Properties of a Semiflexible Urethane Foam System

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THE FACTORS which influence the physical properties of urethane foams are numerous; however, investigations (*1, 4, 5*) have shown that basic correlations of physical properties to fundamental foam structure do exist and can be characterized. The ability to predict accurately and preselect properties presents an appealing picture to the foam chemist.

One major problem has been to find a single system which could give data covering a broad range of physical properties without having to make extensive changes in resins and catalysts. Lack of such a system has necessitated a selection of data from a number of related systems with the interrelationships not being fully known.

The system described in this study provides data covering a fairly broad range of physical properties in a previously unreported area while maintaining controlled conditions of catalyst, silicone oil, density and other factors. Foams were prepared by both "quasi-prepolymer" and "one-shot" methods but had essentially the same characteristics. The portion of the study used in this report was done by the one-shot method because of its flexibility and simplicity.

EXPERIMENTAL

Raw Materials. A commercial 80 to 20 ratio of the 2,4- and 2,6-isomers of tolylene diisocyanate, Mondur TD-80 (Mobay Chemical Co.), was used as the diisocyanate. The resins used were Niax Triol LG-56 (Union Carbide Corp.), a polyoxypropylene triol based on glycerol, with a molecular weight of 3000, and Quadrol (Wyandotte Chemical Co.), *N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine. The foams reported were made using resins containing 12.5 or 15% Quadrol. The catalyst was *N,N'*-dimethylpiperazine (Jefferson Chemical Co.) and the silicone oil stabilizer was XL-520 (Union Carbide Corp.).

Foaming. All foams were prepared using a Mobay foam machine (*6*). Each of the four components—i.e., the polyether resin, diisocyanate, silicone oil, and a water-catalyst mixture, were metered simultaneously to the mixing chamber. Foaming was done in open pan molds, and the foams were cured for 20 hours in a 70° C. oven before testing.

Concentrations of catalyst and silicone oil in the foam mixture were maintained in the ranges of 0.7 ± 0.15 and 1.5 ± 0.1 weight % of the total foam components, respectively. While not providing optimum conditions of curing time, rise time, etc., under all conditions studied, this combination gave good foams throughout a broad range while eliminating the variables of catalyst and silicone oil.

Assuming that 1 mole of water reacts with isocyanate to produce 1 mole of carbon dioxide, various foam densities could be selected by varying the amount of water. The final foam volume was assumed to approximate the volume of carbon dioxide produced when the available water reacted with the isocyanate. Equation 1 was based on the ideal gas law and was used to select formulations quickly to give a desired density.

$$DWT = 1370 \tag{1}$$

D is the foam density in pounds per cubic foot, W is per cent water in the foam mix, and T is the maximum exotherm temperature in degrees Kelvin. T can generally be taken as about 400° K. This leads to Equation 2, applicable to most one-shot foams above 2 pounds per cubic foot density.

$$DW = 3.5 \tag{2}$$

Table I compares predicted and measured foam densities for a series of foams. Equations 1 and 2 are useful in selecting foam densities but do not reflect the probable complexity of the foaming reaction as evidenced by the discrepancies encountered with 120 index foams.

Table I. Measured vs. Predicted Foam Densities

Density, Lb./Cu. Ft.		
Calculated	Measured	Isocyanate Index[a]
2.2	2.2	90
2.7	2.8	90
3.1	3.1	90
3.9	3.9	90
2.2	2.3	100
2.7	2.7	100
3.2	3.3	100
4.0	4.1	100
2.4	1.9	120
2.9	2.4	120
3.4	2.7	120
4.1	3.5	120

[a] Percentage of theoretical isocyanate used, based on water and hydroxyl number of resin mixture.

Test Methods. Density, tensile strength, elongation, constant deflection compression set (calculated on original thickness), and compression load deflection were tested according to the Cellular Plastics Division of the Society of Plastics Industry approved methods (*7*). An Instron tester was used for tensile, elongation, and compression-deflection tests.

A Clash-Berg apparatus was used to determine torsional stiffness. Foam samples 1 inch wide × 0.5 inch thick were tested in a manner similar to ASTM D 1043-51 (*2*). Silicone oil was the medium used.

To measure the accelerated hydrolysis resistance, samples were placed for 5 hours in a steam autoclave at 250° F. and 15 p.s.i. steam pressure. After this period, samples were again tested by the methods indicated. Accelerated oxidation aging was tested by exposing samples in a 150° C. circulating air oven for 24 hours. When this treatment was completed, samples were tested by the methods indicated.

The swell index was obtained by immersing a 15 × 1 ×1-cm. foam sample in acetone for 24 hours at room temperature. The per cent volume swell was calculated from the linear swell observed. Data in Table II are average values for four samples for each experimental condition.

Table II. Volume Swell of Foams in Acetone Related to Aging of the Foam

	Isocyanate Index		
	90	100	120
Calculated M_c	1630	1070	690
Vol. swell, %			
Original	116	90	83
After 5 hr. steam autoclave	140	132	155
After 24 hr. dry air, 150° C.	188	150	116
Net change, autoclave, %	24	42	72
Net change, oven, %	72	60	33

For aniline degradation experiments, a 10.0 ×0.5 × 0.5-cm. foam sample was immersed in portions of dimethylacetamide (DMA) at room temperature until a constant sample length was achieved. The sample was gently pressed between layers of absorbent paper to remove excess dimethylacetamide, then placed in a tube of aniline which had been preheated to 140° C. and was maintained at that temperature. After 2 minutes the sample was removed and rinsed in portions of dimethylacetamide. When free from aniline, the foam swell was again measured in dimethyacetamide and the change noted.

RESULTS AND DISCUSSION

Calculation of Branching. Equation 3 represents an extension of a method described by Bolin and others (*4*) and was used to calculate M_c, the value for average molecular weight per branch point.

$$M_c = \frac{100 - 2.44\,W - K}{\frac{\text{grams } A}{\text{mol. wt. } A}(B_A) + \frac{\text{grams } B}{\text{mol. wt. } B}(B_B) \pm \frac{\text{grams TDI}}{87}} \qquad (3)$$

W is the grams of water per 100 grams of total foam mix, K is the grams of nonfunctional components—i.e., silicone oil, catalyst, etc.—per grams of foam mix, and B_A and B_B are the number of branch points in a molecule of A and B respectively. The grams of TDI refer to the excess or deficiency of diisocyanate present in the initial 100 grams of foam mix compared to the theoretical amount needed in 100 grams of foam mix; the term is added in the case of excess diisocyanate and subtracted in the case of deficiency. The second term of the numerator is a correction for weight loss due to carbon dioxide evolution.

All materials were considered to have their reported functionality. One branch point per molecule was attributed to the triol, two branch points per molecule were attributed to the tetrol.

The diisocyanate was assumed to react first with hydroxyl groups and water to form urethane and urea linkages. If the requirement for hydroxyl and water was filled the excess diisocyanate, as occurs with index values over 100, was assumed to form biuret or allophanate linkages; hence, the final term in the denominator of Equation 3 represents changes in the number of branch points which result from excess or deficiency of diisocyanate. These groups may not be formed in such an entirely selective manner, but because an adequate quantitative evaluation connot be made with present methods, deviations from the theory could not be considered. Comparison with other data (*4*) suggested that deviations were minor or essentially compensated for by other factors.

Structure and Foam Properties. TENSILE AND ELONGATION. The relationship of tensile modulus and ultimate elongation to the calculated molecular weight per branch point is shown in Figure 1. Values of tensile modulus for low M_c samples (120 index) were not in the 65 to 80 p.s.i. range as was expected; this was attributed to tear occurring in these stiff foams. Values of tensile modulus were extrapolated to 100% elongation where necessary for comparison with other data (*4*) (shown as broken lines on Figure 1).

COMPRESSION DEFLECTION. Compression deflection was dependent on density and M_c. To make a realistic evaluation, compression deflection data were compared at like densities. To accomplish this, compression deflection values corresponding to 2.5, 3, and 4 pounds per cubic foot densities were read from a plot of density *vs.* compression deflection (Figure 2) and are shown in Figure 3 as a function of M_c. Figure 4 shows the relationship of reciprocal compression deflection values to M_c. No direct relationship of diisocyanate content (hence aromatic content) with compression deflection was found. Because per cent TDI and M_c values are so interrelated, as are TDI and density, these data did not allow a conclusion as to whether aromatic content, independent of other factors, had any effect on compression deflection values.

COMPRESSION SET. The conditions imposed by the SPI test method for constant deflection compression set (*7*) enabled a correlation to be made between this property and M_c. In this test, foam samples were compressed to half their thickness for 22 hours at a temperature of 70° C. and under controlled humidity conditions. The samples

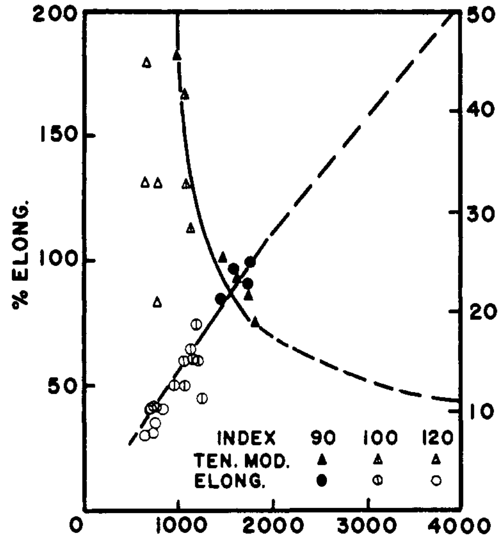


Figure 1. Elongation *vs.* M_c and tensile modulus *vs.* M_c

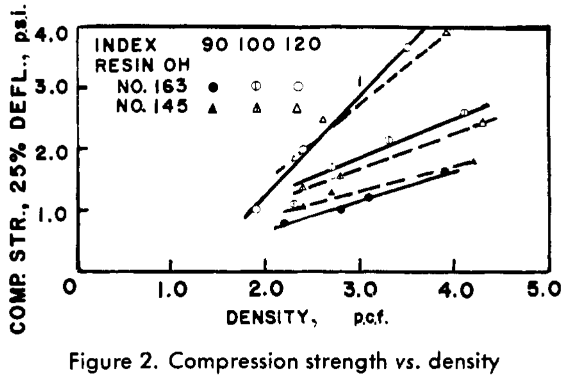


Figure 2. Compression strength *vs.* density

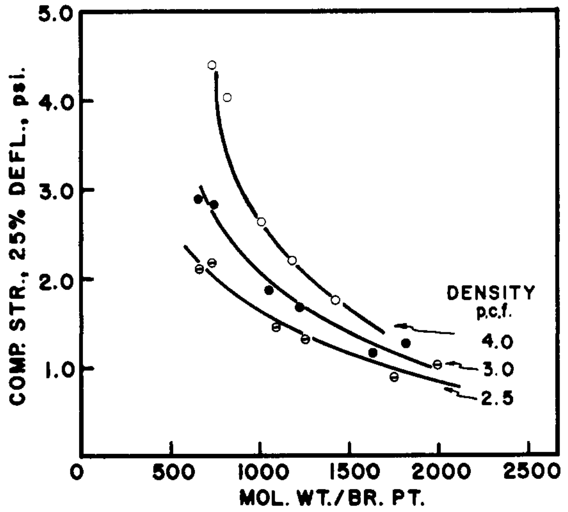


Figure 3. Compression strength vs. M_c

were taken from the oven and the plates removed. After a 30-minute recovery period at room temperature, the sample thicknesses were measured. If the samples having poor set were given longer recovery periods, the sets continued to improve with a recovery rate dependent upon the M_c value for the foam. As M_c values decreased, recovery from compression occurred at slower rates. Similarly, all foams showed good set values (about 5%) if allowed to recover in the 70° C. oven for 30 minutes. Inspection of Figure 5 revealed a possible explanation. Foams having higher M_c values have a relatively flat modulus curve in the 25 to 70° C. range encompassed by the set test. Low M_c foams have a greater slope in this region, indicating a more temperature-sensitive condition.

Slow recovery in the standard compression set test, hence high set values, are believed to result from compression of the foam while in the elastic state (70° C.), followed by recovery in a state approaching the glassy state (25° C.). A correlation was obtained between M_c values and the glass transition regions (Figure 5) as well as between M_c values and compression sets (Figure 6).

Clash-Berg Torsional Stiffness. Besides providing insight into compression set behavior, Clash-Berg torsional stiffness curves were used to study certain phases of polymer structure. Foams having low M_c values are associated with a stiffer polymer which displays greater temperature-

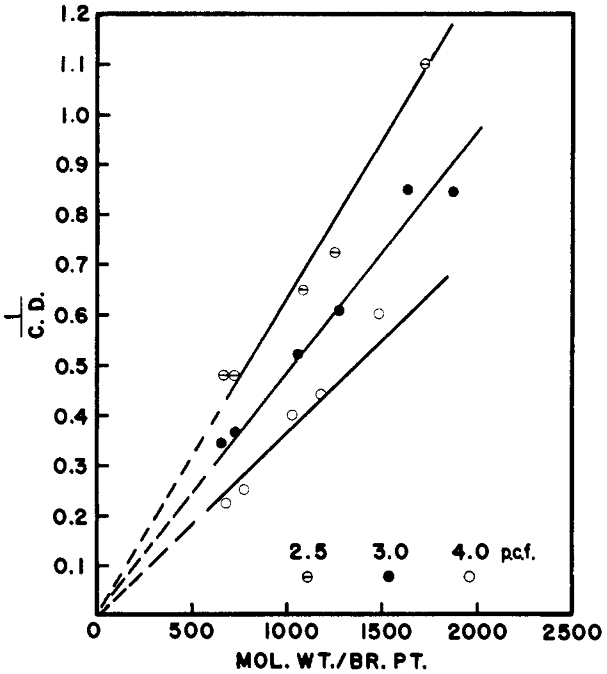
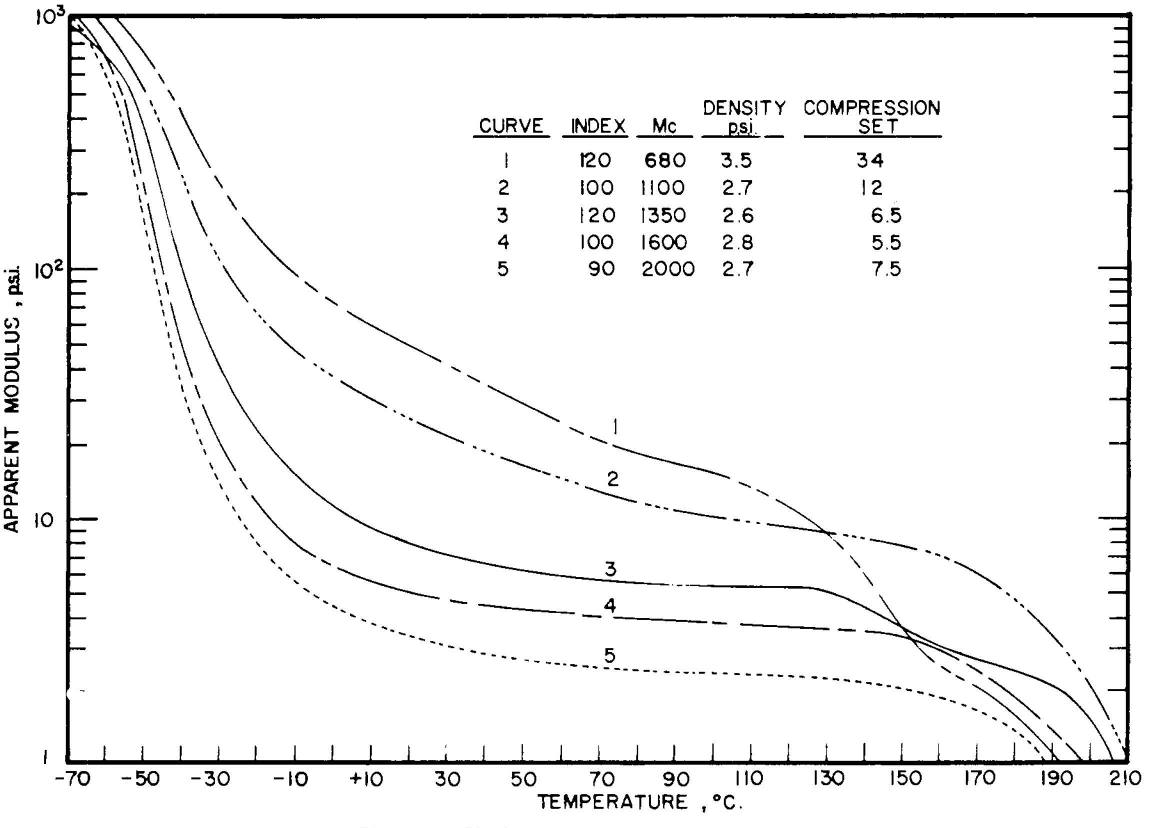


Figure 4. M_c vs. reciprocal compression strength at 25% deflection



CURVE	INDEX	Mc	DENSITY psi	COMPRESSION SET
1	120	680	3.5	34
2	100	1100	2.7	12
3	120	1350	2.6	6.5
4	100	1600	2.8	5.5
5	90	2000	2.7	7.5

Figure 5. Clash-Berg torsional stiffness curves

sensitive compression deflection characteristics (Figure 5). Near 130° C., the curve for high isocyanate index foams shows a deflection which indicates a breakdown of a portion of the polymer linkages. It is believed that the linkages which were broken were biuret and/or allophanate cross links. The presence of one or both of these relatively weak cross links in the high isocyanate index foams was shown by the following experiment.

Biuret and allophanate bonds are broken by hot (140° C.) aniline at a much faster rate than the urethane and urea linkages (*3*). Aniline degradation experiments (Table II) showed that 140° C. aniline had little effect on 90 to 100 index foams. In contrast, the 120 index foam showed significantly greater solvent swelling after the aniline treatment than originally, in agreement with the expected presence and rupture of biuret or allophanate cross links in the 120 index foam.

Dry Oven and Hydrolysis Aging. Figure 7 shows both the relationship of volume swell in acetone to M_c and the effects of dry air and hydrolysis aging on these samples. Table II summarizes these data to show the over-all effect of isocyanate index on aging. Apparently the biuret and/or allophanate linkages present in the high index foams are susceptible to hydrolysis. Conversely, the use of excess isocyanate helps samples resist dry air oven aging, perhaps by effecting a continuing curing action to partially offset the aging process. An examination of samples aged in the hot air oven shows a trend within each of the index groupings. The principal difference among foams of a particular group is the water percentage, hence urea group content and probably free amino end groups. Increased urea content and free amino content may increase oxidation resistance.

Acetone was used as a swell solvent, so a direct comparison with previous data (*4*) could not be made. However, volume swell in dimethylacetamide for selected foams showed that one-shot foams were consistently less cross linked (higher swell index) than the comparable prepolymer foams (*4*). This phenomenon, observed at M_c values of 750 to 5000, indicates that fewer of the branch points in the raw materials are built into cross links in the one-shot foams than in prepolymer foams.

CONCLUSIONS

Foams were prepared having calculated values of M_c in the 700 to 2000 range. At like densities the relationship $M_c \times$ compression deflection = constant was found to hold. Elongation and swell index decreased linearly as M_c decreased. Tensile modulus was an inverse function of M_c, but at lower values of M_c, tear occurred which prevented optimum values of tensile modulus from being achieved. Compression set, as measured by the SPI method, increased sharply below an M_c value of about 1250 because of the increasing viscosity of the polymers at the recovery temperature.

The presence of biuret and/or allophanate linkages in high isocyanate index foams was demonstrated and correlated to dry oven and hydrolysis aging characteristics.

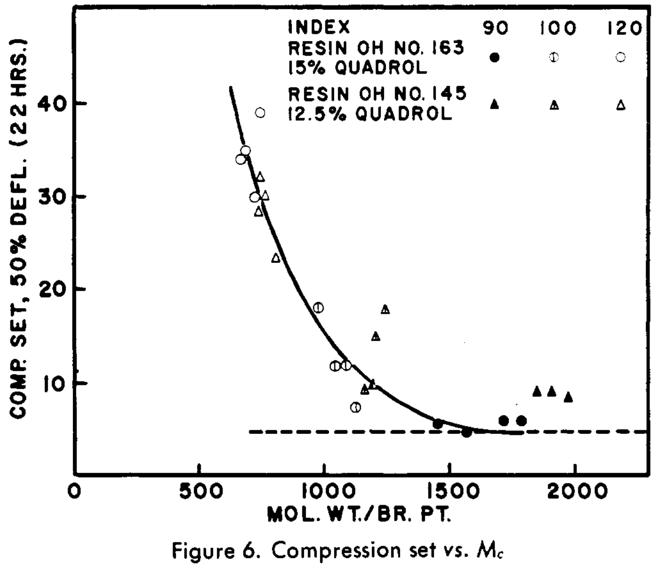


Figure 6. Compression set vs. M_c

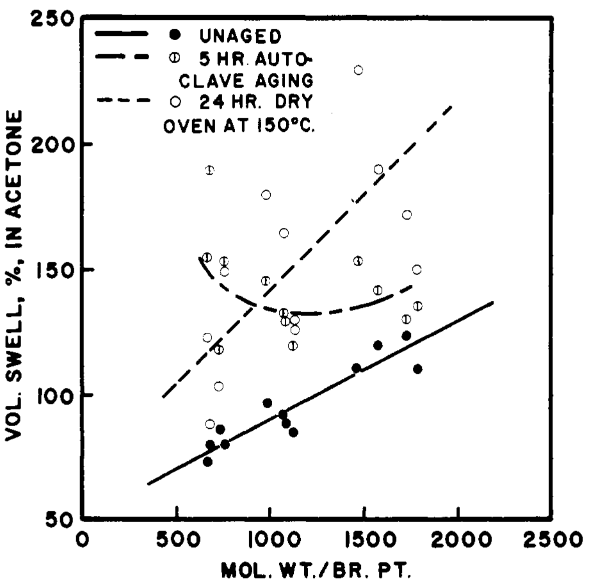


Figure 7. M_c vs. volume swell in acetone

Table III. Degradation of Foams in Aniline, Related to Isocyanate Index

Isocyanate Index	Calculated M_c	Foam Sample Length, Cm. Original, dry	In DMA	In DMA, after aniline treatment	Time in Aniline at 140° C., Minutes
90	1730	10.0	13.9	14.1	2
100	1100	10.0	13.5	13.7	2
120	660	10.0	12.8	14.3	2
90	1730	10.0	13.9	14.4	5
100	1100	10.0	13.4	14.4	5
120	660	10.0	12.6	16.5	5

ACKNOWLEDGMENT

The authors thank the Mobay Physical Testing and Evaluation Group, under the direction of Samuel Steingiser and W.C. Darr for testing the foams prepared during this investigation, also James Wharton and Paull Berger for their contributions to the study.

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RECEIVED for review July 8, 1959. Accepted October 22, 1959.