

Effect of Molecular Structure on the Thermal Aging Properties of Flexible Urethane Foams*

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Synopsis

A series of flexible urethane foams was formulated from diisocyanate-terminated polyether prepolymers, using both a polyether diol and an ethylenediamine tetraglycol as extenders. The long-term compression set characteristics and the compression deflection properties of these foams were studied. The swelling effect in a solvent, the free isocyanate content, and the role of a carbon black filler on the flexible urethane foam formulation were also evaluated. It was concluded that the total amount of diisocyanate used in the formulation, rather than a variation in the type of isocyanate, has the greatest influence on molecular structure.

INTRODUCTION

Flexible urethane foams possess an extremely complicated molecular arrangement. This is primarily due to the very broad spectrum of available starting materials and the countless chemical reactions that may occur during the foam formation. The final polymer contains a great diversity of chemical structures, making available a very wide range of polymer properties. A comprehensive knowledge of the relationship between polymer structure and physical properties is important to fully utilize the engineering capabilities of flexible urethane foams.

Prior work in our laboratory has shown the effect of molecular structure, particularly the diisocyanate, on the load-bearing ability of flexible urethane foams.¹ Additional work has now been completed, to extend this type of information into the area of thermal aging.

Previous investigators have studied the thermal stability properties of both polyester- and polyether-based urethane polymers.²⁻⁴ They have studied the effects of catalyst, chemical linkages, and "secondary bonds" (van der Waal forces) on the aging characteristics of flexible urethane foams.⁵⁻⁷ The work presented here describes the results of a study to determine the role of the diisocyanate and polyol extender, used in flexible urethane foam formulations, in the heat-aging properties of these materials.

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There are several methods that lend themselves to the study of the thermal aging characteristics of flexible urethane foams. For our work, we decided upon a long-term compression-set test, in combination with a determination of the effect of aging on the compression-deflection properties of the foam. Our reasoning for this procedure was that by keeping the foam in a compressed state at an elevated temperature, we would be able to determine not only the stability of the various chemical linkages in the foam, but also the effect of hydrogen bonds present. To further clarify the relationship between polymer structure and aging properties in foams, other methods of investigation were used including: solvent absorption, free isocyanate determination, and the role of a carbon black filler.

All our foams were molded to a desired density by using an isocyanate prepolymer-water-extender formulation. Two different types of extenders were used. The isocyanate prepolymers were based on a polyether triol, terminated with secondary hydroxyl groups. Four different commercially available diisocyanates were evaluated in this study.

EXPERIMENTAL PROCEDURE

Physical Testing

To determine aging characteristics of the urethane formulations, a compression-set test in combination with a determination of the effect of aging for 72 and 168 hr. on the compression-deflection properties of the foams, were conducted. Specimens used were 2 in. in diameter and cut from the cured foam slabs approximately 0.125 in. thick. First a compression-deflection test, to 50% of the original thickness, was performed at ambient temperature ($77 \pm 10^\circ\text{F}$). The specimens were then compressed to 50% deflected thickness in a compression set fixture as described in ASTM D-395.¹⁰ The compressed specimens were aged at $160 \pm 5^\circ\text{F}$. for the specified times (72 and 168 hr.). Upon completion of the aging period, the specimens were cooled to ambient temperature while in the compressed state. The specimens were then removed from the compression-set fixture and allowed to recover for 30 minutes at ambient temperature. The recovered thickness was then measured by using a dial-type gage having a stem and foot weight of 25 g. and a foot 1.125 in. in diameter. A compression-deflection test, to 50% of the original thickness, was performed at ambient temperature on the aged specimens. All tests were performed in duplicate and the results averaged.

Isocyanate Content

The free isocyanate content of both filled (carbon black) and unfilled flexible urethane foam samples was determined by the method of Kubitz.⁸ All the samples were first tested qualitatively and then quantitatively.

The qualitative identification of free isocyanate was accomplished by treating a sample of the material with a test solution containing 0.2% of an *n*-butylamine-malachite green derivative in a 50:50 mixture of cumene

and mineral oil. The presence of a green color is a positive test for as little as 0.005 mmole of isocyanate. The shade of green is an indication of the amount present, but is not sensitive enough for a quantitative analysis.

The quantitative determination involved the following steps: (1) a weighed foam sample was reacted with an excess of a standard solution of *n*-butylamine; (2) an aliquot containing unreacted butylamine was withdrawn; (3) a solution of malachite green was added to react with the *n*-butylamine; (4) the malachite green intensity was measured with a spectrophotometer; (5) the amount of *n*-butylamine that reacted with isocyanate was calculated from a calibration curve (for the decolorization of malachite green by *n*-butylamine).

Solvent Absorption

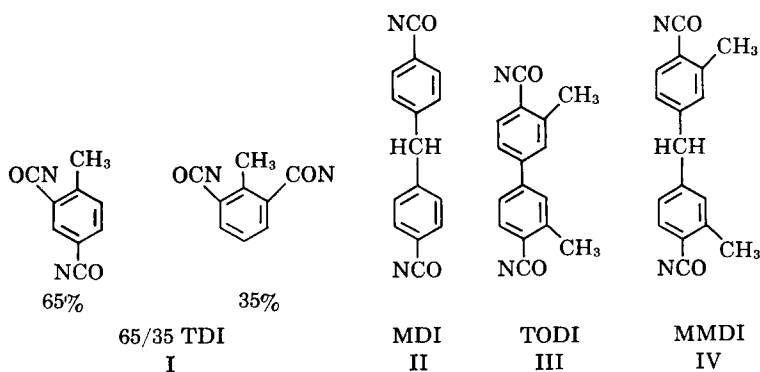
The conventional method for absorption measurements on crosslinked polymers consists of immersing weighted or measured specimens into suitable solvents and observing the gain in weight or volume over a period of time. The ideal solvent is one that would cause swelling, but no solution, of the specimen when immersed. For our work with flexible urethane foams, we elected to expose the samples to vapors of pyridine (a known solvent).

Samples of the flexible urethane foam were reduced in particle size to approximately 1–2 mm., and 0.2 g. was weighed into a tared 5-ml. beaker. The foam samples were then placed into an 8-in. desiccator which contained 400 ml. of pyridine. At various periods of time, the samples were removed from the desiccator, weighed as quickly as possible, and then returned to the desiccator. This weighing operation required approximately 30 sec. for each sample. The per cent weight gain was determined after 2, 4, 6, 8, 24, 26, 32, and 48 hr. exposure to the pyridine vapor.

CHEMISTRY AND FOAMS

Prepolymer Preparation

The four diisocyanates used for this study are shown in structures I–IV. These structural formulas include the single benzene ring as illustrated by



the toluene diisocyanate (TDI) isomers. A fused biphenyl compound is represented by 3,3'-dimethyl-4,4'-diphenyl diisocyanate (TODI). Two separated ring diisocyanates, methylene-bis(4-phenylisocyanate) (MDI) and methylenebis(3-methyl-4-phenyl isocyanate) (MMDI) were also evaluated.

The polyether used in the prepolymer preparation was Niax Triol LHT-67, a polyoxypropylene derivative of 1,2,6-hexanetriol having an average molecular weight of approximately 2500.

The isocyanate prepolymers were prepared by a method similar to that described by Davis et al., certain modifications being necessary for the solid diisocyanates.⁹ The following is a typical prepolymer recipe. Niax Triol LHT-67, 1.0 mole; diisocyanate (first portion), 1.53 mole; diisocyanate (second portion), 2-6 mole. The second portion of isocyanate was varied to adjust the amine equivalent of the finished prepolymer to the desired range of 455 ± 10 . In the case of prepolymers prepared from a combination of diisocyanates, chain extension was accomplished by the first addition while the capping reaction was performed by the second addition.

Shown in Table I are the diisocyanates and combination of diisocyanates used in prepolymer preparation, along with amine equivalents, formulation number, and viscosities of the finished prepolymers.

TABLE I
Typical Properties of Prepolymers Made Using Various Diisocyanates

| Formulation number | Diisocyanate | Amine equivalent | Viscosity (25°C.), cp. |
|--------------------|----------------|------------------|------------------------|
| 254-69 | 65/35 TDI | 462 | 15,500 |
| 254-80 | MDI | 461 | 14,000 |
| 254-91 | TODI-65/35 TDI | 445 | 13,100 |
| 254-101 | MMDI-65/35 TDI | 455 | 10,500 |

Foam Formulation

Two extenders were evaluated in the foam formulations. One was Tetric 701 (EDTG), a tetrafunctional oxypropylene-oxyethylene derivative of ethylenediamine. This polyether polyol is terminated with primary hydroxyl groups and has a molecular weight of approximately 2750. The other extender used was Pluronic L-61 (PPG), a polyether diol of approximately 2000 molecular weight, having a center block of oxypropylene units, and on each end blocks of oxyethylene units; again the polyether polyol was terminated with primary hydroxyl groups.

Blowing was accomplished through the reaction of water with the free isocyanate groups on the prepolymer to release CO₂. A filler, FT carbon black, was added to the formulation at a ratio of approximately 10% based on total foam weight. A cell stabilizer, DC-199, an alkylsilane-polyoxyalkylene copolymer, was also incorporated into the formulations.

A tertiary amine catalyst, *N,N,N',N'*-tetramethyl-1,3-butanediamine (TMBD) was employed in the foaming formulation. The foaming systems using EPTG as an extender are designated by formulation numbers terminating in -A and those with PPG are coded -B. A typical foaming recipe, based on a prepolymer having an amine equivalent of 450 and with EDTG as an extender, is as follows: prepolymer, 100 parts (by weight); EDTG, 48.5 parts; distilled water, 1.38 parts; catalyst (TMBD), 0.24 parts; FT carbon black, 19.4 parts; DC-199, 1.0 parts. The foaming mixture was prepared by combining the extender with the carbon black, water, catalyst, and cell stabilizer. These components were blended together and then combined with the prepolymer. The mixer used for this operation was a high-speed air-driven stirrer with a 1-in. triblade propeller.

Foam Sample Preparation

The foamed test slabs prepared for both physical and chemical testing had dimensions $6 \times 6 \times 0.125$ in. and an approximate density of 0.34 g./cc. A mold release agent, Garan 225 (Ram Chemical Co.), was used to facilitate the removal of the cured foam from the aluminum molds.

The foaming formulation was prepared as described earlier. The liquid mixture was poured into the preweighed mold stationed on a laboratory balance. The balance was set to measure the correct amount of material needed to arrive at the predetermined density. After the correct quantity of foaming mixture had been transferred into the mold cavity, the mold was removed from the balance and the top plate fastened in place. Room temperature molds were used for most of the foaming formulations. The molds were allowed to stand for 1 hr. at room temperature (giving the foam time to gel), then the molds were heated for 2 hr. at $225 \pm 5^\circ\text{F}$. in a forced-draft oven. The molds were then removed from the oven and allowed to cool to room temperature. The samples were removed from the molds and given an additional cure of 6 hr. at $225 \pm 5^\circ\text{F}$.

RESULTS AND DISCUSSION

Shown in Table II are the results of the compressive aging tests at 165°F . for the various flexible urethane foam formulations. These data indicate that in general the diol (PPG)-extended foams had lower compression set and higher load-retention properties than did the tetrafunctional (EDTG)-extended formulations. Formulations 254-91A and 254-91B were the only materials tested that displayed an increase in per cent load retention upon heat aging at 168 hr. Formulation 254-80B (MDI + PPG) displayed exceptionally low compression set and retained over 50% of its load-bearing capacity.

The results of the qualitative tests for free isocyanate content were positive for both the filled (carbon black) and unfilled flexible urethane foams incorporating the diol (PPG) extender. No tests for free isocyanate content were performed on the EPTG-extended formulations, due to their

TABLE II
Compressive Aging Properties of Flexible Urethane Foam at 165°F.

| Formulation number | Chain extender | Diisocyanate | Density, g./cc. | Free thickness, in. | Compression set, % | | Retention of load, % | |
|--------------------|----------------|----------------|-----------------|---------------------|--------------------|---------|----------------------|---------|
| | | | | | 72 hr. | 168 hr. | 72 hr. | 168 hr. |
| 254-69A | EDTG | 65/35 TDI | 0.340 | 0.129 | 13.8 | 26.0 | 54.6 | 50.0 |
| 254-69B | PPG | 65/35 TDI | 0.365 | 0.122 | 20.6 | 25.0 | 52.7 | 46.6 |
| 254-80A | EDTG | MDI | 0.341 | 0.132 | 52.6 | 79.8 | 91.4 | 90.2 |
| 254-80B | PPG | MDI | 0.340 | 0.125 | 9.8 | 9.8 | 57.8 | 56.2 |
| 254-91A | EDTG | TODI-65/35 TDI | 0.342 | 0.128 | 97.0 | 91.4 | 25.0 | 39.7 |
| 254-91B | PPG | TODI-65/35 TDI | 0.356 | 0.126 | 60.5 | 33.4 | 37.7 | 38.7 |
| 254-101A | EDTG | MMDI-65/35 TDI | 0.349 | 0.126 | 11.8 | 49.6 | 70.3 | 48.4 |
| 254-101B | PPG | MMDI-65/35 TDI | 0.355 | 0.124 | 13.0 | 87.4 | 71.6 | 60.0 |

poor showing in the compression-aging test. The qualitative test for free isocyanate content is quite sensitive and would show the presence of NCO at a minimum of 0.005 mmole of sample. All foam samples, except formulation 254-80B, showed the same intensity of green color, indicating the same level (approximately) of NCO.

Table III gives the results of the quantitative determinations for the free isocyanate content of the flexible urethane foam formulations tested. The standard deviation for duplicate determinations was $\pm 0.023\%$. It is evident from Table III that the carbon black filler does not affect the free isocyanate content in the foam formulations. The samples containing MDI were much higher in their free NCO content than any of the samples tested.

TABLE III
Free Isocyanate Content of Diol-Extended Flexible Urethane Foams

| Formulation number | Filler | Diisocyanate | NCO content, % | |
|--------------------|--------------|----------------|----------------|---------|
| | | | Duplicates | Average |
| 254-69B | Unfilled | 65/35 TDI | 0.000, 0.034 | 0.02 |
| 254-69B | Carbon black | 65/35 TDI | 0.057, 0.036 | 0.05 |
| 254-80B | Unfilled | MDI | 0.139, 0.144 | 0.14 |
| 254-80B | Carbon black | MDI | 0.128, 0.109 | 0.12 |
| 254-91B | Unfilled | TODI-65/35 TDI | — 0.031 | 0.03 |
| 254-91B | Carbon black | TODI-65/35 TDI | 0.055, 0.070 | 0.07 |
| 254-101B | Unfilled | MMDI-65/35 TDI | 0.046, 0.024 | 0.04 |
| 254-101B | Carbon black | MMDI-65/35 TDI | 0.050, 0.033 | 0.04 |

The per cent weight gain due to solvent absorption for the diol extended flexible urethane foam formulations is shown in Table IV. Both filled (carbon black) and unfilled samples were used. Figure 1 shows the difference in solvent absorption between a filled and unfilled foam samples.

When considering the results given in Table IV, the possibility of polymer degradation in the process of dissolution by pyridine cannot be ruled out. Why pyridine appears to be a selective solvent is not fully understood at this time. However, it appeared from our work that if degradation did take place at all, it certainly was not extensive. It was assumed that the urethane polymer must be fairly low in molecular weight in order to obtain solution. The fact that different solution times have been observed, as listed in Table IV for the various formulations, gives rise to evidence of variation in crosslinking.

The data in Table IV show that a definite difference exists between the filled (carbon black) and unfilled urethane foams. The unfilled samples all exhibited a greater solvent absorption than did the carbon black-filled materials. As for the basic formulations themselves, the MDI-containing foams did not show as great a gain in weight as did the TDI-containing foams.

TABLE IV
Solvent Absorption in Pyridine for Diol-Extended Urethane Foams

| Formulation number | Filler | Diisocyanate | Weight gain at various exposure times, % | | | | | | | |
|--------------------|--------------|----------------|--|-------|-------|-------|--------|--------|--------|--------|
| | | | 2 hr. | 4 hr. | 6 hr. | 8 hr. | 24 hr. | 26 hr. | 32 hr. | 48 hr. |
| 254-69B | Unfilled | 65/35 TDI | 17.6 | 24.5 | 30.4 | 34.6 | 70.7 | 70.2 | 74.1 | 91.3 |
| 254-69B | Carbon black | 65/35 TDI | 16.9 | 24.7 | 28.9 | 33.0 | 66.0 | 65.2 | 69.0 | 85.5 |
| 254-80B | Unfilled | MDI | 17.9 | 25.0 | 30.4 | 34.6 | 68.6 | 68.2 | 72.5 | 90.4 |
| 254-80B | Carbon black | MDI | 17.3 | 23.2 | 27.6 | 31.5 | 62.9 | 61.9 | 65.8 | 82.4 |
| 254-91B | Unfilled | TODI-65/35 TDI | 18.2 | 25.4 | 31.1 | 35.6 | 69.7 | 69.3 | 73.5 | 91.4 |
| 254-91B | Carbon black | TODI-65/35 TDI | 16.6 | 23.4 | 28.6 | 32.6 | 63.8 | 63.6 | 67.2 | 83.2 |
| 254-101B | Unfilled | MMDI-65/35 TDI | 17.6 | 24.7 | 30.6 | 35.2 | 69.6 | 69.4 | 73.8 | 91.9 |
| 254-101B | Carbon black | MMDI-65/35 TDI | 16.6 | 23.5 | 28.9 | 33.2 | 64.8 | 64.0 | 67.4 | 83.1 |

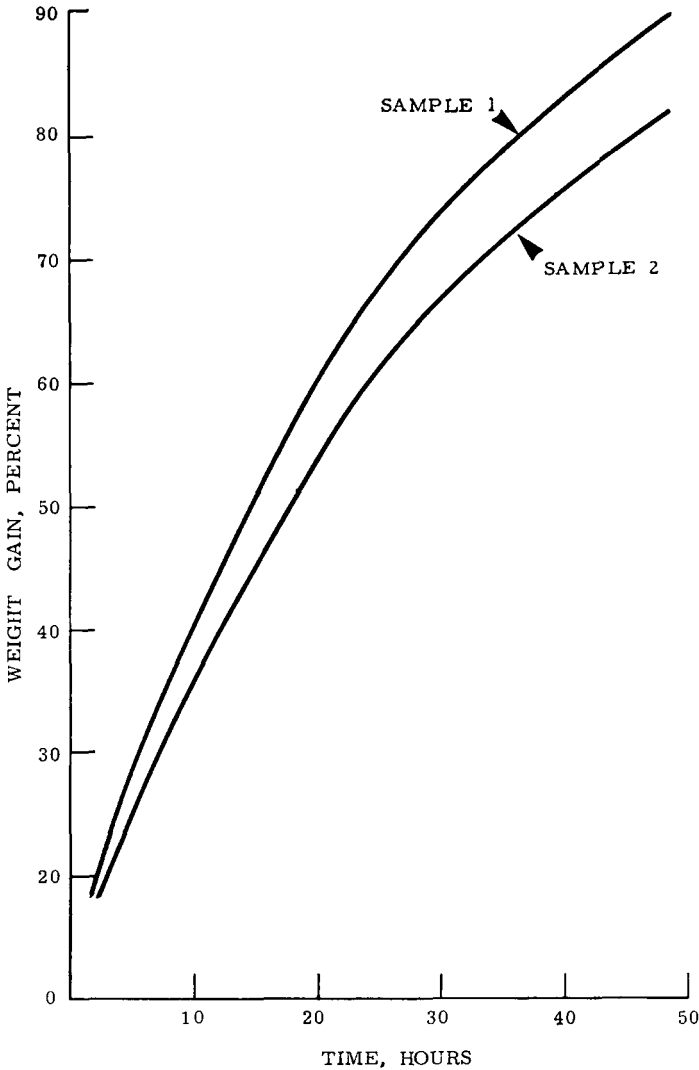


Fig. 1. Solvent absorption for flexible urethane foams: (1) formulation 254-80B (unfilled); (2) formulation 254-80B (carbon black-filled).

Figure 1 more clearly shows the difference between the solvent swelling of the filled (carbon black) and unfilled foam samples. The lower solvent absorption of the carbon black-filled sample could not be attributed to a greater chemical crosslink density, since the free isocyanate contents of the two samples were, for all practical purposes, identical. This difference was presumably caused by secondary bonding forces between the polymer and the carbon black. Since the different diisocyanates used in the foam formulations seem to give rise to different degrees of crosslinking (as evidenced from solution times in pyridine) the combination of isocyanate

and carbon black would give rise to what might be termed effective cross linking.

To further evaluate the role of each component in the diol-extended flexible urethane foam formulation, Table V lists the components for each formulation on a per cent by weight basis. All components are of the same approximate concentration except for the MDI. The actual per cent of MDI is much higher than for any other of the diisocyanates used.

TABLE V
Formulations for Diol-Extended Flexible Urethane Foams

| Material | Vendor | Composition, wt.-% | | | |
|------------------|---------------|--------------------|---------|---------|----------|
| | | 254-69B | 254-80B | 254-91B | 254-101B |
| LHT-67 | Union Carbide | 40.47 | 35.77 | 36.59 | 37.38 |
| L-61 | Wyandotte | 42.88 | 41.36 | 45.31 | 43.81 |
| TDI | Mobay | 15.19 | | 10.42 | 10.64 |
| MDI | Mobay | | 21.63 | | |
| MMDI | Carwin | | | | 6.71 |
| TODI | Carwin | | | 6.26 | |
| H ₂ O | — | 0.76 | 0.78 | 0.73 | 0.75 |
| TMBD | Union Carbide | 0.11 | 0.14 | 0.13 | 0.13 |
| DC-199 | Dow Corning | 0.56 | 0.29 | 0.53 | 0.55 |
| Benzoyl chloride | Fisher | 0.03 | 0.03 | 0.03 | 0.03 |
| Carbon black | Vanderbilt | 9.89 | 9.89 | 9.85 | 9.87 |

CONCLUSIONS

Even though detailed information regarding the chemical structure of flexible urethane foams has not been obtained from this work, several general conclusions can be made.

(1) A diol extender appears to produce a more thermally stable flexible urethane foam than does an ethylenediamine tetrafunctional polyol extender.

(2) The diisocyanate used in the chain extension reaction for the prepolymer does not affect the molecular structure nearly as much as the "capping-off" diisocyanate used in the blowing and crosslinking reactions.

(3) The total amount of diisocyanate, rather than the type or reactivity of the diisocyanate, appears to govern the amount of crosslinking in the polymer.

(4) Flexible urethane foams seem to have only a few crosslinking sites, which can be attacked by a strong nucleophilic reagent such as pyridine.

(5) Flexible urethane foams will dissolve in pyridine, and the rate of dissolution is apparently related to the degree of crosslinking.

(6) The presence of carbon black filler definitely increases the effective crosslinking of the polymers through secondary bonding forces at the carbon black surface.

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Résumé

Une série de mousse d'uréthane flexibles a été formulée au départ de prépolymères polyéther, terminés avec du diisocyanate, utilisant un diol-polyéther et une éthylène-diamine-tétraglycol comme réactifs d'allongement de chaînes. On a étudié les caractéristiques de compression à terme long et les propriétés de déflexion à la compression de ces mousses. L'effet de gonflement dans le solvant, la teneur en isocyanate libre et le rôle de la charge de noir de carbone sur la flexibilité de la mousse d'uréthane ont également été évalués. On en a conclu que la quantité totale du diisocyanate utilisée dans la formulation, plutôt que la variation du type d'isocyanate, exerce l'influence la plus considérable sur la structure moléculaire.

Zusammenfassung

Eine Reihe flexibler Urethanschaumstoffe wurde aus Polyätherpräpolymeren mit Diisocyanatendgruppen mit einem Polyätherdiol und einem Äthylendiamintetraglycol als Reaktionspartner hergestellt. Das Verhalten bei Langzeitkompression und die Verformungseigenschaften dieser Schaumstoffe wurden untersucht. Weiters wurde der Quellungseffekt in einem Lösungsmittel, der Gehalt an freiem Isocyanat und die Rolle eines Rußfüllstoffes bei der Herstellung eines flexiblen Urethanschaumstoffes ermittelt. Man kommt zu dem Schluss, dass die Gesamtmenge des bei der Herstellung verwendeten Diisocyanates und nicht eine Variierung des Isocyanattyps den grössten Einfluss auf die Molekülstruktur besitzt.

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