

Determination of the Molecular Weight Between Cross-links of Elastomeric Stocks by Tensile Retraction Measurements. II. Polyurethanes

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Synopsis

Tensile retraction measurements of M_c were made on a variety of polyurethanes or polyurethane-ureas. These samples were prepared using a number of prepolymer MW and functionalities. In addition, the stoichiometry of the cure was allowed to range widely. In all cases, excellent linear correlation coefficients were obtained between the M_c and the Λ_{\max} of the test. The slope and M_r (the value of M_c extrapolated to $\Lambda_{\max} = 1$) determined from this was used to characterize the polymer. These data allowed the determination of χ for each of the different systems such that comparable values of M_c could be measured by swelling. Identical formulations cured at different temperatures were shown to have measurable differences in M_c , slope, and percentage set. These variations appear to relate to the perfection of the network and morphology of the hard domains.

INTRODUCTION

The general determination of the molecular weight between cross-links (M_c) of polyurethane elastomers by swelling has posed certain very specific problems in the past. For instance, the functionality of the polyol, polyamine, and polyisocyanate can be varied individually or in combination from one to three or greater in small increments. Not only that, but the ratio of OH or NH_2 to NCO can be controlled widely about the equivalence point. As a result, a variety of solvent-polymer interaction constants χ would be needed even to attempt to obtain M_c on such varied systems. The temperature of cure and varying compatibilities of the hard and soft segment can lead to unknown quantities of allophanates and biurets in samples. Thus, swelling with good solvents for the hard segment (e.g., DMF, DMAc, DMSO, and so on) will give highly swollen rubbers that will often not be at equilibrium because of the slow hydrolysis of the biuret and allophanate cross-links. In addition, the good solvents will extract hard block oligomers and thereby contribute to the difficulty of data interpretation.

Even if a true equilibrium swelling could be obtained with solvents for the hard domains, it would not resemble the M_c present in the original sample. The high elongation imposed by swelling would be the equivalent of over 100% strain in the sample, which would effectively remove the contribution of many entanglements. In addition, the high sol fraction observed in such a system would represent the removal of a material that could have a different composition than the gel fraction and thus make it difficult to calculate the overall cross-link density.

Although the high sol fraction and attainment of equilibrium swelling do not appear a major problem with solvents that are good for the soft segment and poor for the hard segment, these data generally are not generated. Little importance has been placed on swelling of the soft segments since the value of the M_c calculated should be that of the average molecular weight of the soft segment employed. However, such an evaluation should give data that would more closely approximate the conditions of use of such an elastomer.

The present work allows the determination of M_c by nonswelling techniques such that the true cross-link density of polyurethanes can be determined by making measurements based upon the application of rubber elasticity theory to the retraction curve of a tensile test (see Part I).¹

EXPERIMENTAL

Test Procedure

A 0.25-in. strip 6 in. long was cut out of a 0.040–0.100 in. thick plaque of the desired stock. A 2-in. span was clamped in the Instron, and successive maximum elongations of 10, 25, 50, 100, 200, 300, 400, and 500% were run while adjusting the chart speed and crosshead speed to give from 6 to 30 in. chart travel at a speed of 0.50–5 in./min. The load cell range was selected to allow the maximum travel on the chart to be between 30 and 90% of full scale.

Testing was done on a fresh strip for each desired maximum strain in the initial work. Alternatively, each test was run in succession without reclamping. Both procedures gave equivalent results. The initial width, thickness, and span were used in all calculations.

The percentage set was taken as the percentage elongation at which the return curve returned to zero stress. This point is taken as the origin for all subsequent measurements of stress and strain.

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

POLYMERS TESTED

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

RESULTS AND DISCUSSION

In the previous paper, the M_c of an SBR sample was shown to be obtainable by proper application of the correct equations to tensile-retraction (T-R) data. For polyurethanes the necessary equation is expressed by eq. 1.

$$M_c = \frac{XdRT}{C_1} \quad (1)$$

TABLE I
Formulation of Polyurethane Stocks

Sample	% NCO	NH ₂ /NCO	Cure temperature (°C)	<i>d</i> (g/ml)	<i>v_f</i> ^a
Polyether diol ^b					
1	6.40	1.025		1.076	0.244
2	6.40	0.80		1.070	0.228
Polyether glycol ^c (6000 MW)					
3	12.0		130 ^d	1.13	0.386
4	12.0		130 ^d	1.13	0.386
5	12.0		170	1.13	0.386
6	12.0		180	1.13	0.386
7	12.0		150	1.13	0.386
Polyether glycol (4400 MW) ^e					
8	11.24		170	1.125	0.377
9	11.24		160	1.125	0.377
10	11.24		140	1.125	0.377
11	11.24		180	1.125	0.377
12	12.5		180	1.14	0.420

^a *v_f* is the volume fraction of filler (hard segment).

^b Based on isocyanate end capped 1000 MW polyether diol (average functionality *f* = 2.0) cured at 120°C for 1 h with an aromatic diamine.

^c Based on a methylene dianiline diisocyanate (MDI) end capped 6000 MW polyether glycol (*f* = 2.4) cured 30 min. with 1,4-butanediol (BDO) at an index of 1.05.

^d Catalyst added.

^e Based on a MDI end capped 4400 MW polyether glycol (*f* = 2.2) cured 30 min with BDO at an index of 1.0.

where *X* is the filler factor, *d* is the sample density, and *R* and *T* are the gas constant and absolute temperature, respectively. The *M_c* is the molecular weight between all types of cross-links measured at a strain level λ_{max}. The value of *C*₁ is a constant for any given λ_{max} and for these samples is obtained by evaluation of eq. (2) using at least five points on the last 70% of the T-R curve.

$$C_1 = \frac{\sigma}{2(\Lambda - \Lambda^{-2})} \quad (2)$$

where σ is the stress based on the undeformed dimensions at a strain of λ. The strain amplification factor Λ² was determined from the known volume fraction of filler *v_f* and eq. (3).

$$\Lambda = \epsilon (1 + 2.5v_f + 14.1v_f^2) + 1 \quad (3)$$

where ε is the extension ratio.

In the case of polyurethanes, the *v_f* was calculated by assuming all of the

diisocyanate and diol or diamine chain extender was not subject to elastic deformations and thus must all be considered filler.³

The Guth-Gold⁴ filler factor X ,

$$X = 1 + 2.5v_f + 14.1v_f^2 \quad (4)$$

must also be applied to the apparent M_c measured in these filled systems in order to compensate for the effect of the filler on the measured properties. Although X was derived for unattached spheres, the use of this correction allows the determination of the most reasonable value of M_c for this system, even though these fillers are not spherical.

The value of the extrapolation of the M_c versus Λ_{\max} plot to $\Lambda_{\max} = 1$ represents the molecular weight between polymer chain restrictions (M_r) in the unperturbed sample.

The linear correlation coefficient obtained by this treatment of a plot of M_c versus Λ_{\max} gave even better results than obtained previously from SBR (see Part I). For the most part, this improved correlation (e.g., 0.999+ from 0.98+) is probably due to the improved uniformity of the dispersion of the filler in the polyurethane system, possibly by an associated decrease in the number of trapped defects in the polyurethane stocks.

RATE OF TESTING

In order to determine if these high-modulus elastomers are at equilibrium during the T-R testing, a polyurethane-urea, sample 1, was tested at strain rates from 10 to 500% per minute at 25°C and λ_{\max} of 3. The data listed in Table II were obtained. No apparent trend can be seen in the variation of C_1 with test speed outside of the accuracy of the measurement. Thus, it must be concluded that, in the testing speed range employed, an equilibrium condition appears to be present and the application of rubber elasticity theory can be justified.

Figure 1 shows a plot of the logarithm of the test rate versus the percentage set data from Table II. The relaxation of the deformed polymer chains during the test would be expected to give the observed straight line. It is interesting to note that the slope of this line is negative for this mul-

TABLE II
Determination of Variation of C_1 with Speed of Testing for a Polyurethane Urea, Sample 1

Strain rate (%/min)	C_1 (psi)	% Set
10	55.04 ± 1.21	52.2
25	53.68 ± 1.22	50.3
50	53.07 ± 1.20	49.3
100	52.82 ± 2.77	48.0
250	53.43 ± 1.13	46.3
500	53.03 ± 0.67	45.5
Average	53.51 ± 0.81	

tiblock polyurethane network employed. This system would be expected to behave differently from a filled hydrocarbon rubber, since the filler portions, which are the cross-link sites, are distributed along the backbone.⁵ In contrast, the continuous rubbery portion of an SBR with random adjacent interactions with fillers and cross-link site has been shown to give a positive slope in a similar type of plot (see Part I).

A typical T-R curve used for calculations is shown in Fig. 2. Here, sample 1 was tested at 100°C to a λ_{\max} of 1.25. The points shown on the return curve indicate the value of C_1 at that point. In all cases at least five values were averaged and a standard deviation of less than 5% was calculated for each constant.

Plots of T-R data at two test temperatures are shown in Figs. 3 and 4. As would be expected from the previous discussion, the $\Lambda_{\max} = 1$ intercept for both temperatures were almost identical, and the slope of the higher temperature test showed a decrease in polymer-filler strength as indicated by the higher slope values.

Reducing the aromatic diamine curative content such that a NH_2/NCO of only 0.80, sample 2, was utilized, gave the similar type of results shown

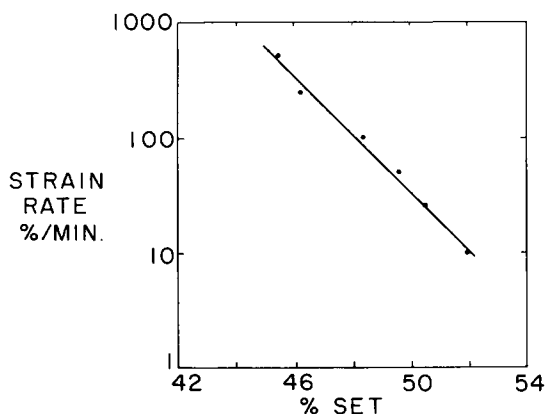


Fig. 1. Tensile retraction percentage set versus strain rate for a polyurethane sample 1.

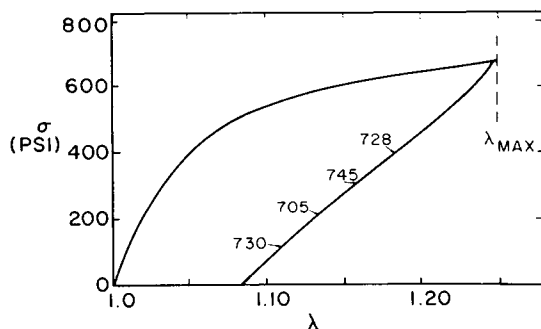


Fig. 2. Stress-strain tensile retraction curve for sample 1 at 100°C. The numbers indicated on the retraction curve are the value of C_1 calculated at that point.

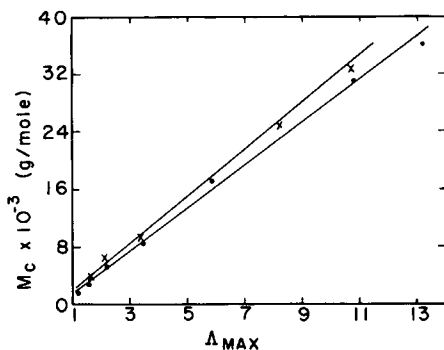


Fig. 3. Tensile retraction data for sample 1, $\text{NH}_2/\text{NCO} = 1.025$, tested at 25°C (●) and at 100°C (×).

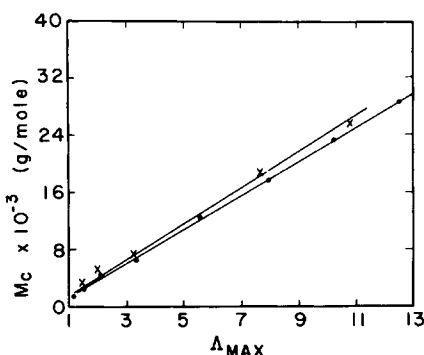


Fig. 4. Tensile retraction data for sample 2, $\text{NH}_2/\text{NCO} = 0.80$, tested at 25°C (●) and at 100°C (×).

in Fig. 4. In this case, even closer agreement between the M_c were observed and only small changes in slope were noted. This is as would be expected from the attachment of the terminal NCO groups as biuret or allophanates to give a network with very few loose ends and a multifunctional hard segment.

When the 25°C data shown in Figs. 3 and 4 are plotted together in Fig. 5, an interesting situation becomes apparent. That is, the six data points of the 0.80 NH_2/NCO , sample 2, give almost a perfect straight line (correlation coefficient = 0.9998) and the first three data points of this polymer, and the first six of the 1.025 NH_2/NCO , sample 1, also give a near perfect (correlation coefficient = 0.9996) straight line. The last two data points of sample 1 most nearly give a straight line parallel to the ideal line of sample 2. Table III summarizes the slope, intercept, and correlation coefficient for these plots. Such a relationship could be explained in that sample 2, with 0.80 NH_2/NCO , has almost a perfect network with almost no hard segment attached with less than two chemical bonds. Any defects in the filler-filler interaction were all destroyed by extension to 50%. The remainder of the hard segments now are bonded to the soft segments to give the lowest slope possible for this type of system (2337). In the case of sample 1, with 1.025

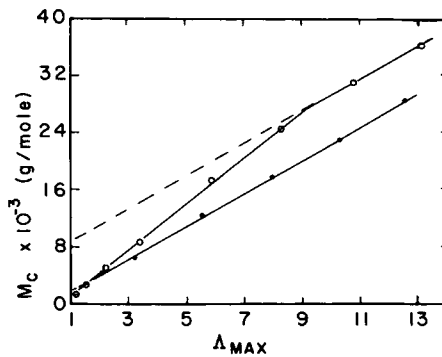


Fig. 5. Tensile retraction data for samples 1 (○) and 2 (●) tested at 25°C: fitting the best line through the last six points of 2 and another fit of the best line through the first six points of 1 along with the first three points of 2.

TABLE III
Slopes and Intercepts from Polyurethane Ureas

Sample	Temperature (°C)	M_r	Slope	Correlation coefficient
2	25	1410	2364	0.9996
2	100	1510	2582	0.9997
1	25	1720	2944	0.9975
1	100	2060	3225	0.9998
2 ^a	25	1100	2337	0.9996
1 ^b	25	1724	3229	0.9998

^a For six points from $\lambda = 1.5$ to 5.0.

^b For six data points from $\lambda = 1.1$ to 3.0 plus the first three data points of sample 3, from $\lambda = 1.1$ to 1.5.

NH₂/NCO, a significant number of these defects exists in the hard segment up to 200% elongation. The pulling out of these defects shows a slope of 3229 during their destruction. Most probably, the last few points are now controlled by a defect-free structure observed in sample 2.

If such an interpretation is correct, it should be possible to calculate the percentage of unbounded filler (*UF*) in the sample by first taking the ratio *R* of the slope of the imperfect sample to that of the slope of the perfect sample. This should be equal to *X* if no bonding between the filler and matrix had taken place.

The volume fraction of the unattached filler v_{UF} should then be obtained by solving eq. (5):

$$R = 14.1v_{UF}^2 + 2.5v_{UF} + 1 \quad (5)$$

and from this, the percentage *UF* would be

$$\%UF = \frac{100v_{UF}}{v_F} \quad (6)$$

TABLE IV
Calculation on Unbonded Filler in Samples 1 and 2

NH ₂ /NCO	Range	Slope	v_{UF}	v_F	% UF
0.80	1.5-5.0	2337	0.0	0.2284	0.0
0.80	1.1-5.0	2364	0.0045	0.2284	2.0
1.025	1.1-5.0	2944	0.0735	0.2437	30.2
1.025	1.1-3.0	3229	0.0982	0.2437	40.3

Applying these calculations to the polyurea urethane samples gave the data in Table IV.

The values of UF calculated appear reasonable considering about 23% of the isocyanate in the prepolymer used is free to form end groups or even free filler with excess diamine. In the case of NH₂/NCO being 0.80, this free isocyanate will be attached by means of biuret or cyclic trimer linkages into the ideal structure that is free of end groups.

These calculations are possible in the case of polyurea urethane samples because the soft segments definitely establish that the base M_c must be similar, whereas for hydrocarbon rubbers this cannot be assumed.

Polyurethanes from MDI/BDO

Three polyurethanes of exactly the same composition, samples 5, 6, and 7, were prepared, except that the temperature of the cure was 170, 180, and 150°C, respectively. The T-R plots are shown in Fig. 6. Here, despite identical formulations, three different M_c were measured with at least two different slopes also being determined.

It has been reported by Castro et al.⁶ that the urethane produced from MDI/BDO has limited solubility in the prepolymer. However, in this work the temperatures employed for the cures were up to 100°C above those used by Castro. Thus, in this temperature range, it seems reasonable that greater solubility of oligomers should occur and vary the anticipated chemistry. This could also result in morphological variations as well. Such changes of morphology by variations in the size of the hard blocks along with the

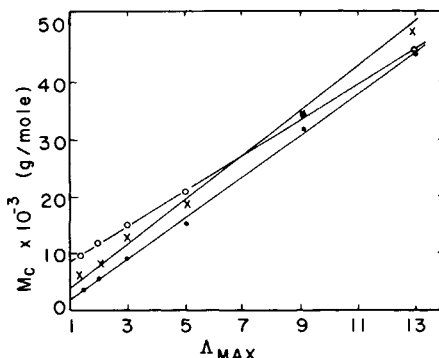


Fig. 6. Tensile retraction data for a polyurethane cured at 150°C (●), sample 7; 170°C (×), sample 5; and 180°C (○), sample 6.

distribution of repeat units has been proposed⁵ for samples heated in the 80–200°C range. These changes appear to be readily observed by a T-R measurement of M_r . When catalyzed samples 3 and 4 (again of the same formulation) were considered along with the above-discussed uncatalyzed higher temperature cures, the observation of Castro that the catalyst only changes the time scale of the reaction appears to hold true at least up to cure temperatures of 170°C. Sample 7 was not completely cured by the 150°C molding and as a result did give unusual results.

Similar results are obtained with samples 8, 9, 10, and 11, which were based on a lower MW polyol with lower functionality. Again, identical formulations were prepared with curing at 170, 160, 140, and 180°C being the only change in the preparation. Again, everything except the 180°C cured sample 11 gave similar results. Here the M_r from the 180°C cure was again about double that determined at the lower cure temperatures.

Percentage Set Measurements

The size and distribution of hard domains has been suggested to have an effect on the percentage set measured from a tensile measurement.⁵ Although the primary interest of the T-R technique was not the measurement of the percentage set, it does appear that the data obtained can help in further explaining the morphology produced. Although the percentage set has been shown to change with the rate of strain at a given λ_{\max} , those tests run at the same rate and λ_{\max} should be directly comparable. Such data are listed in Table V.

As suggested,⁵ the percentage set gives an indication of the deformation of the hard domains during elongation to give an orientated structure that, because of the long relaxation times involved, is manifested as irrecoverable flow. Here it can be seen that such reorientation appears to occur the least

TABLE V
Variation of % Set Observed at $\lambda_{\max} = 4.0$ Testing at 250%/min

Sample	% Set	Cure temperature (°C)
6000 MW prepolymer, $f = 2.4$		
3	100.4	130 + cat
4	103.0	130 + cat
5	89.2	170
6	75.7	180
7	121.2	150
4400 MW prepolymer $f = 2.2$		
8	111.6	170
9	110.6	160
10	102.4	140
11	94.6	180
12	94.1	180

at the higher cure temperatures, indicating the formation of a different and possibly more stable morphology.

Swelling

The soaking of these polyurethanes in toluene at 25°C gave a true equilibrium swelling. The ν_r calculated from this swelling is shown on Table VI along with the calculated value of χ derived from these data and the M_r (Part I). For these relatively narrow molecular weight soft segment samples, no trend of changing χ with different values of ν_r can be observed. An average value of χ of 0.470 ± 0.018 was obtained for the samples 3–12 prepared with the higher MW polyether prepolymer. A slightly higher average was obtained for samples 1 and 2, which were based on 1000 MW polyether diols, although data to obtain a statistically meaningful difference are lacking.

It is of interest to note that both the T-R and swelling data show the same trend of changes in the M_c of these polymers. Thus, it appears that differences in morphology can be seen by these techniques. The use of T-R should be particularly helpful with a study of these morphological changes since not only the M_r but also the slope of the plot used to obtain it show significant variations (see Table VII). The slopes, M_r , correlation coefficients and values of X measured at 25°C on the samples reported in this paper are summarized in Table VII.

CONCLUSIONS

Tensile-retraction measurements have been shown to give a good determination of the M_c of segmented polyurethane elastomers. This procedure has the advantage over swelling in that the M_c obtained represents the total of the physical, chemical, and hydrogen-bonded interchain attractions. If a series of polyurethanes of the same composition are to be prepared, this will allow the proper evaluation of χ when concurrent swelling measurements are made. In addition to the M_c measurement, the determination of slope of the associated line and the percentage set at a specific λ_{\max} appear to give

TABLE VI
Calculation of χ for Polyurethanes from M_r

Sample	M_r	ν_r	χ
1	1720	0.420	0.504
2	1410	0.428	0.475
3	4260	0.312	0.485
4	3810	0.321	0.481
5	4220	0.318	0.493
6	8510	0.233	0.465
7	1720	0.382	0.424
8	2600	0.350	0.461
9	2990	0.336	0.464
10	2590	0.354	0.467
11	5130	0.285	0.473
12	8770	0.244	0.483

TABLE VII
Summary of Tensile Retraction Data on Polyurethanes

Sample	M_r ($\times 10^{-3}$)	Slope ($\times 10^{-3}$)	Correlation coefficient	X
1	1.72	2.94	0.9975	2.45
2	1.41	2.36	0.9996	2.31
3	4.26	3.23	0.9972	4.06
4	3.81	3.32	0.9996	4.06
5	4.22	3.80	0.9998	4.06
6	8.51	3.12	0.9996	4.06
7	1.72	3.63	0.9995	4.06
8	2.60	4.59	0.9943	3.95
9	2.99	4.56	0.9929	3.95
10	2.59	4.69	0.9995	3.95
11	5.13	5.34	0.9995	3.95
12	8.77	4.08	0.9996	4.53

a means of measuring unbounded filler and changes in morphology of the cured sample.

The author would like to express his thanks to Mr. P. W. Boerner for preparation and curing of the various polyurethane elastomers and Mr. J. M. Doshak for running the Instron and collecting much of the data using the digitizer. Valuable discussions with Dr. S. L. Cooper of the University of Wisconsin and Dr. T. Ward of VPI were appreciated. In addition, thanks is given to the Firestone Tire & Rubber Co. for permission to publish this work.

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Received September 24, 1985.

Accepted December 6, 1985.