

Dependence of Physical Properties on Composition in a Series of High Load-Bearing Polyurethane Foams. Part II. Effects of Variations in Reactant Ratios

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Synopsis

Data and interpretations are presented on the effects of chemical variations on the physical properties, and in particular, the compression-deflection characteristics of a series of high load-bearing, open-celled, shock-mitigating polyurethane foams. The load-bearing capability of the foam is considered to be a function of density and intrinsic stiffness of the polymer. Polyol components of the formulations consisted of a poly-(oxypropylene triol) of approximately 4000 molecular weight and ethylene glycol. The blowing agents were water and trimerized linseed fatty acids. A solution of polymethylene polyphenylisocyanate and tolylene diisocyanate comprised the isocyanate mixture. Stannous octoate and *N*-ethylmorpholine were the dual catalysts. Load-bearing capability of the foam was raised by increasing the concentrations of the isocyanates, poly-(oxypropylene triol), stannous octoate, and by employing higher ratios of polymethylene polyphenylisocyanate to tolylene diisocyanate. Decrease in compressive strength resulted from increasing the quantity of blowing agents and *N*-ethylmorpholine. Increasing the quantity of ethylene glycol gave load-bearing properties which increased to a maximum and then decreased. Chemical variations are analyzed in terms of their effects on the properties of the polymeric networks. These include crosslink density, number and distribution of hydrogen bonds, chain orientation and mobility, and relative selectivity of the various reactions. Effects on the overall bulk properties of the foam are discussed in terms of the chemical composition.

INTRODUCTION

This paper is concerned with the effects of chemical variations on the physical properties, in particular, the compression-deflection characteristics of a shock-mitigating foam. The required properties of this foam and the philosophy employed in the development of the basic formulation to meet those requirements have been described in an earlier issue of this journal.¹ Variables studied here include the composition of the polyol and isocyanate streams and the quantity of water and isocyanates.

EXPERIMENTAL

Measurements of the physical properties have been described in detail.¹⁻³ In essence, the compression-deflection characteristics were meas-

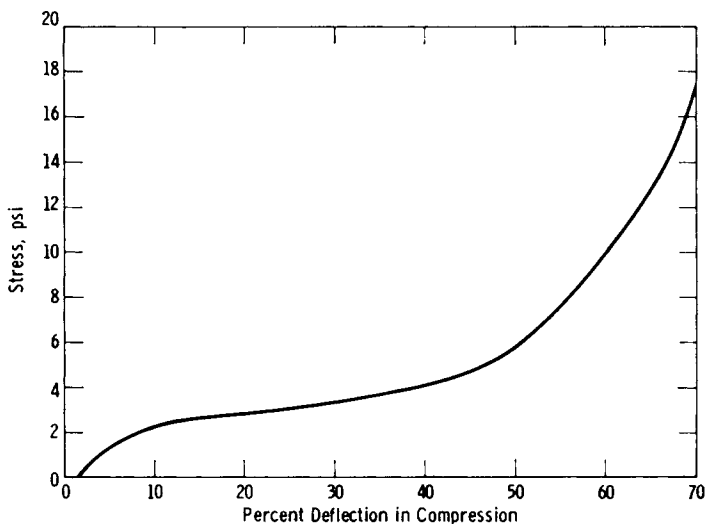


Fig. 1. Typical stress-strain data for four-cycle test, fourth cycle loading curve.

ured with a Southwark-Tate-Emery testing machine, similar to an Instron universal tester, by applying the load to the complete area of the top and bottom faces of the sample, as opposed to the more usual indentation method. The sample of foam, 6 in. \times 6 in. and 2 in. in height is compressed to 25% of its original height and then unloaded without pause. A total of four deflection cycles, applied at the rate of 2 in./min. are imposed on the sample with essentially zero time lag between cycles. Data are recorded on the fourth loading cycle. A typical fourth-cycle stress-strain curve is shown in Figure 1.

RESULTS AND DISCUSSION

Density and Intrinsic Compressive Stiffness

A polyurethane foam is a highly complex heterogeneous form of matter, therefore it is impossible to isolate completely effects of chemical variables. Studies of sensitivities of physical properties to chemical compositions, complex as they are, are much more amenable to understanding in the case of clear casting resins or varnish films. Additional physical variables which control the properties of the foam are imposed as a consequence of change of chemical composition. For example, the rheology of the system, interfacial tensions, gas solubility, rates of diffusion of the forming gas, number of nucleating centers, etc., are often altered with chemical changes in the formulation. Furthermore, chemical changes alter the kinetics and thermodynamics of all the phases of the foam formation. The above factors affect the resultant density and cell structure of the foam and thus influence many of the physical properties. Therefore, chemical structure sensitivity studies that are reported here should be considered primarily qualitative in nature.

The major portion of this study is concerned with the effect of various chemical variations on the compression-deflection or load-bearing characteristics of the foam. In this study, the load bearing is considered to be a

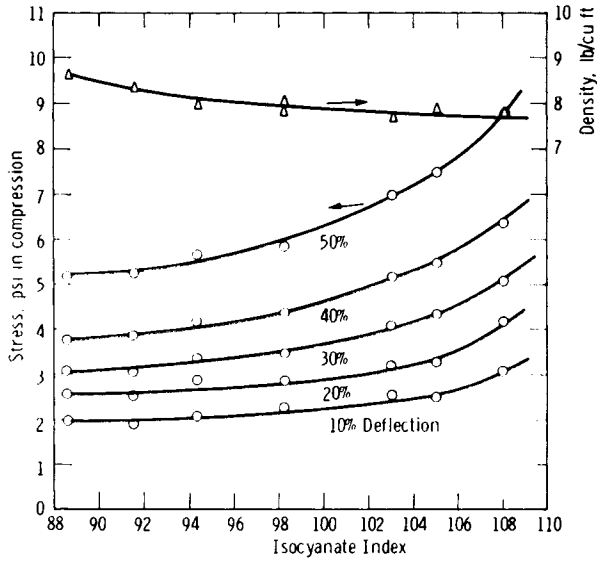


Fig. 2. Effect of isocyanate index on load-bearing capacity and density; 0.38 parts H_2O , 0.0675 parts $SnOct$.

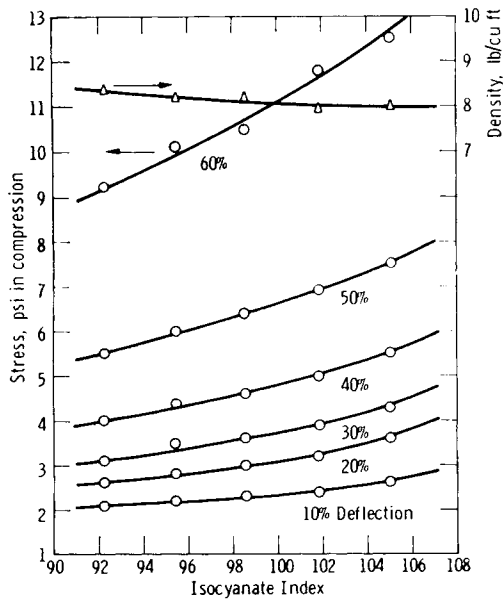


Fig. 3. Effect of isocyanate index on load-bearing capacity and density; 0.41 parts H_2O , 0.135 parts $SnOct$.

function of density and intrinsic compressive stiffness. The latter term has been created in an attempt to separate the effect of density from that of the actual stiffness of the polymeric structure, since changes of density occur with variations in chemical composition. Chemical structure of the

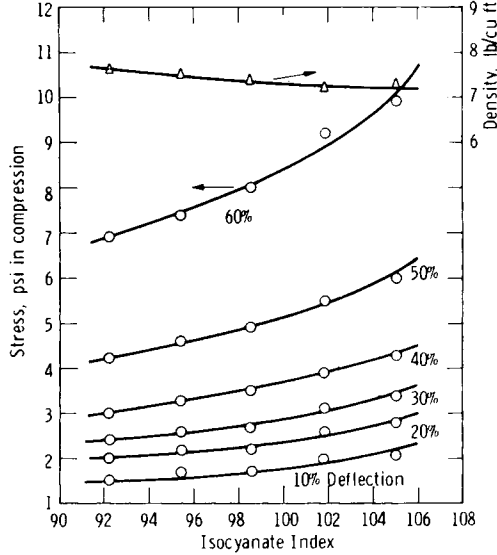


Fig. 4. Effect of isocyanate index on load-bearing capacity and density; 0.41 parts H₂O, 0.0675 parts SnOct.

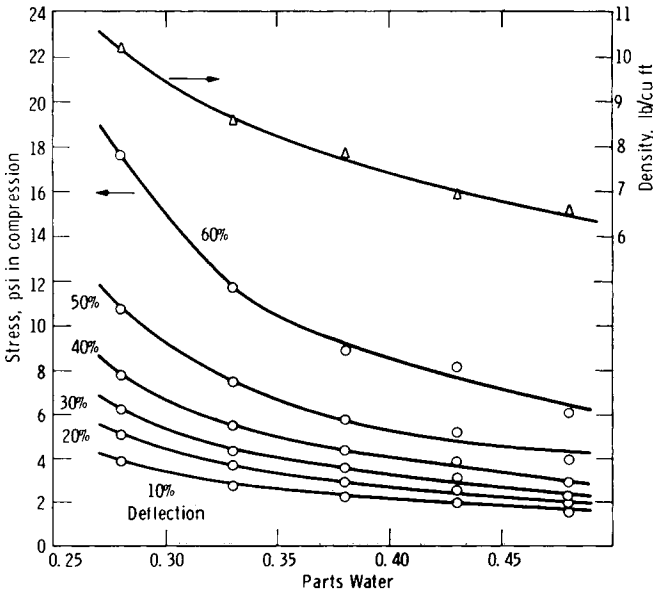


Fig. 5. Effect of water concentration at constant isocyanate index on load-bearing capacity and density.

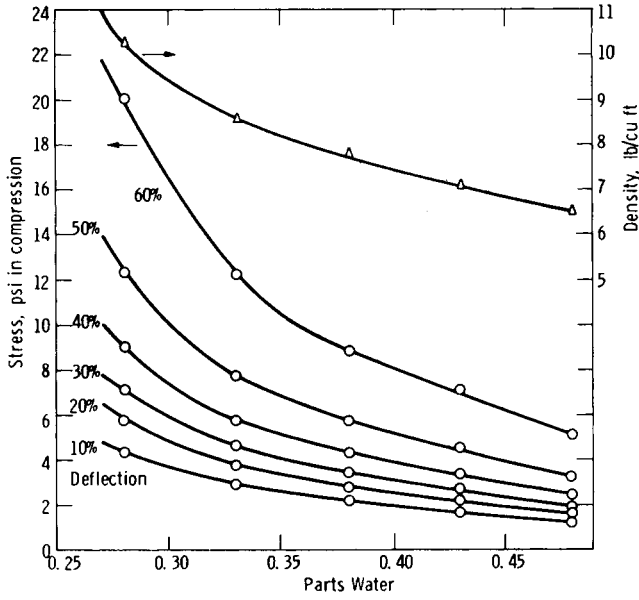


Fig. 6. Effect of water concentration at constant isocyanate level on load-bearing capacity and density.

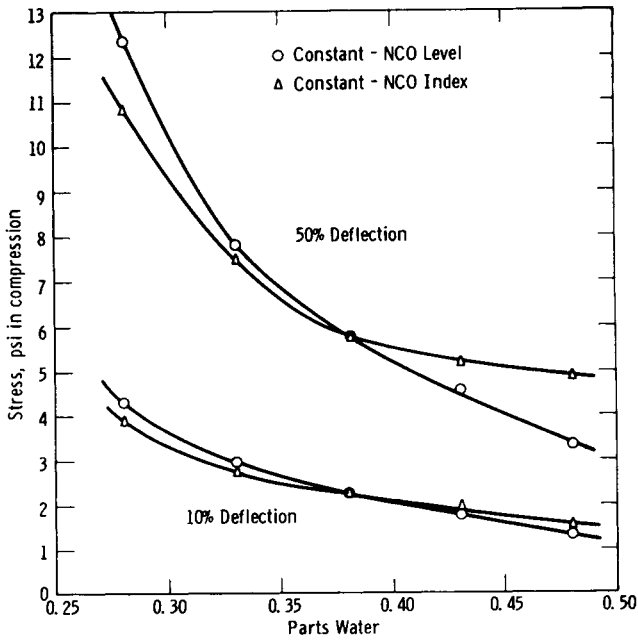


Fig. 7. Effect of water concentration at constant isocyanate level and isocyanate index on load-bearing capacity.

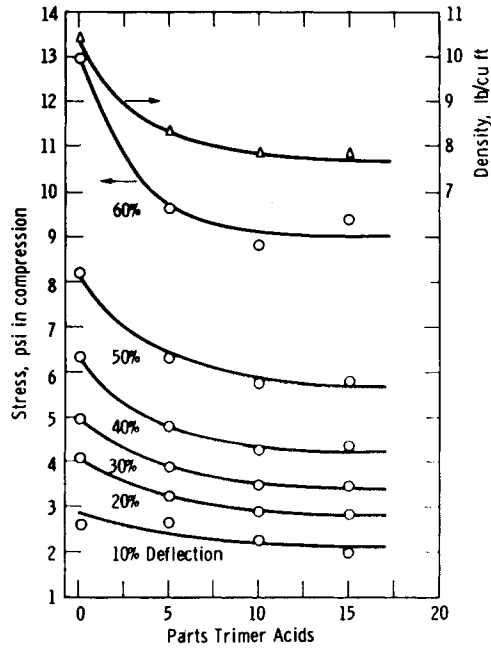


Fig. 8. Effect of trimer acids concentration on load-bearing capacity and density.

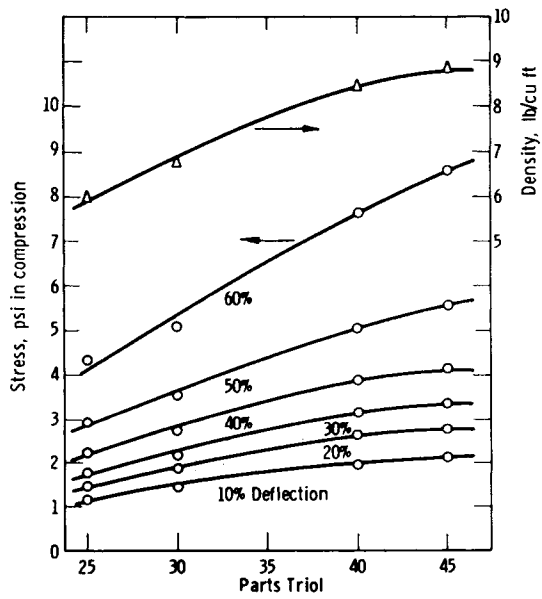


Fig. 9. Effect of poly(oxypropylene triol) concentration on load-bearing capacity and density.

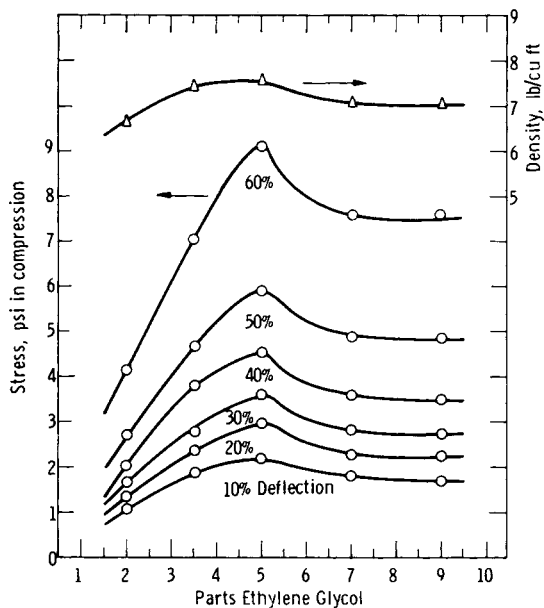


Fig. 10. Effect of ethylene glycol concentration on load-bearing capacity and density.

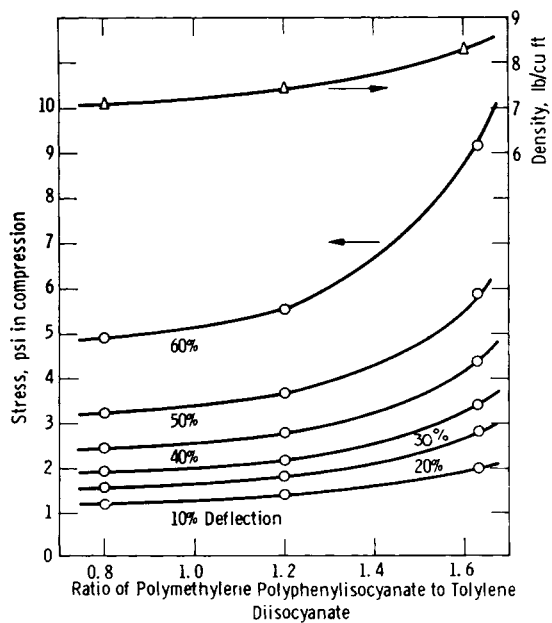


Fig. 11. Effect of isocyanate composition on load-bearing capacity and density.

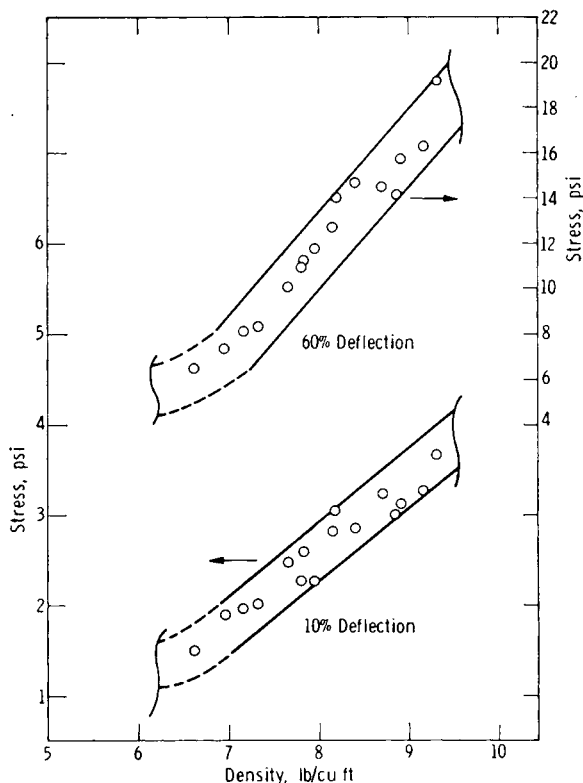


Fig. 12. Correlation between density and load-bearing capacity for foams of same formulation except for different catalyst concentrations.

polymer is thus largely reflected in the intrinsic compressive stiffness; however, this concept is nevertheless largely qualitative, since the nature of the cell structure and its effect has not been isolated. These effects are minimized, though, since all of the foams described in this study appear to have similar cell structures, except for the first one listed in Table VII.

In Figures 2-11, the gross effects of the chemical variations on the compression-deflection characteristics and density of the foam are shown. Using the basic formulation (Table I) and varying the rates of foam gelation and blowing by changing the catalyst quantities and ratios (Table II), we obtained a series of 16 foams. These foams had essentially the same chemical composition but different densities. (Some variation in composition of the polymers is expected due to the effects of catalyst concentration and composition on formation of allophanate and biuret linkages. Furthermore, the catalysts can influence the quantity and nature of the unreacted endgroups.) A plot of the density versus load-bearing capacity for the 10% and 60% deflection points is shown in Figure 12. Even though the points display too much scatter for clearly defining the nature of the density-load bearing relationship, they provide suitable envelopes for making compari-

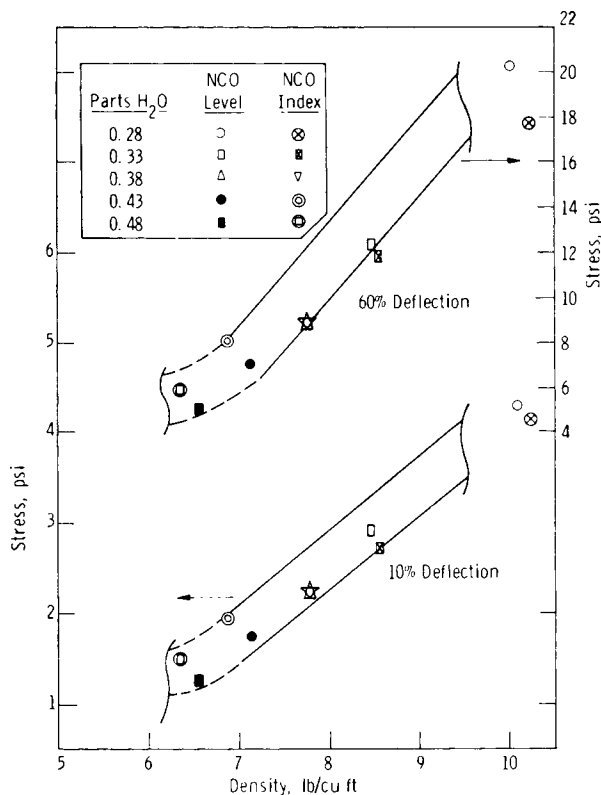


Fig. 13. Effect of quantity of water at constant isocyanate level and index on density-load bearing relationship.

sons with foam of slightly different chemical compositions. The scatter in the data is due to experimental error^{1,2} and to the effect that the differences in catalyst quantities and composition have on the various phenomena which control the nature of the cell structure. Nevertheless, catalyst variations are one of the most convenient means of isolating the effects of density while maintaining essentially the same chemical structure. In Figures 13-18, an attempt is made to compare qualitatively the relative intrinsic compressive stiffness of foams of slightly different chemical structures to the series of Figure 12 (Table II). The envelope shown in Figure 12 is reproduced in Figures 13-18. Intrinsic compressive stiffness is determined by comparing load-bearing capacity of a given foam at a certain density with the envelope at the same density.

Variations in Quantity of Isocyanate

The effect of isocyanate index, defined as 100 times the ratio of isocyanate employed to that theoretically required to react with all of the active hydrogen compounds, was studied at two different water and tin levels (Figs. 2-4, Table III). These figures show that the load-bearing capacity

TABLE I
Typical Formulation of Protective Foam

Stream		Parts of components ^a	Total parts of stream ^a
1	Polyoxypropylene triol (POPT) ^b (mol. wt. approximately 4000)	35	45.2
	Tribasic fatty acids (TA) ^c	10	
	<i>N</i> -Ethylmorpholine (NEM)	0.2	
2	Ethylene glycol (EG)	5.00	5.8 + X
	Hydroquinone	0.80	
	Water	X	
3	Tall oil fatty acids ^d	0.2025	0.27
	Stannous octoate (SnOct)	0.0675	
4	Polymethylene polyphenylisocyanate (PMPPI) ^e	18.8	30.3
	Tolylene diisocyanate (TDI) ^f	11.5	

^a X = quantity of H₂O added adjusted to give desired compression-deflection properties. Most common values are 0.38-0.41 parts water.

^b Polyoxypropylene triol, Voranol CP-4000; manufactured by Dow Chemical Company. Similar results are expected with the use of other 4000 mol. wt. poly(propylene ether triols).

^c Tribasic fatty acids: trimer acids, Empol 1040, manufactured by Emery Industries, consists of approximately 90% of C₅₄ tribasic acids and 10% of C₃₆ dibasic acids.

^d Tall oil fatty acids: Acintol FA-1, manufactured by Arizona Chemical Company. Other fatty acids can be substituted.

^e Polymethylene polyphenylisocyanate; Mondur MR, manufactured by Mobay Chemical Company. Similar results are expected from PAPI, manufactured by the Carwin Company. Materials believed to have an average functionality of about 2.75.

^f Tolyene diisocyanate consists of approximately 80% of 2,4-tolyene diisocyanate and 20% of 2,6-tolyene diisocyanate.

TABLE II
Relationship Between Density and Load-Bearing Capability of Foam^a

Catalyst composition		Stress at various deflections, psi		Density, lb./ft. ³
NEM, parts	SnOct, parts	10%	60%	
0.2	0.065	2.24	11.73	7.95
0.2	0.130	3.02	14.15	8.85
0.2	0.195	3.25	16.28	9.15
0.2	0.260	3.66	19.11	9.30
0.4	0.065	1.96	8.12	7.15
0.4	0.130	2.26	10.87	7.80
0.4	0.195	2.85	14.65	8.40
0.4	0.260	3.11	15.75	8.90
0.6	0.065	1.89	7.40	6.95
0.6	0.130	2.46	10.05	7.65
0.6	0.195	2.81	12.66	8.15
0.6	0.260	3.23	14.50	8.70
0.8	0.065	1.49	6.52	6.60
0.8	0.130	2.00	8.31	7.32
0.8	0.195	2.58	11.13	7.81
0.8	0.260	3.04	13.98	8.18

^a Basic formulation, Table I.

^b NEM = *N*-ethylmorpholine, SnOct = stannous octoate.

increases and density shows a slight decrease with increasing isocyanate (NCO) level. The density effect can be attributed to increased availability of NCO for the CO₂-generating reactions. Since the load-bearing capacity of this series of foams increases at decreasing densities, it is apparent that the increased quantities of NCO give a stiffer polymer. This effect is further illustrated in Figure 14, in which the compressive stress-density relationship is shown against the 10% and 60% deflection parameters. Foams prepared from formulations having higher NCO indices gave stress values near the top of the parameter areas, whereas the low-index foams clearly showed a reduced intrinsic compressive stiffness. At the lower NCO indices, the polymer chain length is shorter due to the deficiency of the available NCO to react with all of the hydroxyl-containing compounds. As the index increases, greater intrinsic compressive stiffness results due to increased molecular weight, formation of additional crosslinks due to allophanate and biuret linkages, crosslinks resulting from the increased quantity of the polyfunctional polymethylene polyphenylisocyanate, and a higher concentration of aromatic groups in the polymer chains.

TABLE III
Effect of Isocyanate Index on Load-Bearing Capability and Density

Run ^a	NCO blend, parts	NCO index	Stress at various deflections, psi						Density, lb./ft.
			10%	20%	30%	40%	50%	60%	
1	27.3	88.5	2.0	2.6	3.1	3.9	5.2	—	8.6
2	28.2	91.5	1.9	2.5	3.0	3.9	5.2	—	8.35
3	29.1	94.3	2.1	2.8	3.3	4.2	5.6	—	8.0
4	31.8	103.0	2.5	3.4	4.1	5.2	7.0	—	7.7
5	32.4	105.0	2.5	3.5	4.3	5.5	7.5	—	7.85
6	33.3	108.0	3.0	4.2	5.0	6.4	8.8	—	7.8
7	30.3	98.2	2.2	2.9	3.5	4.4	5.8	—	8.05
8	30.3	98.2	2.2	2.9	3.5	4.3	5.8	—	7.8
9	30.6	98.2	2.3	3.0	3.6	4.6	6.4	10.5	8.2
10	31.6	101.3	2.4	3.2	3.9	5.0	6.9	11.8	7.9
11	32.6	104.5	2.6	3.6	4.3	5.5	7.5	12.5	8.0
12	29.6	94.8	2.2	2.8	3.5	4.4	6.0	10.2	8.2
13	28.6	91.6	2.1	2.6	3.1	4.0	5.5	9.2	8.4
14	30.6	98.2	1.7	2.2	2.7	3.5	4.9	8.0	7.4
15	31.6	101.3	2.0	2.6	3.1	3.9	5.5	9.2	7.2
16	32.6	104.5	2.1	2.8	3.4	4.3	6.0	9.9	7.3
17	29.6	94.8	1.7	2.2	2.6	3.3	4.6	7.4	7.5
18	28.6	91.6	1.5	2.0	2.4	3.0	4.2	6.9	7.6

^a Runs 1-8: 0.38 parts H₂O, 0.0675 parts SnOct; runs 9-13: 0.41 parts H₂O, 0.135 parts SnOct; runs 14-18: 0.41 parts H₂O, 0.0675 parts SnOct.

Variations in Quantity of Ethylene Glycol

In view of the above discussion, the results obtained with varying quantities of ethylene glycol (EG) are somewhat enigmatic. From Figure 10 and Table IV it can be seen that the load-bearing capacity and density increase with EG content to a peak at about 5 parts EG, then decrease with

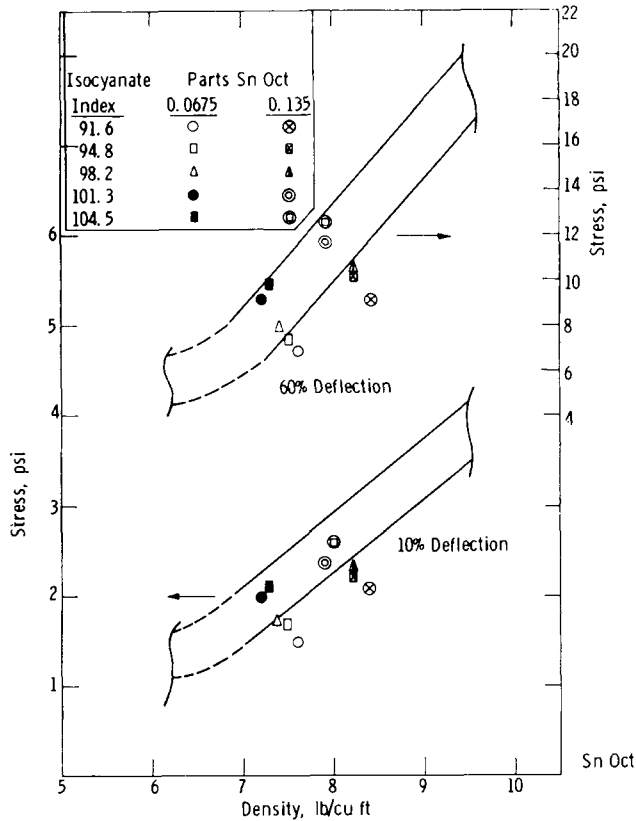


Fig. 14. Effect of isocyanate index on density-load bearing relationship.

increased glycol content. The relative intrinsic compressive stiffness of the foams containing 9, 7, and 5 parts EG are about the same and then show a decrease for 2.0 and 3.5 parts EG (Fig. 17).

As the quantity of EG is raised, the rates of foam gelation are increased due to more crosslinks and greater exotherm. These additional crosslinks can consist of allophanate and biuret linkages which result from the required increased quantity of the isocyanate stream. The polymethylene polyphenylisocyanate component provides crosslinking through urethane linkages. However, the higher exotherm and greater isocyanate concentration also favor the blowing reactions. Hence, there are two opposing trends, and over the range of concentrations studied, the overall gelation process appears to be optimized with respect to the blowing reactions when the quantity of EG is between 4 and 5 parts where the density is at a maximum.

On increasing the quantity of EG from 2 to 5 parts, the increased hydrogen bonding is largely responsible for the stiffening of the polymer chains. As the hydrogen bonding is increased further, it becomes more difficult for the polymer chains to align themselves so as to take advantage of the

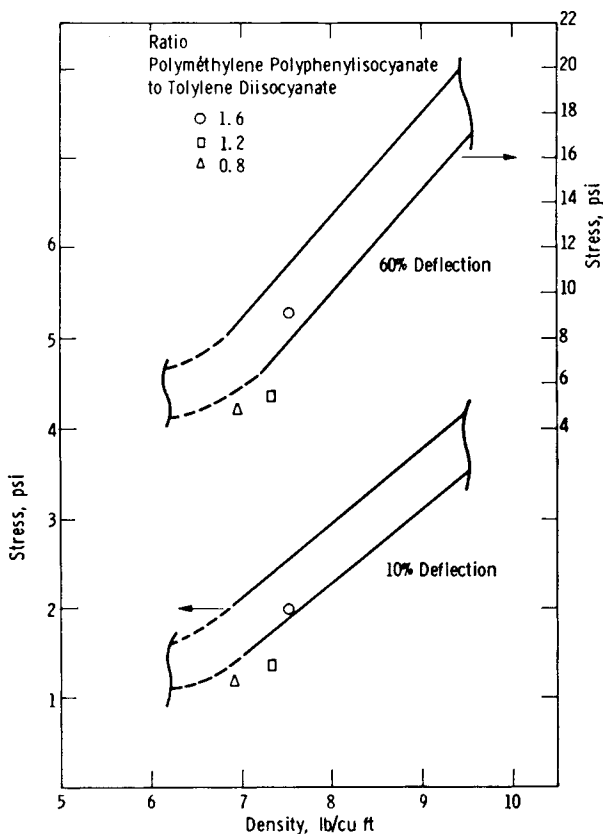


Fig. 15. Effect of isocyanate composition on density-load bearing relationship.

additional hydrogen bonding. Increased crosslinking resulting at higher EG concentrations also interferes with the ability of the chains to align.

Since the EG is more reactive and is the source of about six times the hydroxyl equivalents (based on a formulation with 5 parts EG) compared to the poly(oxypropylene triol), the product consists of a block-type polymer. Thus, long polyether chains are interspersed between multi-consecutive segments of compact and highly polar urethane-containing groups. Hence, the hydrogen bonding occurs in clusters or bunches, rather than being uniformly distributed along the polymer chains. If the number of hydrogen bonds in the bunches is increased, for example, from that corresponding to use of 5 parts EG to 9 parts EG, there might not be an appreciable difference in chain stiffening, since the clusters could have been close to their maximum rigidity at 5 parts EG. One might also consider that the polyether which comprises a large proportion of the volume of the polymer is relatively unaffected and behaves in a manner analogous to a buffer.

Another possible contribution to the lack of stiffening of the polymer chains at the upper range of the EG concentration studied is that there

may be more unreacted groups since the quantity of material of low equivalent weight is increased. This is a familiar occurrence in many types of polymeric systems where the ends of the many but relatively low molecular weight, entangled polymer chains are somewhat restricted in their motions due to the required coordination with other segments of the network. In addition, the greater exotherm resulting when more EG is used may contribute to the dissociation of some of the already reacted secondary hydroxyl groups from the polyether.

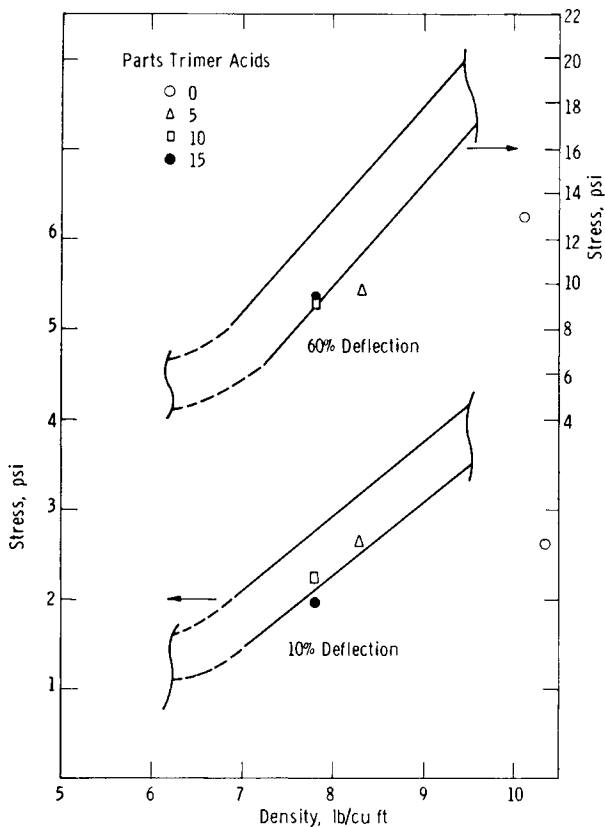


Fig. 16. Effect of trimer acids on density-load bearing relationship.

That the load-bearing capacity of this series of foams increased with EG content from 2 to 5 parts is attributed to both the increase in bulk density of the foam and stiffness of the polymer chains. The subsequent decrease in load-bearing capacity with increasing the EG from 5 to 9 parts resulted from the decrease of density. The tensile strength (Table IV) also peaks at about 5 parts EG, reflecting primarily the increased density. Elongation was essentially the same for 9 to 5 parts EG and then rose rapidly with decreasing EG concentration due to the fewer crosslinks.

TABLE IV
Effect of Ethylene Glycol Content on Physical Properties^a

Ethylene glycol, parts	NCO blend, parts	Stress at various deflections, psi				Density, lb./ft. ³	Tensile strength, psi	Elongation, %		
		10%	20%	30%	40%				50%	60%
9	44.2	1.7	2.2	2.7	3.5	4.9	7.6	7.0	27	70
7	37.4	1.8	2.3	2.8	3.6	4.9	7.6	7.0	32	80
5	30.3	2.2	2.9	3.6	4.5	6.1	9.4	7.5	41	77
3.5	25.2	1.7	2.3	2.8	3.8	4.7	7.0	7.7	31	97
2.0	19.9	1.1	1.4	1.6	2.0	2.7	4.1	6.7	23	110

^a 0.41 parts H₂O, 0.0675 parts SnOct.

TABLE V
Effect of Poly(oxypropylene Triol) Content on Physical Properties^a

Triol, parts	NCO, parts	Stress at various deflections, psi				Density, lb./ft. ³	Tensile strength, psi	Elongation, %		
		10%	20%	30%	40%				50%	60%
45	31.1	2.1	2.8	3.3	4.2	5.5	8.6	8.8	34	85
40	30.7	1.9	2.6	3.1	3.9	5.1	7.6	8.4	36	90
30	29.9	1.5	1.9	2.2	2.7	3.5	5.1	6.8	31	80
25	29.5	1.2	1.5	1.8	2.2	2.9	4.3	6.0	27	77

^a 0.38 parts H₂O, 0.0675 parts SnOct.

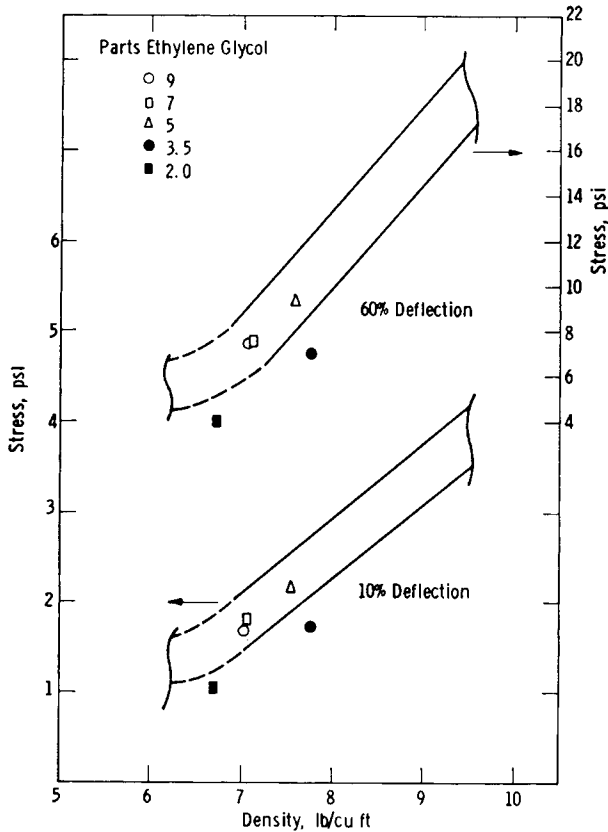


Fig. 17. Effect of ethylene glycol on density-load bearing relationship.

Variations in Quantity of Poly(oxypropylene Triol)

Load-bearing capacity and density increased with increasing poly-(oxypropylene triol) (POPT) content (Fig. 9 and Table V). This can be attributed to a bulk or dilution effect, since the ratio of the quantity of gas evolved to the total mass of the foam decreased with increasing POPT concentration. Since the POPT is primarily responsible for the flexibility of the polymer chains, it can be seen that the intrinsic compressive stiffness decreases with increasing POPT content (Fig. 18). Of the two above opposing trends, dilution and softness, that of dilution appears to predominate with respect to overall load-bearing capability. Within experimental error, the general trend for both elongation and tensile strength is to increase with the POPT. Even though the calculated crosslink density increases slightly with the POPT (\bar{M}_c 1450, 1400, 1300, and 1250 for 45, 40, 30, and 25 parts POPT, respectively), this apparently is overshadowed by the decrease in hydrogen-bond concentration, as indicated by the generally reduced intrinsic compressive stiffness (Fig. 18). Higher elongation values at greater POPT concentrations are also consistent with

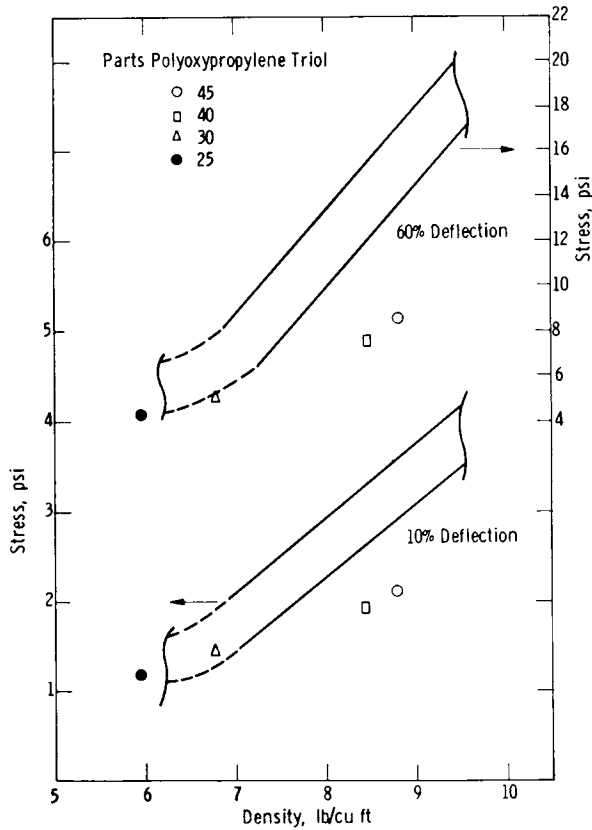


Fig. 18. Effect of poly(oxypropylene triol) on density-load bearing relationship.

this view. The tensile effect can be largely attributed to the density variation.

Variations in Quantity of Water

The effect of water concentration on load-bearing capacity and density was studied (Table VI), both at a constant NCO index (Fig. 5) in which the NCO content was adjusted according to the quantity of water and at a constant NCO level (Fig. 6) which gives a varying NCO equivalence. In both cases, the density and load-bearing capacity decrease with increasing water; however, the changes in load-bearing capability are more sensitive to water concentration when the NCO level is maintained constant (Fig. 7). At high water content, the load-bearing capacity is relatively lower at the constant NCO level, whereas for low water concentration the reverse occurs (Figs. 7, 13). This can be attributed to the greater NCO concentrations that occur for both the low water concentration at constant NCO level and the higher water content at the constant NCO index for the previously discussed reasons. The greater sensitivity of the

constant NCO level series to the effect of water concentration (Fig. 7) occurs because at the low water content the actual NCO index is higher, thus giving an increased intrinsic compressive stiffness, whereas at higher water concentrations the resultant lower NCO index gives a softer foam.

TABLE VI
Effect of Water Content on Load-Bearing Capability and Density^a

Run	Water, parts	NCO blend, parts ^b	Stress at various deflections, psi						Density, lb./ft. ³
			10%	20%	30%	40%	50%	60%	
1	0.28	30.3	4.3	5.8	7.1	9.0	12.3	20.2	10.1
2	0.33	30.3	2.9	3.8	4.6	5.8	7.8	12.2	8.5
3	0.38	30.3	2.2	2.9	3.5	4.3	5.8	8.8	7.8
4	0.43	30.3	1.7	2.2	2.7	3.4	4.6	7.1	7.05
5	0.48	30.3	1.3	1.6	2.0	2.5	3.3	5.2	6.6
6	0.28	29.1	3.9	5.1	6.2	7.9	10.8	17.6	10.25
7	0.33	29.7	2.7	3.6	4.4	5.5	7.4	11.7	8.55
8	0.38	30.3	2.2	2.9	3.5	4.3	5.8	8.8	7.8
9	0.43	30.9	2.0	2.5	3.0	3.8	5.1	8.1	6.9
10	0.48	31.5	1.5	1.9	2.3	2.9	3.9	6.1	6.4

^a 0.0675 parts SnOct.

^b Runs 1-5 constant NCO level; runs 6-10 constant NCO index of 98.2.

Variations in Quantity of Trimer Acids

Load-bearing capacity and density decrease with increasing trimer acids (TA) concentration (Fig. 8 and Table VII). Since the reaction product of an organic acid with NCO groups generates CO₂, an increase in the TA content gives more blowing and hence lower density foams. Increased TA gives a more open-celled foam, as evidenced by the increase of breathability¹ with the TA concentration (Fig. 19 and Table VII). This phenomenon is attributed to the previously described kinetic effect.¹⁻³ It appears that the intrinsic compressive stiffness of the foam is almost independent of the TA concentration over the range of 5-15 parts. Omission of TA causes a major change in the rheological characteristics and cell

TABLE VII
Effect of Trimer Acids Content on Load-Bearing Capability, Breathability, and Density

Trimer acids, parts ^a	Stress at various deflections, psi						Density, lb./ft. ³	Breathability, psi ^b
	10%	20%	30%	40%	50%	60%		
0	2.6	4.1	5.0	6.4	8.2	12.9	10.4	5.0
5	2.6	3.2	3.9	4.8	6.3	9.6	8.3	2.8
10	2.2	2.9	3.5	4.3	5.8	8.8	7.8	1.1
15	2.0	2.8	3.5	4.4	6.0	9.4	7.8	1.2

^a 0.38 parts H₂O, 0.065 parts SnOct.

^b Breathability defined in Part I.¹

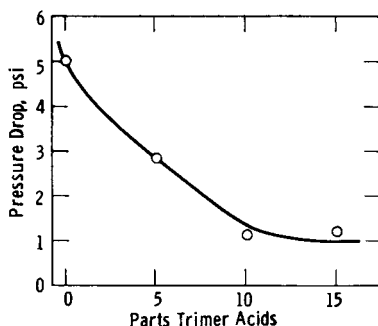


Fig. 19. Effect of trimer acids concentration on breathability.

structure of the foam. The fundamental difference in structure was apparent, since normal linear shrinkage for most of the foams discussed in this paper was about 1.5%, whereas about 5% shrinkage occurred when TA was omitted. As a result, the apparent decrease of intrinsic compressive stiffness of the zero TA foam is not amenable to an explanation based solely on chemical structure sensitivity concepts.

Variations in Isocyanate Composition

The effect of the composition of the isocyanate stream was studied by varying the ratios of the tolylene diisocyanate (TDI) and the polymethylene polyphenylisocyanate (PMPPI) components. Over the range studied, the increased crosslink density, obtained by a higher ratio of PMPPI to TDI, resulted in increased load-bearing properties (Fig. 11 and Table VIII). The intrinsic compressive stiffness of the foam was about the same,

TABLE VIII
Effect of Variations of Isocyanate Composition on Physical Properties

Ratio PMPPI/TDI ^a	Stress at various deflections, psi						Density, lb./ft. ³	Tensile strength, psi	Elonga- tion, %
	10%	20%	30%	40%	50%	60%			
1.6	2.0	2.8	3.4	4.3	5.9	9.2	7.6	39	80
1.2	1.4	1.8	2.1	2.8	3.6	5.5	7.4	32	87
0.8	1.2	1.5	1.9	2.4	3.2	4.9	7.0	34	100

^a Refer to Table I for description of isocyanates.

within experimental error, for the two lower PMPPI ratios and showed the expected increase for weight ratio of 1.63 parts PMPPI per part TDI. Elongation increased, as expected, with a decrease in crosslink density. As the PMPPI ratio is increased further, beyond about 2.5, the foams tend to become friable and begin losing load-bearing capability, as measured on the fourth loading cycle, due to rupture of cell ligaments.⁴

SUMMARY AND CONCLUSIONS

A study of the sensitivity of physical properties and especially load-bearing capability to chemical structure has been made on a series of polyurethane foams. Since the foams represent heterogeneous nonideal systems, the interpretations were qualitative, and some were speculative in nature. A more fundamental study would involve ideal systems employing thin films of polymeric materials. However, since the physics and chemistry of foam formation and structure cannot be divorced, it was considered that the results of a structure-sensitivity study of actual foams would be a useful contribution to the field of applied foam technology. A further extension of this work that would help elucidate many of the discussed phenomena is a detailed study of the polymeric structure and end-group analyses of the material of actual foams.

Since density is of major importance in controlling load-bearing capacity an attempt has been made to determine qualitatively the contributions of the stiffness of the polymeric structure independent of the bulk density of the foam. This led to the development of the concept of intrinsic compressive stiffness accompanied with discussions of the effects of chemical structure on it.

This study involved variations in the chemical structure of a high load-bearing, shock-mitigating polyurethane foam. The basic formulation in weight per cent around which the variations were made is approximately that of 42.7% poly(oxypropylene triol) (M.W. \sim 4000), 12.2% trimerized fatty acids, 0.2% tall oil fatty acids, 6.1% ethylene glycol, 1.0% hydroquinone, 23.0% polymethylene polyphenylisocyanate, 14.1% tolylene diisocyanate (80% 2,4-tolyene diisocyanate-20% 2,6-tolyene diisocyanate), 0.2% *N*-ethylmorpholine, and 0.1% stannous octoate. Results indicate that within the concentration limits studied increased isocyanate content, higher functionality of the isocyanate mixture, and greater poly(oxypropylene triol) concentration give increased load-bearing capability to the foam. The latter two cause an increase in the bulk density of the foam, whereas the density decreases slightly with increasing isocyanate index. Increased quantity of trimerized fatty acids gives a reduction in compressive stress and density and higher breathability. The density and load-bearing capacity decrease with increasing water content and appear to reach a peak midway in the studied concentration range of the ethylene glycol.

References

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Résumé

On présente des résultats d'expériences et leur interprétation à propos de l'étude de l'effet de la variation de la composition chimique sur les propriétés physiques. En particulier, on s'est intéressé aux caractéristiques de la déflexion en compression d'une série de mousses de polyuréthane, à haute capacité de charge, à cellule ouverte, prévue pour absorber des chocs. La résistance à la charge d'une mousse semble être une fonction de la densité et de la rigidité intrinsèque du polymère. Les composants polyol consistaient en un triol de polyoxypropylène d'un poids moléculaire de 4000 environ et d'éthylène-glycol comme agents de gonflement, on a utilisé l'eau et des acides gras d'huile de lin trimérisée. Le mélange d'isocyanate était composé d'une solution de polyméthylène polyphénylisocyanate et de toluène diisocyanate et les deux catalyseurs étaient respectivement l'octoate d'étain et la *N*-éthylmorpholine. La résistance à la charge de la mousse a été élevée en augmentant la concentration en isocyanates, en polyoxypropylène-triol, en octoate d'étain et en augmentant les proportions de polyméthylène polyphénylisocyanate dans la solution avec le toluène diisocyanate. On diminue la résistance à la compression en augmentant la quantité d'agents de gonflement et la *N*-éthylmorpholine. Si l'on augmente la quantité d'éthylène-glycol, la résistance à la charge augmente d'abord puis décroît. On a analysé l'effet de la variation de la composition chimique en fonction de leur influence sur les propriétés du réseau polymérique. Parmi celles-ci, on note la densité de pontage, le nombre et la distribution de liaisons d'hydrogène, l'orientation de la chaîne et sa mobilité, et la sélectivité relative des diverses réactions. On discute des propriétés globales de la mousse en fonction de sa composition chimique.

Zusammenfassung

Ergebnisse und Interpretationen für den Einfluss chemischer Änderungen auf die physikalischen Eigenschaften und im besonderen die Kompressionsdurchbiegung charakteristik einer Reihe hochbelastbarer, offenzelliger, stossdämpfender Polyurethanschaumstoffe werden vorgelegt. Die Belastungsfähigkeit des Schaumstoffs wird als Funktion der Dichte und der inneren Steifigkeit des Polymeren betrachtet. Die Polyolkomponente des Systems bestand aus Polyoxypropylentriol mit einem Molekulargewicht von etwa 4000 und Äthylenglycol. Die Treibmittel waren Wasser und trimerisierte Leinölfettsäuren. Eine Lösung von Polymethylenpolyphenylisocyanat und Toluylendiisocyanat bildete die Isocyanatmischung. Zinnoctanoat und *N*-Äthylmorpholin bildeten die dualen Katalysatoren. Die Belastungsfähigkeit des Schaumstoffs wurde durch Erhöhung der Isocyanat-, Polyoxypropylentriol-, Zinn-II-octanoatkonzentration sowie durch Anwendung eines höheren Verhältnisses von Polymethylenpolyphenylisocyanat zu Toluylendiisocyanat erhöht. Durch Erhöhung der Menge des Treibmittels und des *N*-Äthylmorpholins wurde eine Abnahme der Kompressionsfestigkeit erhalten. Eine Erhöhung der Äthylenglycolmenge ergab Belastbarkeitseigenschaften, welche zu einem Maximum anstiegen und dann abnahmen. Die chemischen Veränderungen werden in bezug auf ihren Einfluss auf die Eigenschaften des Polymernetzwerks analysiert. Dazu gehören die Vernetzungsdichte, Anzahl und Verteilung der Wasserstoffbindungen, Kettenorientierung und -beweglichkeit sowie die relative Selektivität der verschiedenen Reaktionen. Der Einfluss der Bruttoeigenschaften der Schaums substanz wird in Beziehung zur chemischen Zusammensetzung diskutiert.

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