

# Semi- and Fully Interpenetrating Polymer Networks Based on Polyurethane–Polyacrylate Systems.

## I. The Polyurethane Networks

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### Synopsis

The polyurethane networks based on a commercial prepolymer, Adiprene L-100, and trimethylol propane (system 1) and on toluene diisocyanate, polypropylene glycol, and trimethylol propane (system 2) were prepared and characterized in a number of ways. The materials constitute the first formed networks in a series of interpenetrating polymer networks and semi-interpenetrating polymer networks to be reported in subsequent papers in this series. System 1 networks were characterized by swelling tests which showed the  $\bar{M}_c$  values to be sensitive to the amount of polyurethane present in the polymerization solvent. Stress–strain, stress–relaxation, and dynamic mechanical analyses were also conducted. For system 2,  $\bar{M}_c$  was measured, by both the swelling and the Mooney–Rivlin techniques, for materials in which the diol-to-triol ratios had been altered. The latter showed  $C_1$  increasing as  $\bar{M}_c$  decreased while  $C_2$  was small and changed only slightly indicating approximately ideal behavior. These  $\bar{M}_c$  values were about 13% larger than predicted by swelling.

### INTRODUCTION

Although interpenetrating polymer networks (IPNs) are a branch of polyblends, they comprise a rather broad area and, consequently, have many diverse aspects. In general, it can be said that an IPN has been formed when a pair of polymeric networks are synthesized in intimate contact with one another. The ideal, but never realized, situation is that one network fully interpenetrates the other to form many physical, but no chemical, crosslinks. The situation most likely to lead to such a state is when one network is totally compatible with the other. This is, of course, a rarity for pairs of different polymers, but IPNs can be synthesized where both networks are the same polymer. Such IPNs are called Millar IPNs,<sup>1</sup> and those so far investigated<sup>2</sup> show that even they do not correspond to the idealized concept of two fully interpenetrating networks. In reality, what is found in most cases, is a comprehensive degree of phase separation in which substantially pure domains of each network exist. Thus, extensive physical crosslinking is localized at the phase boundaries. Therefore, in order to optimize interpenetration, it is desirable that the phases be as small as possible.

If only one polymer is crosslinked, the material is called a semi-IPN. A semi-IPN of the first kind (semi-1-IPN) is where the first formed polymer is crosslinked.

There are a number of distinct ways of synthesizing IPNs. Subsequent papers shall be concerned largely with sequential IPNs.<sup>3</sup> This refers to the case where network 1 is formed first. In a simultaneous IPN<sup>4</sup> both networks are synthesized

at the same time. It is an obvious precondition for simultaneous IPNs that the networks are formed by different mechanisms, e.g., condensation and free radical addition polymerizations. Certain sequential IPNs are capable of being prepared by the simultaneous route. The polyurethane-polyacrylate system to be discussed in this series is such a case. IPNs may also be prepared using emulsion polymerization techniques.<sup>5</sup> The first network is synthesized and the second monomer and crosslinker is then added, but no new soap is used. The belief, though there seems to be no direct evidence in the literature, is that no new particles are generated. A consequence is that core-shell latex particles may be formed. An outstanding practical advantage of latex IPNs, as long as the extent of crosslinking is relatively low, is that each particle is an individual IPN which can be molded like a thermoplastic. The other methods so far mentioned lead to thermosets. Recently, Sperling<sup>6</sup> has made use of the network forming mechanisms of the thermoplastic elastomers and ionic polymers to generate truly thermoplastic IPNs. Such an approach could have substantial processing advantages. Another method of generating IPNs is to mix already formed latexes.<sup>7</sup> This leads to rather gross morphologies.

In this series of papers both semi- and full IPNs based on polyether urethanes, and mainly, but not exclusively, polymethyl acrylate will be investigated from a wide variety of points of view. For example, the effect of the tightness of the networks, the composition, and the synthesis conditions, plus a number of other aspects will form the subject matter of later papers. Much emphasis will be placed on dynamic mechanical analysis and electron microscopy in the attempt to understand the morphologies produced and relate these to properties.

As, in all cases, the polyurethane component will have one of two very similar structures, it is convenient to treat this component separately. The polyurethanes are made either by reacting Adiprene L-100 with trimethylol propane (system 1) or by reacting toluene diisocyanate with polypropylene glycol and trimethylol propane (system 2). The latter system was used when it was desired to have a polyurethane network which is more crosslinked than can be achieved with Adiprene L-100.

## EXPERIMENTAL

### Materials

Adiprene L-100 was kindly donated by DuPont (U.K.), Ltd. This commercial prepolymer<sup>8</sup> had a number average molecular weight of 1990 g/mol and a weight average molecular weight of 3980 g/mol. The polypropylene glycol had corresponding values of 2000 and 2200 g/mol, respectively. Toluene diisocyanate and butane-1,4-diol were supplied by B.D.H., Ltd. while the trimethylol propane was an Aldrich Chemicals product. All materials were very carefully dried prior to use.

### Synthesis

All polyurethanes were prepared using the same procedure and conditions as for the gelation of the polyurethane component in the semi- and full IPN syntheses. The polyurethane precursors were mixed in inhibited methyl acry-

late, or whatever monomer was used to produce the second component of the system, containing di-*n*-butyl tin dilaurate (B.D.H., Ltd.) as polyurethane catalyst (2% w/w of polyurethane) and 1% w/w of 2,4-dihydroxybenzophenone (Aldrich Chemicals) as stabilizer. All the polyurethane precursors and additives were soluble in the stabilized monomer. The mixture was carefully degassed and then poured into a metal mold sealed with a Teflon-coated rubber gasket. The mold was closed with a metal top plate which was bolted into position and fitted with springs to allow for contraction during polymerization.

The polyurethane was allowed to gel for 24 h at 20°C. The monomer was then slowly removed to yield the pure network. The last traces of monomer were removed by placing the sheets in a vacuum oven at room temperature for 10 days.

Linear polyurethanes were prepared in an identical manner by omitting the triol component (system 2) or replacing it with butane-1,4-diol (system 1).

In all polyurethanes prepared the NCO:OH ratio was 1.1:1.

### Techniques

The stress-strain measurements were made at 20°C and a strain rate of 2.5 cm/min using a Howden tensometer. Standard dumbbell test pieces were used. The same instrument, fitted with an environmental chamber, was used for the stress-relaxation measurements. A strain rate of 38 cm/min was used to achieve the desired strain level for these relaxation tests. The strain in both types of measurement was defined as the change in length over the original length. The dynamic mechanical data were obtained with a Rheovibron dynamic mechanical viscoelastometer (Model DDV-II-B) at a heating rate of approximately 1°C/min.

## RESULTS AND DISCUSSION

### System 1

#### *Molecular Weight between Crosslinks by Swelling*

Swelling experiments were conducted on small rectangular specimens (ca. 0.3 g) in nine different liquids ranging in solubility parameter  $\delta$  from  $14.8 \times 10^3$  (J/m<sup>3</sup>)<sup>1/2</sup> (*n*-hexane) to  $29.7 \times 10^3$  (J/m<sup>3</sup>)<sup>1/2</sup> (methanol). The swelling coefficients  $Q$  were evaluated using

$$Q = \frac{m - m_0}{m_0} \times \frac{1}{d} \quad (1)$$

$m$  is the weight of the swollen sample,  $m_0$  is the original weight, and  $d$  is the density of the swelling agent. Figure 1 shows  $Q$  vs.  $\delta^3$  for a polyurethane prepared from Adiprene L-100 and trimethylol propane in 40% w/w of inhibited methyl acrylate. According to this figure the polyurethane solubility parameter is  $19.2 \times 10^3$  (J/m<sup>3</sup>)<sup>1/2</sup>. The same value was found for system 2 materials.

In order to determine  $\chi$ , the polymer-solvent interaction parameter, the Bristow and Watson<sup>10</sup> semiempirical equation was used:

$$\chi = \beta_1 + (V_s/RT)(\delta_s - \delta_p)^2 \quad (2)$$

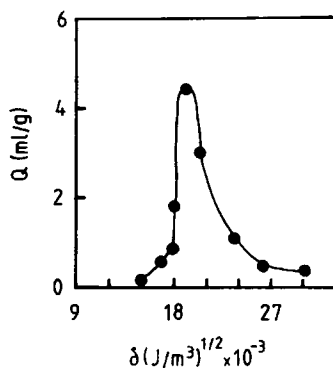


Fig. 1. Swelling coefficient vs. solubility parameter plot for the system 1 polyurethane synthesized in 40% w/w of inhibited methyl acrylate.

$\beta_1$  is the lattice constant, usually about 0.34,  $V_s$  is the molar volume of solvent,  $R$  is the universal gas constant, and  $T$  is absolute temperature. The subscripts  $s$  and  $p$  refer to the swelling agent and polymer, respectively.

The average molecular weight between crosslinks,  $\bar{M}_c$ , was calculated from the Flory-Rehner<sup>11-13</sup> equation:

$$\nu_e = -\frac{1}{V_s} \left[ \frac{\ln(1 - v_r) + v_r + \chi v_r^2}{v_r^{1/3} - 2v_r/F} \right] \quad (3)$$

$\nu_e$  is the number of polymer chains per unit volume,  $F$  is the functionality of the system, which in this case is 3, and  $v_r$  is the volume fraction of polymer in the swollen gel at equilibrium.  $\nu_e$  and  $\bar{M}_c$  are related by the polymer density  $\rho$ :

$$\nu_e = \rho/\bar{M}_c \quad (4)$$

As the polyurethanes were crosslinked in the swollen state, the effect this had on  $\bar{M}_c$  was taken into account by using the Tobolsky front factor,<sup>14,15</sup> which can be replaced by  $\phi_r^{2/3}$ .  $\phi_r$  is the volume fraction of rubber present at the time of crosslinking. Thus, eq. (4) is modified as follows:

$$\nu_e = (\rho/\bar{M}_c)\phi_r^{2/3} \quad (5)$$

Table I summarizes the results of swelling tests and also density measurements for three system 1 samples of crosslinked polyurethanes prepared at different concentrations of inhibited methyl acrylate. According to these results, the  $\bar{M}_c$

TABLE I  
Swelling<sup>a</sup> and Density Data

Weight fraction of polyurethane in inhibited methyl acrylate	$\chi$	$v_r$	$\bar{M}_c$ (g/mol)	Density (kg/m <sup>3</sup> )
0.6	0.35	0.169	4700	1091
0.4	0.35	0.142	5500	1082
0.2	0.35	0.107	6400	1075

<sup>a</sup> In chloroform.

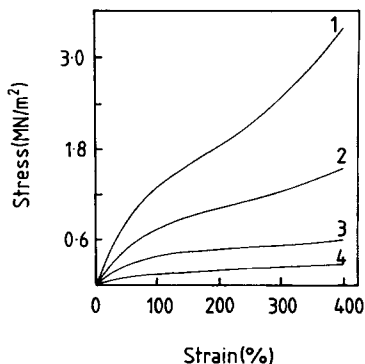


Fig. 2. Stress-strain plots (20°C) for system 1 polyurethanes with  $\bar{M}_c$  values (g/mol) of 4700 (1), 5500 (2), and 6400 (3) and for a linear polyurethane (4) based on Adiprene L-100.

values of the polyurethanes significantly decreased with increasing the weight fraction of polyurethane in the original gel. A similar increase in  $\bar{M}_c$  with dilution was observed by Allen et al.<sup>16</sup> and Shen and Tobolsky.<sup>17</sup> They attributed the effect to a decrease in the physical entanglements at higher dilutions. Table I also shows that there was a slight increase in the density of the polyurethanes when  $\bar{M}_c$  decreased.

#### *Stress-Strain Behavior*

Figure 2 shows the stress-strain behavior of a linear polyurethane prepared using Adiprene L-100 and butane-1,4-diol and of the same crosslinked polyurethanes as in Table I. It is clear from this figure that the modulus of the polyurethane increases, as expected, with decreasing  $\bar{M}_c$ .

#### *Dynamic Mechanical Analysis*

The properties of segmented polyurethane elastomers are principally controlled by the relative amounts of soft and hard segments.<sup>18-20</sup> The soft blocks consist of long chain polyethers or polyesters while the hard blocks are relatively inflexible and are often capable of strong intermolecular forces of attraction through urea and urethane groups. The hard segments can group themselves into domains.<sup>21</sup>

A number of authors have reported<sup>22,23</sup> dynamic mechanical data for various polyurethanes.

Figure 3 shows the  $\tan \delta$ -temperature data for the three networks already discussed and for the linear polyurethane. The glass transition of the soft segments is clearly observed. These and other dynamic mechanical data are shown in Table II. The glass transition temperature  $T_g$ , half-peak width and  $\tan \delta_{\max}$  are all sensitive to the degree of crosslinking.

Dynamic storage moduli  $E'$  and dynamic loss moduli  $E''$  vs. temperature plots are shown in Figures 4 and 5, respectively. The expected minor variations with crosslink density are shown.

DSC thermograms showed a glass transition at about  $-34^\circ\text{C}$ , but the complete absence of crystallinity.

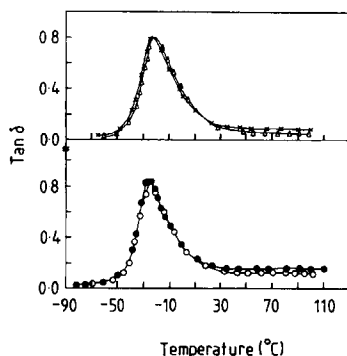


Fig. 3.  $\tan \delta$ -temperature plots for system 1 polyurethanes with  $\bar{M}_c$  values (g/mol) of 4700 ( $\Delta$ ), 5500 (X), and 6400 (O) and for a linear polyurethane ( $\bullet$ ) based on Adiprene L-100. Frequency was 11 Hz.

### Stress-Relaxation

Figure 6 shows, at three different strains, the logarithmic plots of stress  $\sigma$  as a function of time for the system 1 crosslinked polyurethane with  $\bar{M}_c$  equal to 6400 g/mol. The curves are almost parallel over the strain range investigated. Soft polymeric materials often show<sup>24,25</sup> this feature whether they are crosslinked or uncrosslinked.

Figure 7 shows logarithmic plots of relaxation modulus  $E_r(t)$  against time for the linear and two of the crosslinked polyurethanes. The rates of stress-relaxation,  $[d \log E_r(t)]/(d \log t)$ , of the linear part of the isotherms are shown in Table III. From Table III it is clear that there is an increase in the rate of relaxation with increasing  $\bar{M}_c$  of the polyurethane. The linear polyurethane relaxes faster than the crosslinked ones. This may be explained by the fact that in the networks the chains cannot pass through the backbones of one another.

### System 2

Three system 2 materials were prepared with different  $\bar{M}_c$  values by altering the diol-to-triol ratio while holding the toluene diisocyanate content constant. The networks were prepared in 80% w/w of inhibited methyl acrylate. The resulting polyurethane networks were investigated using the Mooney<sup>26</sup> theory.

The Gaussian theory of rubber elasticity quantitatively predicts<sup>24</sup> the relationship between stress and strain for a deformed network at constant temperature. The statistical theory, originally formulated by Meyer et al.,<sup>27</sup> relates

TABLE II  
Dynamic Mechanical Properties of the Polyurethanes

$\bar{M}_c$ (g/mol)	$T_g$ (°C)	Half peak width (°C)	$\tan \delta_{\max}$
Linear	-26	31	0.85
6400	-25	32	0.83
5500	-23	34	0.80
4700	-21	35	0.79

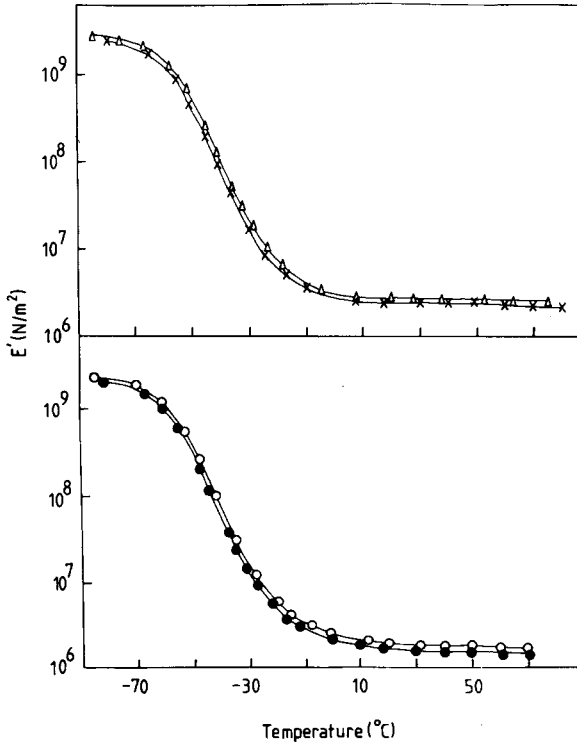


Fig. 4.  $E'$  vs. temperature plots for system 1 polyurethanes with  $\overline{M}_c$  values (g/mol) of 4700 ( $\Delta$ ), 5500 (X), and 6400 (O) and for a linear polyurethane ( $\bullet$ ) based on Adiprene L-100. Frequency was 11 Hz.

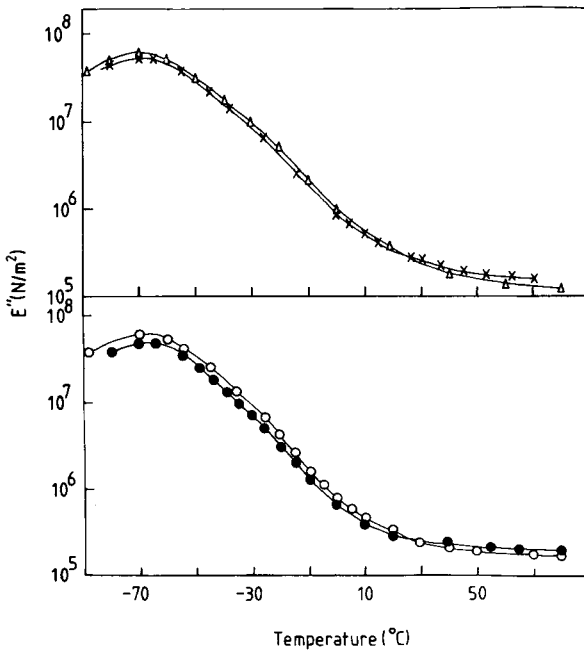


Fig. 5.  $E''$  vs. temperature plots for system 1 polyurethanes with  $\overline{M}_c$  values (g/mol) of 4700 ( $\Delta$ ), 5500 (X), and 6400 (O) and for a linear polyurethane ( $\bullet$ ) based on Adiprene L-100. Frequency was 11 Hz.

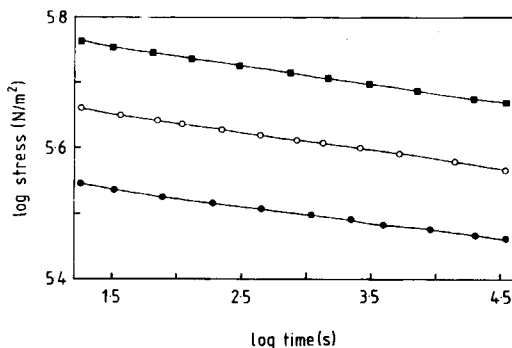


Fig. 6. Log stress vs. log time plots (20°C) at 100% (●), 150% (○), and 200% (■) applied strain for the system 1 polyurethane with  $\bar{M}_c$  equal to 6400 g/mol.

the elasticity of rubber to statistical properties of the polymer molecules which undergo continual conformational fluctuation under the influence of thermal agitation. From a simplified network model it is possible to derive the stress-strain relations corresponding to any particular type of strain. Thus, Wall<sup>28</sup> derived eq. 6 for simple extension represented by an extension ratio  $\lambda$ , which is equal to the length over the original length:

$$F = NkT(\lambda - \lambda^{-2}) \quad (6)$$

$F$  is the force per unit unstrained area,  $N$  is the number of network elements per unit volume, and  $k$  is the Boltzmann constant. It can be shown<sup>15</sup> that, for a rubber crosslinked in the swollen state,

$$\bar{M}_c = (\rho R/Nk)\phi_r^{2/3} \quad (7)$$

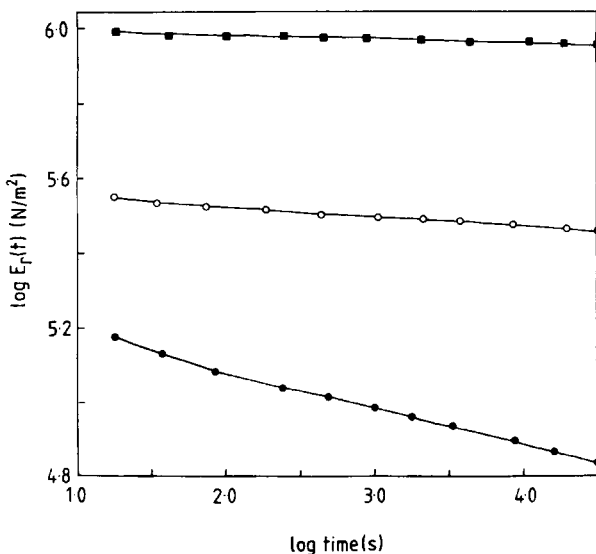


Fig. 7. Log  $E_r(t)$  vs. log time plots (20°C) for the system 1 polyurethanes with  $\bar{M}_c$  (g/mol) equal to 6400 (○) and 4700 (■) and for a linear polyurethane (●) based on Adiprene L-100. The applied strain was 100%.



TABLE III  
Stress-Relaxation Rates

System	$\frac{d \log E_r(t)}{d \log t}$
Linear	0.096
$\bar{M}_c = 6400$	0.027
$\bar{M}_c = 4700$	0.012

Experimental studies<sup>24</sup> have shown the above theoretical predictions to hold approximately, though there are significant minor deviations in stress-strain relations. Deviations from prediction become appreciable for most polymer networks if the system is strained to greater than about 20% in simple tension. The deviations from the statistical theory in simple tension may be satisfactorily represented on the basis of the phenomenological theory of Mooney.<sup>26</sup> This takes the following form:

$$F = 2C_1(\lambda - \lambda^{-2}) + 2C_2(1 - \lambda^{-3}) \quad (8)$$

$C_1$  and  $C_2$  are empirical constants. The first is the same as that derived from the statistical theory with  $2C_1$  equal to  $\rho RT/\bar{M}_c$ , while the second term involving the constant  $C_2$  represents the deviation from this theory. The Mooney equation does not provide any information on the physical interpretation of observed deviations for an actual rubber from the one-constant equation derived from the statistical theory. Certain hypotheses have, however, been advanced. Guth and Wang<sup>29</sup> attribute the deviations to internal effects which are not taken into account in the statistical theory. Gumbrell et al.<sup>30</sup> have shown a characteristic variation of  $C_2$  with degree of swelling, irrespective of the type of rubber or nature of the swelling liquid. However, there are several suggestions for the molecular

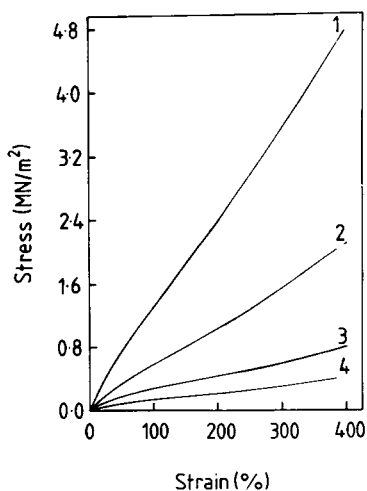


Fig. 8. Stress-strain plots (20°C) for system 2 polyurethanes with  $\bar{M}_c$  values from swelling measurements (g/mol) of 1700 (1), 3800 (2), and 6900 (3) and for a system 2 based linear polyurethane (4).

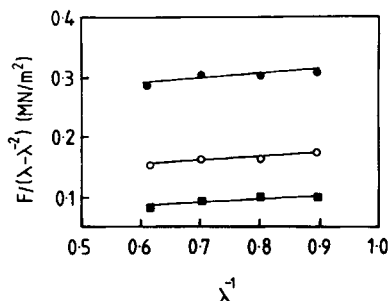


Fig. 9.  $F/(\lambda - \lambda^{-2})$  vs.  $\lambda^{-1}$  plots (20°C) for system 2 polyurethanes with  $\bar{M}_c$  (swelling) values (g/mol) of 1700 (●), 3800 (○), and 6900 (■), respectively.

interpretation of the constant  $C_2$ , including considerations of local packing,<sup>31,32</sup> internal energy,<sup>33,34</sup> and entanglements.<sup>35,36</sup>

It is convenient to write the Mooney equation in the following form:

$$F/2(\lambda - \lambda^{-2}) = C_1 + C_2/\lambda \quad (9)$$

A plot of  $F/2(\lambda - \lambda^{-2})$  against  $1/\lambda$  yields a straight line of slope  $C_2$  and with an intercept of  $C_1 + C_2$  on the vertical axis at  $1/\lambda$  equal to unity.

The stress-strain curves of the three crosslinked polyurethanes and a linear polyurethane synthesized using toluene diisocyanate and polypropylene glycol are shown in Figure 8. As expected, when the amount of triol is increased the modulus of the polyurethane is also increased. The data were plotted as  $F/2(\lambda - \lambda^{-2})$  against  $\lambda^{-1}$  curves (see Fig. 9) and both the Mooney-Rivlin constants and  $\bar{M}_c$  were calculated for the crosslinked polyurethanes.

The results obtained from the Mooney-Rivlin plots and from swelling experiments are shown in Tables IV and V. In agreement with Blokland,<sup>37</sup>  $C_1$  increased with decreasing  $\bar{M}_c$ , but  $C_2$  is small and only changed slightly when  $\bar{M}_c$  of the polyurethane decreased. Sperling<sup>38</sup> and Landel<sup>39</sup> obtained very small

TABLE IV  
Data Obtained for the Three Polyurethanes Using Mooney-Rivlin Plots

Sample	$C_1 \times 10^{-5}$ (N/m <sup>2</sup> )	$C_2 \times 10^{-5}$ (N/m <sup>2</sup> )	$\bar{M}_c^a$ (g/mol)
I	2.72	0.53	1900
II	1.24	0.51	4300
III	0.68	0.50	7800

<sup>a</sup> Front factor correction  $\phi_f^{2/3}$  applied.

TABLE V  
Results Obtained from the Swelling<sup>a</sup> of the Three Polyurethanes

Sample	$\chi$	$\nu_r$	$\bar{M}_c$ (g/mol)
I	0.35	0.199	1700
II	0.35	0.133	3800
III	0.35	0.103	6900

<sup>a</sup> In chloroform.

values for  $C_2$  when they characterized different polyurethanes. They argued, therefore, that the elastomers appeared to behave nearly ideally.

Comparing Tables IV and V, the  $\bar{M}_c$  values of the polyurethanes measured by elongation tests were about 13% higher<sup>38</sup> than those measured by swelling tests.

### References

1. J. R. Millar, *J. Chem. Soc.*, **263**, 1311 (1960).
2. D. L. Siegfried, J. A. Manson, and L. H. Sperling, *J. Polym. Sci.*, **16**, 583 (1978).
3. L. H. Sperling and D. W. Friedman, *J. Polym. Sci.*, **7**, 425 (1969).
4. L. H. Sperling and R. R. Arnsts, *J. Appl. Polym. Sci.*, **15**, 2317 (1971).
5. L. H. Sperling, T. W. Chui, C. Hartman, and D. A. Thomas, *Int. J. Polym. Sci.*, **1**, 331 (1972).
6. D. L. Siegfried, D. A. Thomas, and L. H. Sperling, *J. Appl. Polym. Sci.*, **26**, 177 (1981).
7. H. L. Frisch and D. Klempner, *Macromol. Rev.*, **1**, 149 (1970).
8. D. J. Hourston and Y. Zia, *Polymer*, **20**, 1497 (1979).
9. G. Gee, G. Allen, and G. Wilson, *Polymer*, **1**, 456 (1960).
10. G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, **54**, 1731 (1958).
11. P. J. Flory, and J. Rehner, *J. Chem. Phys.*, **11**, 521 (1943).
12. J. P. Bell, *J. Polym. Sci.*, **A-2**, **8**, 417 (1970).
13. G. Krause, *Rubber World*, **135**, 67 (1956).
14. A. V. Tobolsky, D. W. Carlson, and N. Indicator, *J. Polym. Sci.*, **54**, 175 (1961).
15. C. Price, G. Allen, F. De Candia, M. C. Kirkham, and A. Subramanian, *Polymer*, **11**, 486 (1970).
16. G. Allen, M. J. Bowden, D. J. Blundell, F. G. Hutchinson, G. M. Jeffs, and J. Vyvoda, *Polymer*, **14**, 597 (1973).
17. M. C. Shen and A. V. Tobolsky, *J. Polym. Sci.*, **A-2**, **2**, 2513 (1964).
18. S. L. Cooper and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **10**, 1837 (1966).
19. G. M. Estes, D. S. Huh, and S. L. Cooper, *Block Copolymers*, Plenum, New York, 1970.
20. L. L. Harrell, *Macromolecules*, **2**, 607 (1969).
21. J. A. Manson and L. H. Sperling, *Polymer Blends and Composites*, Heyden, London, 1976.
22. J. Ferguson, D. J. Hourston, R. Meredith, and D. Patsavoudis, *Eur. Polym. J.*, **8**, 369 (1972).
23. T. Kajiyama and W. J. MacKnight, *Macromolecules*, **2**, 254 (1966).
24. S. S. Labana, *Chemistry and Properties of Crosslinked Polymers*, Academic, New York, 1972, p. 431.
25. W. V. Chang, R. Bloch, and N. W. Tschoegl, *Rheol. Acta*, **15**, 367 (1961).
26. M. Mooney, *J. Appl. Phys.*, **11**, 582 (1940).
27. K. H. Meyer, G. Von Susich, and E. Valko, *Kolloid Z.*, **59**, 208 (1932).
28. F. T. Wall, *J. Chem. Phys.*, **10**, 485 (1942).
29. E. Guth and M. C. Wang, *J. Chem. Phys.*, **20**, 1144 (1952).
30. S. M. Gumbrell, L. Mullins, and R. S. Rivlin, *Trans. Faraday Soc.*, **49**, 1495 (1953).
31. E. A. Di Marzio, *J. Chem. Phys.*, **36**, 1563 (1962).
32. J. L. Jackson, M. S. Shen, and D. A. McQuarrie, *J. Chem. Phys.*, **44**, 2388 (1966).
33. R. J. Roe and W. R. Krigbawn, *J. Polym. Sci.*, **61**, 167 (1962).
34. K. Yamamoto, S. Kusamizu, and J. Fujita, *Macromol. Chem.*, **99**, 212 (1966).
35. B. M. E. Van Der Hoff and E. J. Buckler, *J. Macromol. Sci. (Chem.)*, **1**, 747 (1967).
36. G. Kraus and G. A. Moczogema, *J. Polym. Sci. A*, **2**, 277 (1964).
37. R. Blokland, *Elasticity and Structure of Polyurethane Materials*, Rotterdam University Press, Rotterdam, 1968.
38. L. H. Sperling, *Polymer Alloys*, Plenum, New York, 1977.
39. R. F. Landel, *Polymer Networks. Structures and Mechanical Properties*, Plenum, New York, 1971.

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