**, 739–746 (1980).
21. W. J. Macknight and M. Yang, *J. Polym. Sci. C*, **42**, 817–832 (1973).
22. E. Guth and R. Simha, *Kolloid-Z.*, **74**, 266 (1936).
23. D. Gold, Thesis, Vienna, 1937.

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