A Statistical Study of the Effect of Formulation Variables on the Properties of Sorbitol Polyether-Based Rigid Urethane Foam

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INTRODUCTION

Their unique combination of properties makes rigid polyurethane foams useful in a variety of applications. These foams have a rare combination of high strength, good thermal stability, excellent electrical properties, and excellent thermal and acoustical insulation properties. One of their principal uses to date has been for structural applications in aircraft. Combination metal/foam structures in aircraft have shown excellent vibration and shock resistance for both the foam and the bond between foam and metal. Rigid polyurethane foam is rapidly growing in importance as an insulating material for home refrigerators and freezers. Its usage as a core material for sandwich structures in building and construction is on the increase. For each end application, a specific set of foam properties is required or desired. It was the objective of the present investigation to obtain reliable information concerning the effect of formulation factors on measured foam properties, subject to the limitations on foam ingredients and foam preparation techniques discussed below.

The chemical reactions involved in the production of urethane foams have been discussed elsewhere[1-3] and will not be reviewed here. The fundamental polymer chain-forming reaction is the addition of an isocyanate group to a hydroxyl group to form a urethane linkage. Toluene diisocyanate is usually employed as the ingredient which supplies the isocyanate groups The other major component of rigid foams is a highly branched polyhydroxy compound (polyol), which reacts with the diisocyanate to form a highly crosslinked, rigid, three-dimensional space network. The other necessary ingredients in a typical foam formula are the blowing agent, the catalyst, and the dispersing agent (surfactant).

Foam properties are affected strongly by the choice of the polyol component, which may be a polyester or a polyether. In the German pioneering work[4] on rigid foams, branched polyesters prepared from adipic acid, phthalic anhydride, and trimethylol propane were used. Polyesters were also used in the early work on rigids done in this country by Lockheed Aircraft[5] and Pittsburgh Plate Glass.[6]

More recently there has been a trend toward the use of polyethers in the production of rigid urethane foam.[7] One class of polyethers used for this purpose is prepared by adding propylene oxide to sorbitol.[7,8] As successive molecules of propylene oxide are added to sorbitol, the molecular weight of the product increases, and the hydroxyl number decreases. The hydroxyl number is defined as the milligrams of potassium hydroxide equivalent to the hydroxyl groups present in one gram of the compound being analyzed. Table I presents the properties of typical propylene oxide/sorbitol adducts used in the preparation of rigid urethane foams. As the hydroxyl number increases from 285 to 650, the degree of crosslinking and the brittleness of

TABLE I
General Properties of Sorbitol Polyethers

Properties	G-2406	G-2408	G-2410	G-2414	G-2421
Hydroxyl Number	650	549	490	375	285
Viscosity at 25°C. (Hoeppler), centipoises	115,000	18,000	10,000	3000	1500
Molecular weight	530	650	760	965	1340
Acid number	0.30	0.30	0.30	0.30	0.30
Water (max.), %	0.10	0.10	0.10	0.10	0.10
Normal ash content (max.), %	0.0025	0.0025	0.0025	0.0025	0.0025
Color (Hess-Ives)	5	5	5	5	5

the resulting foam increases. An increased degree of crosslinking also results in better retention of compressive strength and dimensional stability during humid aging at elevated temperatures (see the comparison of G-2410 and G-2406 given below).

PREPOLYMER SYNTHESES AND PROPERTIES

The first step in the production of a foam is the preparation of the "quasi-prepolymer" or "semi-prepolymer," which may be referred to as the prepolymer for the sake of brevity. In a foam based on G-2410, for example, the prepolymer is prepared by reacting all of the toluene diisocyanate (TDI) with a portion of the G-2410. The prepolymer is then stored for periods of time ranging upward to a year or more. In order to make the foam, the prepolymer is mixed thoroughly with the remainder of the G-2410 required, plus blowing agent, catalyst, and dispersing agent.

The technique of preparing the prepolymer is of importance, because it has a considerable influence on the physical and chemical properties of the final foam. Hence a preliminary study was made of prepolymer preparation techniques prior to carrying out the main body of the statistical investigation of formulation factors.

In all cases the prepolymer work was carried out in a closed reaction flask under an atmosphere of nitrogen. The reaction is highly exothermic, and the reaction flask was kept immersed in a bath of cooling water to provide adequate temperature control.

In order to determine the best technique, a time and temperature study was carried out on the preparation of prepolymer from G-2410, G-2408, and G-2406, with the use of NCO/OH charge ratios of 4.0 and 4.5 and reaction times of 0.5 and 1.0 hr. The results for the runs at 70°C. are presented in Table II.

It is desirable that the reaction does not proceed beyond the point where the per cent free NCO is equal to the computed per cent corresponding to complete reaction of all hydroxyl groups. Excess cooking results in dimerization and trimerization of the TDI, formation of allophanate groups, and other generally undesirable side reactions. All of these secondary reactions reduce the percentage of free NCO in the final prepolymer.

It is also necessary that the viscosity of the prepolymer product remain fairly constant, so that the prepolymer can be stored for several months or a year at room temperature without excessive thickening or gelation.

In a typical prepolymer preparation a three-liter flask was charged with TDI and G-2410 at an isocyanate/hydroxyl equivalent ratio of 4.5/1.0. The following weights were used: TDI, 1957.5 g.; G-2410, 558.5 g. Toluene diisocyanate having a 2,4/2,6 isomer ratio of 79/21 and a hydrolyzable chlorine content of 0.014% was employed throughout the investigation. Both ingredients were added simultaneously with agitation under a nitrogen atmosphere. Earlier trials had shown that gradual addition of the G-2410 to the TDI offered no advantage, while the gradual addition of TDI to G-2410 produced an unwanted viscosity build-up. The temperature was allowed to rise to 70°C., due to the exothermic heat of the reaction and then

TABLE II
Properties of Quasi-Prepolymers Prepared at 70°C.

Polyether	NCO/OH ratio	Reaction time, hr.	Viscosity, 1000 centipoise		Free NCO, %	
			1 Week	2 Months	Actual	Theoretical
G-2410	4.0	0.5	13.1	25.1	27.1	27.3
		1.0	12.8	21.1	26.8	27.3
	4.5	0.5	4.3	6.0	28.7	29.1
		1.0	4.6	5.7	28.6	29.1
G-2408	4.0	0.5	21.8	23.0	28.4	27.9
		1.0	22.9	24.9	27.6	27.9
	4.5	0.5	5.1	6.0	28.8	29.5
		1.0	5.1	7.4	29.2	29.5
G-2406	4.0	0.5	20.4	35.4	28.2	29.1
		1.0	18.3	37.3	28.2	29.1
	4.5	0.5	3.4	6.4	30.0	30.7
		1.0	3.7	4.3	30.2	30.7

maintained at 70°C. for 1 hr. Samples were withdrawn after 0.5 and 1.0 hr. and cooled immediately. The analysis of each sample for per cent free NCO was run immediately after cooling. Viscosity readings were made with a Brookfield viscometer after aging periods of one week and two months.

Runs were made at 10-degree intervals over the temperature range 60–110°C. It was noted that, in general, higher reaction temperatures led to higher product viscosity and a more rapid rate of viscosity increase during prepolymer storage at room temperature. Reaction temperature above 90°C. gave free NCO contents below the theoretical and excessively high viscosity. Both effects probably resulted from undesirable side reactions. An examination of Table II shows the following.

(1) Complete reaction of isocyanate and hydroxyl groups occurred after 0.5 hr. at 70°C. This was true for G-2410, G-2408, and G-2406 at both the 4.0 and 4.5 level of the NCO/OH ratio.

(2) When an NCO/OH ratio of 4.5 was used, the viscosity for the three polyethers remained at a very low level and increased at a very slow rate over a two-month storage period. The use of the 4.0/1.0 ratio gave viscosities which fluctuated over a wide range and did not seem to level off.

PLAN OF THE STATISTICAL INVESTIGATION

Each rigid foam formulation must be carefully designed to meet the key requirements of its specific end use. For example, refrigerator insulation is an application which requires short cure time, low and constant thermal conductivity, over 85% closed cells, low density, and excellent resistance to humid aging. Volume change is one of the critical phenomena in humid aging and must be minimized. The foam should have adequate strength and dimensional stability at low density, since low density means lower ingredient cost per unit volume of foam. The percentage of closed cells must be high, and the retention of the trichlorofluoromethane blowing agent must be excellent in order to obtain low and constant thermal conductivity (K factor) over long periods of time.

While the remarks in the preceding paragraph apply to refrigerator insulation, for an entirely different application it is quite conceivable that it might be desirable to place emphasis on maximum shear strength, or increased cure time, increased density, or some other radical change in properties. Hence what is really needed is an understanding of how each formulation variable or factor affects each foam property. The dependence of physical properties on formulation factors is extremely complicated, and it became evident that the best way to tackle the problem was by a statistical pattern of experimentation. Accordingly a plan was set up to investigate the effect of the following factors and levels:

(1) Catalyst concentration (two levels).

(2) Isocyanate/hydroxyl ratio in quasi-prepolymer (two levels).

(3) Quasi-prepolymer cook time (two levels).

(4) Dispersing agent concentration (two levels).

(5) Isocyanate/hydroxyl ratio in total foam (four levels).

This plan of investigation was designed to obtain the optimum formulation for refrigerator insulation, but the information obtained is of considerable usefulness in other formulation problems. The complete experimental pattern of factor combinations is shown in Table III. Dabco catalyst (Houdry Process) was selected for use in the whole series of experiments, and was employed at 0.4 and 0.8% concentration. Information about the effect of catalyst concentration is important in obtaining the proper balance between cure time and foam properties. Too low a catalyst concentration will give poor physical properties and produce a slow cure. Too high a catalyst concentration will promote excessive exotherm during foaming, and cause cracks and fissures in the foam.

The NCO/OH ratio was evaluated at the 4.0 and 4.5 levels. This ratio is important because of its effect on prepolymer stability, exotherm in foaming, and foam properties. As noted above in the discussion on prepolymers, the 4.5 ratio gives prepolymers having long-term viscosity stability at room temperature; on the other hand, the 4.0 ratio produces less exotherm during foam cure.

The method of prepolymer preparation has an effect on foam properties, since greater or lesser degrees of crosslinking can be introduced in the prepolymer and the effect carries over into the resulting foam. Prepolymer cooking times of 0.5 and 1.0 hr. were used in this investigation. These appeared to be the most feasible cook times, based on the prepolymer work described above.

X-520 (Union Carbide) dispersing agent was employed in the experimental pattern at 0.3 and 0.5% concentration. The dispersant concentration is important, since an adequate concentration is necessary to produce good mixing and uniform cell structure. Dispersing agent in too high a concentration will act as a diluent and decrease the strength of the foam.

TABLE III
Statistical Pattern of Foam Formulations

Foam no.	Catalyst concn., %	NCO/OH ratio (prepolymer)	Prepolymer cook time, hr.	Dispersant concn., %	NCO/OH ratio (total)
1	0.4	4.0	0.5	0.3	0.95
2	0.4	4.0	0.5	0.3	1.10
3	0.8	4.0	0.5	0.3	1.00
4	0.8	4.0	0.5	0.3	1.05
5	0.8	4.0	0.5	0.5	1.10
6	0.8	4.0	0.5	0.5	0.95
7	0.4	4.0	0.5	0.5	1.05
8	0.4	4.0	0.5	0.5	1.00
9	0.8	4.5	0.5	0.3	1.10
10	0.8	4.5	0.5	0.3	0.95
11	0.4	4.5	0.5	0.3	1.05
12	0.4	4.5	0.5	0.3	1.0
13	0.4	4.5	0.5	0.5	0.95
14	0.4	4.5	0.5	0.5	1.10
15	0.8	4.5	0.5	0.5	1.00
16	0.8	4.5	0.5	0.5	1.05
17	0.8	4.0	1.0	0.5	1.05
18	0.8	4.0	1.0	0.5	1.00
19	0.4	4.0	1.0	0.5	1.10
20	0.4	4.0	1.0	0.5	0.95
21	0.4	4.0	1.0	0.3	1.00
22	0.4	4.0	1.0	0.3	1.05
23	0.8	4.0	1.0	0.3	0.95
24	0.8	4.0	1.0	0.3	1.10
25	0.4	4.5	1.0	0.5	1.00
26	0.4	4.5	1.0	0.5	1.05
27	0.8	4.5	1.0	0.5	0.95
28	0.8	4.5	1.0	0.5	1.10
29	0.8	4.5	1.0	0.3	1.05
30	0.8	4.5	1.0	0.3	1.00
31	0.4	4.5	1.0	0.3	1.10
32	0.4	4.5	1.0	0.3	0.95

The NCO/OH ratio in the total foam is of great importance, and was evaluated at four levels: 0.95, 1.00, 1.05, and 1.10. This ratio has a marked effect on humid-aging resistance, which is a key property in refrigerator insulation. Some foam manufacturers recommend a stoichiometric ratio of 1.00, while others suggest a slight excess of isocyanate over hydroxyl. An excess of isocyanate operates to drive the reaction to completion and eliminate unreacted hydroxyl groups. Unreacted hydroxyl groups are known to make the foam hydrophilic and sensitive to humid-aging breakdown.

The method of preparing each foam can be illustrated by a consideration of Foam No. 16 in Table III. The quasi-prepolymer was first prepared by reacting 3561 g. TDI with 1039 g. G-2410 (Hydroxyl No. 491) for 1.0 hr. at 70–75°C. under nitrogen. This charge corresponds to an NCO/OH equivalent ratio of 4.5/1.0. The same lot of G-2410 was used in making all of the foams in the statistical study, since the hydroxyl number of the G-2410 varies slightly from batch to batch. The foam components, A and B, were then made up to have the composition shown in Table IV.

Component A was mixed for 1 min. with an Ohmite stirrer operated at approximately 4000 rpm. Component B was mixed in a similar fash-

TABLE IV

	Weight, g.
Component A	
Quasi-prepolymer	1212.0
X-520 (Union Carbide)	12.0
Trichlorofluoromethane	300.0
Component B	
G-2410	897.0
Dabco (Houdry Process)	19.5

ion. Components A and B were then poured together, mixed for 0.5 min. with the stirrer, and poured into a large cardboard box which served as the mold. This particular foam required 2 min. to foam to its full height. It became tack-free to the touch after 3 min. (tack-free time), and was hard to the touch 5 min. after being poured into the mold (hardness time). It was allowed to cure at room temperature for approximately one week before physical testing. All foams were aged for 67 ± 3 days at room temperature before measuring the K factor.

Certain factors were held constant for all foams involved in the statistical study. The total weight of the formulation was held constant, and 300 g. of trichlorofluoromethane was used in each formula. It is important to hold the amount of blowing agent constant, since this influences the density of the foam, which in turn strongly affects all physical properties. In each foam the catalyst and dispersant were added at the proper percentage, and the balance of the formula made up from prepolymer and G-2410 in correct amounts to give the selected NCO/OH ratio in the total foam. Because of the variation in per cent catalyst and dispersant, this method of procedure requires that the total of prepolymer and G-2410 vary by a small amount which is about $\pm 0.6\%$ on total foam weight. This small variation should have an insignificant effect on foam properties, and hence should cause no trouble in the investigation of the effect of the selected formulation factors.

The experimental design presented in Table III is a fractional factorial pattern. Factorial experiments of this type have been discussed in considerable detail by Davies.[9] The experiment is called fractional because only a fraction of the total possible number of foam samples is prepared and evaluated. An investigation of all factors in Table III in all possible combinations would require the preparation of 64 separate foams. However, by the use of statistical theory, it was found possible to reduce the total number of foams to 32 without losing any pertinent information. In other words, it is possible to investigate the main effect of the factors and their more important interrelationships in a fraction of the number of tests required for the complete factorial experiment. In carrying out such an experiment it is not sufficient to vary only one factor at a time, but all factors must be varied in such a way as to elucidate the effect of each factor and the possible ways in

TABLE V
Summary of Results: Effect of Formulation Factors on Foam Properties

	(1) NCO/OH ratio (total)	(2) Catalyst concn.	(3) NCO/OH ratio (prepolymer)	(4) Prepolymer cook time	(5) Dispersant concn.	(6) Experiment avg.	(7) Two-level effect limits	(8) 95% confidence limits for individual sample measurements
Tensile strength, psi	−5.0	−	−	−	−	63.3	±4.2	±11.9
Shear strength, psi	a,b	a	b	−	−	29.65	±1.36	±3.85
Tack-free time, min.	+	−4.70	−	−1.43	+	5.85	±0.51	±1.44
Humid-aged compressive strength, psi	+	+	−	−4.0	−	29.5	±2.2	±6.2
Humid-aged volume change, %	c	+	c	−	+	19.7	±2.6	±7.4
K factor	0	d	e	e	d	0.131	±0.004	±0.0132
Compressive strength (at 10% comp.), psi	0	4.5	−3.9	−4.7	−	53.3	±3.5	±9.9
Density, lb./ft.³	−	+0.10	−0.06	−0.08	0	2.41	±0.06	±0.17
Water absorption, %	0	−0.61	0	−0.76	0	6.85	±0.30	±0.85
Open cells, %	0	0	0	0	0	5.0	±1.6	±4.5
Moisture vapor transmission, perms/in.	0	0	0	0	0	5.82	±1.90	±5.38

[a] Plot of this effect shown in Figure 1.
[b] Plot of this effect shown in Figure 2.
[c] Plot of this effect shown in Figure 3.
[d] Plot of this effect shown in Figure 4.
[e] Plot of this effect shown in Figure 5.

which the effect of each factor may be modified by varying the other factors. In the analysis of the experimental results, the effect of each factor can be determined with four times the accuracy as if only one factor had been varied at a time. The type of design shown in Table III also enables an estimation of the experimental error for the purpose of assessing the significance of the effects, and enables the determination of confidence limits for both effects created by the variables and by the individual measurements.

Table V summarizes the results of the analysis of the data and shows the magnitude of the significant effects on each property of going from the lower to the higher level in each case for all five factors. Where effects were not statistically detectable, only the probable direction of the effects (if they exist) is indicated. A minus sign indicates that the effect (property) decreases as the level of the factor increases. A plus sign indicates an increase in effect with increasing factor level. Opposite the entry tack-free time, for example, the −4.70 entered under catalyst concentration indicates that an increase in catalyst concentration from 0.4 to 0.8% decreases the tack-free time by 4.7 min. This conclusion (or prediction) is based on results of all 32 foams evaluated, and hence is much

more reliable and precise than the result of any one measurement. Column six in the Table V presents the average of each property for all eleven properties. Column seven shows the precision of the estimated effect of each factor. For example, the effect of increased catalyst concentration on tack-free time is to reduce the time by 4.70 ± 0.51 min. Column eight shows the 95% confidence limits on the individual measurements of each foam sample. Comparison of columns seven and eight shows clearly that the estimate of the effect of each factor is much more precise than the result of each individual measurement. Another way of stating the matter is to say that the application of statistical theory enables us to make accurate estimates of the effects of each factor, regardless of the confusing effect of random sample to sample experimental variation. All of the computations were carried out by use of an I.B.M. Model 650 digital computer.

RESULTS

The following paragraphs summarize the effects of each factor on each foam property.

Tensile Strength

The only factor having a detectable effect on tensile strength was the NCO/OH ratio in the total foam. There was an estimated decrease of 5.0 psi as the ratio increased from 0.95 to 1.10. While this information may have some usefulness in other applications, tensile strength is not a property of major concern in refrigerator insulation. Reference to Table V shows that the other formulation factors had no detectable effect on tensile strength.

Shear Strength

The effects on shear strength are presented graphically in Figures 1 and 2, since several factors are interrelated. Figure 1 illustrates that the shear strength decreases as the NCO/OH ratio increases and lies generally at a higher level for 0.8% catalyst than for 0.4% catalyst. Throughout the present work an increase in catalyst concentration was found to increase physical properties generally, probably because higher catalyst concentration promotes a more complete reaction of all hydroxyl groups with all isocyanate groups and results in a more tightly crosslinked polymer structure. Figure 2 demonstrates that shear strength falls off in any case as the NCO/OH (total) ratio increases, but does so less rapidly when the NCO/OH ratio in the prepolymer has a value of 4.5. Table V indicates that shear strength is not
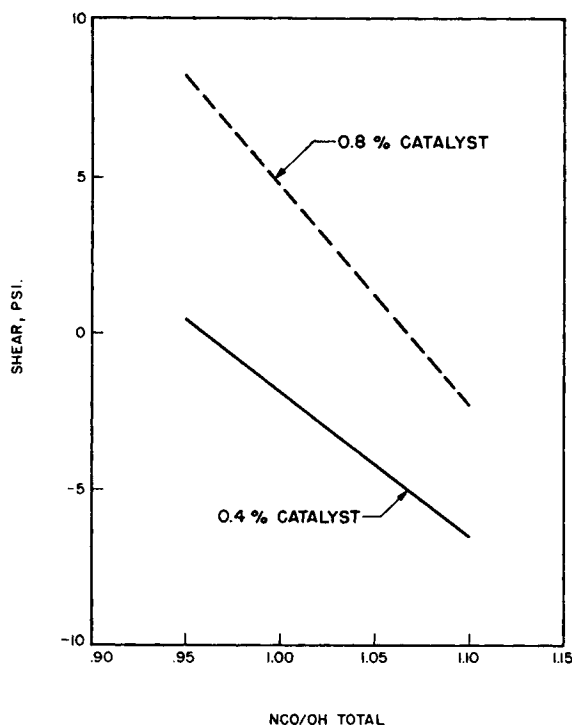

Fig. 1. Effect of NCO/OH ratio in total foam and catalyst concentration on shear strength.
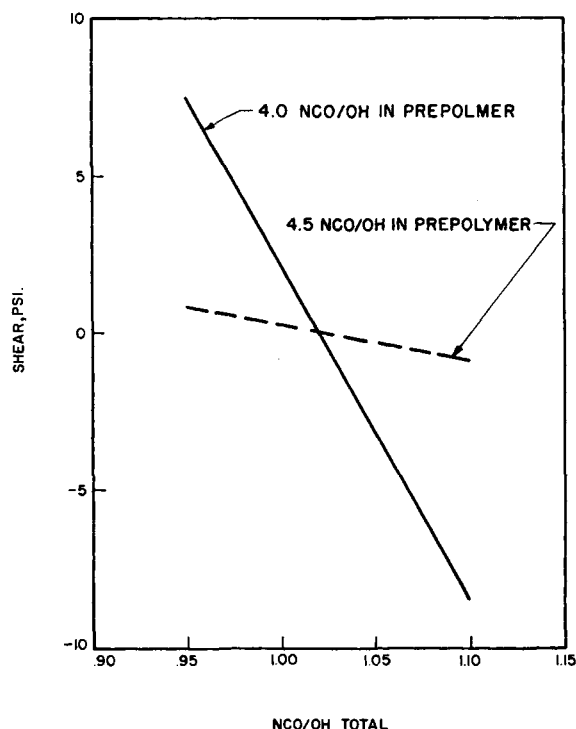
Fig. 2. Effect of NCO/OH ratio in prepolymer and in total foam on shear strength.

affected by a variation of prepolymer cook time or dispersant concentration.

Tack-Free Time

Measurement of tack-free time gives an estimate of the relative rate of cure. Table V shows that an increase in catalyst concentration reduces the tack-free time by 4.7 min., which is in line with the usual observation that increased catalyst speeds up cure. Table V also shows that an increase in prepolymer cook time from 0.5 to 1.0 hr. reduces the tack-free time by 1.4 min. This reduction in cure time apparently results from the fact that longer prepolymer cooking time gives certain crosslinking reactions a head start before the actual pouring of the foam. Table V indicates that dispersant concentration, NCO/OH (total) ratio, and NCO/OH (prepolymer) ratio have little or no effect on tack-free time.

Humid-Aged Compressive Strength

Increasing the prepolymer cook time from 0.5 to 1.0 hr. decreases the compressive strength after humid aging by 4.0 psi. This sensitivity to humid aging probably results from undesired side reactions which occur when prepolymer cooking time is prolonged. It is known that too long a cooking time

produces dimerization and trimerization of the TDI, in addition to the formation of allophanate linkages in the polymer by the reaction of isocyanate groups with urethane groups. The allophanate group is one of the least stable linkages, both hydrolytically and thermally, that can be formed by isocyanate reaction. In spite of these facts, the one hour prepolymer cook time is preferred for reasons given below in the discussion of K factor.

The compressive strength of humid-aged foam was not affected significantly by any of the other formulation factors.

Volume Change on Humid Aging

The volume change caused by humid aging is affected in a complex way by NCO/OH (total) ratio and NCO/OH (prepolymer) ratio. Reference
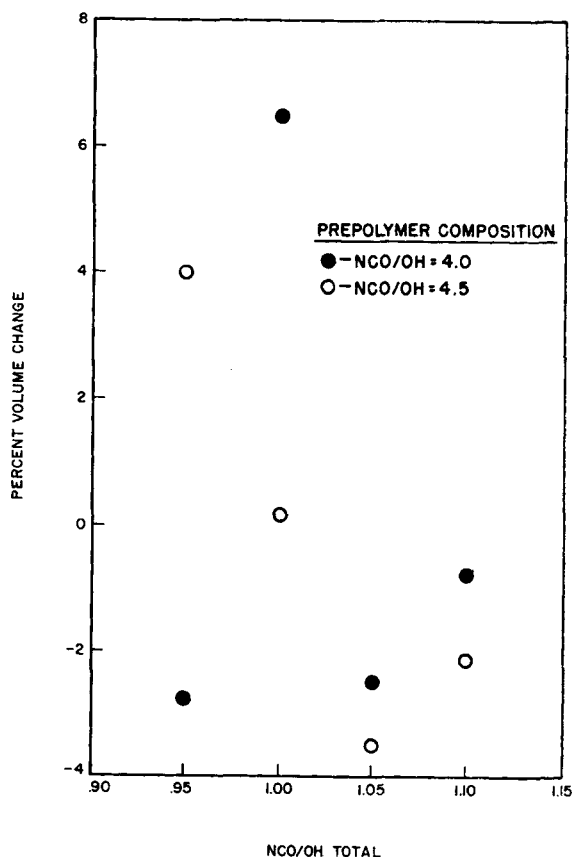

Fig. 3. Effect of NCO/OH ratio in prepolymer and in total foam on volume change during humid aging.

to Figure 3 shows that the minimum volume change occurs when the NCO/OH (total) ratio is 1.05 and the NCO/OH (prepolymer) ratio is 4.5. This result is in agreement with the theory that a slight stoichiometric excess of [NCO] over [OH] tends to

drive the reaction to completion and eliminate hydrophilic, unreacted hydroxyl groups.

Catalyst concentration, prepolymer cook time, and dispersant concentration had little or no effect on volume change.

Thermal Conductivity

There are interrelations between several factors which affect the K factor. Figure 4 demonstrates that the K factor decreases as catalyst concentration increases, and that a combination of 0.5% dispersant concentration with 0.8% catalyst gives the greatest reduction in K factor. Figure 5 indicates that a combination of an NCO/OH (prepolymer) ratio of 4.5 and a prepolymer cook time of 1 hr. produces a reduction in K factor. Since the low K factor is the most important property in refrigerator insulation, the prepolymer cook time of 1 hr. is preferred in spite of the detrimental effect of increased cook time on humid-aged compressive strength cited above.

An explanation of these effects is difficult because of the complexity of the polymer structure and chemistry. A low K factor results from a good retention of trichlorofluoromethane by the foam, which implies a negligible permeation of fluorohydrocarbon through the cell walls. The rate of
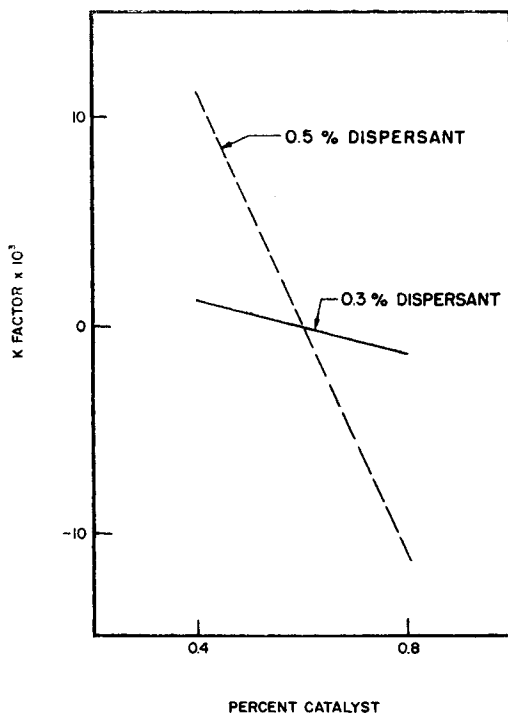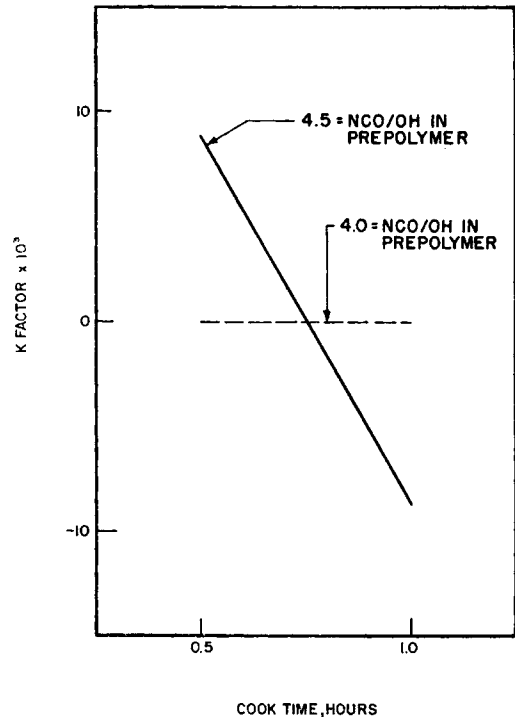

Fig. 5. Effect of prepolymer cooking time and NCO/OH ratio on K factor.

permeation of fluorohydrocarbon depends on (1) the solubility of fluorohydrocarbon in the polymer, and (2) the diffusion constant for fluorohydrocarbon in the polymer. An increased catalyst concentration would be expected to produce a more tightly crosslinked polymer structure and hence reduce the diffusion constant and possibly reduce the solubility. In the same fashion, an increased prepolymer cook time could conceivably lead to a higher degree of crosslinking and thence higher trichlorofluoromethane retention and lower K factor.

Table V shows that NCO/OH (total) ratio has no effect on K factor.

Compressive Strength

The compressive strength increases by 4.5 psi when the catalyst concentration increases from 0.4 to 0.8%. This increase is probably due to a more complete and thorough cure.

Increasing the NCO/OH (prepolymer) ratio from 4.0 to 4.5 reduces the compressive strength by 3.9 psi. However, the 4.5 ratio is preferred because it produces a prepolymer having an essentially constant viscosity at room temperature.

Increasing the prepolymer cook time to 1.0 hr. reduces the compressive strength by 4.7 psi; however, the lower K factor achieved with the longer

Fig. 4. Effect of catalyst and dispersant concentrations on K factor.

cook time outweighs this (Fig. 5) for the present application. The K factor is of primary importance in refrigerator insulation.

The NCO/OH (total) ratio and dispersant concentration have no significant effect on compressive strength.

Density

Small effects on density were associated with catalyst concentration, NCO/OH (prepolymer) ratio, and prepolymer cook time. The relative constancy of the density resulted from the fact that the concentration of trichlorofluoromethane blowing agent was held constant in all formulations.

Water Absorption

An increase in catalyst concentration or in prepolymer cook time resulted in a significant decrease in water absorption.

Per Cent Open Cells and Moisture Vapor Transmission

None of the formulation factors had a significant effect on these properties.

In summary, the statistical investigation showed that the following values of the formulation variables should be chosen to produce the optimum properties for refrigerator insulation:

(1) Catalyst concentration: 0.8%.

(2) Isocyanate/hydroxyl ratio in quasi-prepolymer: 4.5.

(3) Quasi-prepolymer cook time: 1.0 hr.

(4) Dispersing agent concentration: 0.5%

(5) Isocyanate/hydroxyl ratio in total foam: 1.05.

The higher level of catalyst concentration was chosen because it results in increased shear strength, shorter cure time, lower thermal conductivity, and higher compressive strength. A question may arise as to why a still higher catalyst concentration should not be used. The answer is that a separate series of experiments has shown that increasing the catalyst above 0.8% leads to the danger of overheating and cracking when the foam is poured. The 4.5 ratio for NCO/OH in the prepolymer was chosen because this produces a stable prepolymer in storage and results in a foam having a low K factor and the minimum volume change in humid aging. The prepolymer cook time of 1 hr. was chosen because it reduces the tack-free time by 1.4 min. and results in a decrease in K factor. The dispersing agent concentration of 0.5% is best be-

cause it results in a lower K factor. The NCO/OH (total) ratio of 1.05 was chosen because it produces a minimum volume change on humid aging, a property of critical importance in refrigerator insulation.

The ingredients and conditions to be used in producing the optimum foam are summarized in Table VI.

TABLE VI

	Weight, g.
Quasi-prepolymer (NCO/OH = 4.5)[a]	
T.D.I. (80/20)	3561.0
G-2410	1039.0
Component A	
Trichlorofluoromethane	300.0
Quasi-prepolymer	1210.0
X-520 (Union Carbide)	12.2
Component B	
G-2410	898.0
Dabco (Houdry Process)	19.5

[a] Reaction for 1.0 hr. at 70–75°C.

The "optimum foam" formulation does not happen to occur in the pattern shown in Table III. However, the properties of the optimum foam can be computed with considerable reliability from the averages and the effects shown in Table V. The predicted properties are given in Table VII.

TABLE VII
Predicted Properties of Optimum Foam Formulation

Property	
Tensile strength, psi	66.7
Water absorption, %	6.9
Open cells, %	5.0
Tack-free time, min.	2.8
Compressive strength (at 10%), psi	51.3
Humid-aged compressive strength (7 day, 70°C., 100% R.H.), psi	27.5
Humid-aged volume change (7 day, 70°C., 100% R.H.), %	16.2
Shear strength, psi	26.9
Density, lb./ft.³	2.39
Moisture vapor transmission, perms/in.	5.8
Water absorption in 48 hr., %	6.9

The prediction means that if several foams were prepared according to the optimum formulation, the averages of the properties would be the values shown.

Effect of Other Formulation Variables

Other formulation variables which have a marked effect on foam properties are the hydroxyl number of the polyether and the catalyst type. While

TABLE VIII
Effect of Polyether Monomer on Foam Properties

	Formula no. 33	Formula no. 34	Formula no. 16
Component A			
Quasi-prepolymer (NCO/OH = 4.5), g.	1290.0	1032.0	1212.0
Trichlorofluoromethane, g.	300.0	320.0	300.0
Component B			
G-2406 (Atlas Powder), g.	818.0	656.0	—
G-2410 (Atlas Powder), g.	—	—	897.0
TMBD (Union Carbide), g.	—	16.0	—
Dabco (Houdry Process), g.	19.5	—	19.5
X-520 (Union Carbide), g.	12.2	8.0	12.0
Celluflex FR-2 (Celanese), g.	—	496.0	—
Properties			
Density, lb./ft.^{3}	2.17	2.07	2.57
Compressive strength (at 10% comp.), psi	48.0	34.0	50.1
Humid-aged compressive strength (at 10% comp.), psi[a]	39.9	26.8	28.0
Humid-aged volume change, %[a]	+10.9	+6.5	+17.6
K Factor	0.121	0.115	0.129
Tensile strength, psi	39.7	33.0	56.8
Shear strength, psi	25.9	14.4	29.4
Water absorption (48 hr.), %	—	5.4	7.1
Moisture vapor transmission, perms/in.	7.2	—	5.3
Flammability, in./min.	—	Nonburning	—
Tack-free time, min.	8.0	6.0	5.0

[a] Humid-aged one week at 70°C., 100% R.H.

these were not investigated in the statistical pattern, a few observations are included here for the sake of completeness. Generally speaking, an increase in hydroxyl number produces an increase in crosslinking density, increased brittleness, improved compressive strength retention in humid aging, and greater resistance to the plasticizing effect of inert diluents. These points are illustrated in Table VIII. The foams shown are not strictly comparable because of the wide differences in density, but certain conclusions can be drawn. The foam based on G-2406 (No. 33) has a humid-aging volume change of only 10.9%, compared to

17.6% for the G-2410 foam (No. 16). Foam No. 33 retains 83% of its compressive strength during humid aging, compared to only 56% retention for foam No. 16. The effect of adding a fire-retarding diluent (Celluflex FR-2) to a G-2406 foam is shown in the properties of foam No. 34. Comparison of foams 33 and 34 shows that the addition of a diluent to No. 33 produces only a slight decrease in physical strength, part of the drop being attributable to the decrease in density. The nonburning foam, No. 34, has a compressive strength retention of 79% during humid aging, and a volume increase of 6.5%. The difference between the volume change for foams 33 and 34 is not experimentally significant (refer to confidence limits in Table V).

The other important factor affecting foam properties is catalyst type. To date only preliminary investigations have been made of the following catalysts alone and in various combinations: (1) N,N,N',N'-tetramethylbutanediamine (TMBD), Union Carbide; (2) dibutyltin di-(2-ethyl hexanoate) (M-1), Metal and Thermit; (3) dibutyltin dilaurate (D-22), Union Carbide. The TMBD is similar in action to Dabco, and the two are useful in combination. The tin catalysts must be used cautiously and at very low concentration to prevent a very hot foaming reaction and cracking of the foam. On the other hand, there are preliminary indications that the tin catalysts, when properly used, may reduce volume change and improve compressive strength retention in humid aging.

APPENDIX

Foam Property Data

The complete physical test data on the foams evaluated in the statistical study are presented in Tables IX and X.

Physical Property Tests

The following tests were made on each foam employed in the statistical study.

Tensile Strength (ASTM D-1623-59T). The Tinius Olsen Universal Tester was used to apply the load through universal couplings to special spool-shaped samples. The force required to pull each sample apart was measured. Each sample was cylindrical in shape and tapered down to a narrow center cross section. The small, center section had a diameter of 1.129 in. (area of 1 in.²), and was 0.5

TABLE IX
Measured Properties of Experimental Foams

Foam no.	Density, lb./ft.³	Compressive strength, psi	Humid-aged compressive strength, psi	Tack-free time, min.	Humid-aged volume change, %
1	2.32	57.4	24.75	8	+18.3
2	2.23	50.9	30.70	11	+24.8
3	2.73	63.0	27.00	3	+20.19
4	2.58	63.2	32.75	4	+19.21
5	2.33	61.5	22.50	3	+20.30
6	2.41	60.75	31.86	4	+19.80
7	2.29	47.5	30.25	10	+15.93
8	2.57	66.75	37.20	8	+28.5
9	2.53	54.75	36.25	5	+15.0
10	2.48	63.4	33.50	4	+24.05
11	2.43	53.4	30.90	9	+11.9
12	2.35	52.75	32.5	9	+23.8
13	2.43	47.25	29.0	8	+18.0
14	2.38	48.5	30.6	12	+18.9
15	2.55	55.25	33.4	3	+20.1
16	2.57	50.10	27.95	5	+17.6
17	2.44	56.87	32.25	4	+17.4
18	2.41	48.50	31.00	3	+27.42
19	2.36	55.50	26.75	8	+16.88
20	2.52	47.00	29.00	9	+14.12
21	2.40	52.25	35.15	7	+28.79
22	2.37	49.50	25.9	7	+18.25
23	2.55	52.50	29.57	4	+17.43
24	2.48	50.65	27.07	3	+13.65
25	2.22	40.50	23.82	7	+17.75
26	2.25	45.75	21.50	6	+18.05
27	2.41	52.25	25.75	4	+26.6
28	2.20	55.58	24.57	3	+21.35
29	2.37	52.91	25.50	3	+17.20
30	2.27	52.5	24.75	3	+18.38
31	2.38	52.07	29.25	5	+14.62
32	2.25	50.25	28.25	8	+25.57

in. in length. The samples were cut so that the line of applied force was in the direction of foam rise. The samples were conditioned at 73°F. and 50% R.H. prior to testing.

Compressive Strength (ASTM D-1621-59T). Rectangular foam blocks were placed between the parallel plates of the Universal Tester. The force and deformation were recorded as the plates were brought together at a constant rate of speed. The stress was measured at the yield point and at 10, 25, and 50% compressive deflection. Prior to testing the samples were conditioned for 24 hr. at 73°F. and 50% R.H.

Density (ASTM D-1622-59T). Foam blocks were measured with a thickness gage and vernier calipers. Each sample was then weighed on an analytical balance and the density computed in pounds per cubic foot. The samples were condi-

tioned at 73°F. and 50% R.H. prior to measuring and weighing.

Flammability (ASTM D-1692-59T). A foam sample 6 × 2 × ¹/₂ in. was placed in a horizontal position on a wire gauze and ignited at one end with a Bunsen burner. After 1 min. the flame was removed from the sample. If the sample immediately stopped burning it was rated "nonburning" by this test. If the sample continued to burn, its rate of burning in inches per minute was noted.

Compressive Strength After Humid Aging. The compressive strength was measured as described above after the foam sample had been humid-aged for 7 days at 70°C. and 100% R.H. The sample aged was a block measuring 2¹/₂ × 1¹/₂ × 6¹/₂ in. This was cut down to 2 × 2 × 1 in. before running the compressive strength measurement. This is not a standard test, but it has been employed by

TABLE X
Measured Properties of Experimental Foams

Foam no.	Shear strength, psi	Water absorption, vol.-%	Moisture vapor transmission, perm/in.	Open cells, %	Tensile strength, psi	K Factor
1	30.97	7.06	4.21	7.6	69.7	0.125
2	27.30	7.40	4.89	2.45	54.5	0.126
3	31.80	7.29	5.85	10.15	52.93	0.133
4	31.7	7.95	5.73	9.2	66.4	0.132
5	24.33	5.98	5.24	7.85	65.7	0.125
6	35.16	6.83	6.43	6.45	76.2	0.129
7	27.33	7.32	6.39	5.25	66.1	0.143
8	28.66	7.14	5.77	1.5	69.8	0.136
9	31.27	6.87	4.89	4.80	64.7	0.135
10	32.41	6.54	5.67	5.35	76.0	0.144
11	27.85	7.37	4.93	4.10	63.62	0.142
12	30.83	7.69	5.82	4.85	66.59	0.136
13	30.44	8.94	5.48	0.0	68.35	0.138
14	27.08	7.42	5.86	10.4	66.21	0.136
15	29.58	6.77	4.76	5.65	61.31	0.119
16	29.38	7.12	5.28	5.50	56.78	0.129
17	32.7	7.26	5.51	5.70	62.87	0.131
18	30.97	5.55	6.08	3.30	70.61	0.121
19	25.41	7.07	7.36	5.30	58.69	0.129
20	31.97	7.25	10.31	6.30	67.97	0.137
21	28.94	7.00	5.57	5.55	74.42	0.132
22	25.40	7.13	6.60	3.00	60.17	0.136
23	35.14	6.23	5.00	9.2	68.82	0.122
24	23.52	6.44	6.26	4.45	55.55	0.140
25	27.17	6.81	6.29	4.85	58.80	0.137
26	23.47	6.36	6.70	5.3	63.74	0.128
27	33.05	5.72	6.23	7.45	58.47	0.118
28	32.21	6.07	5.67	4.2	61.16	0.121
29	34.71	5.76	5.67	0.25	51.51	0.120
30	30.30	6.37	4.58	0.90	61.75	0.123
31	30.46	6.19	5.83	1.25	53.81	0.127
32	27.50	6.31	5.64	2.65	52.84	0.137

several members of the Cellular Plastics Division of the SPI (Society of the Plastics Industry).

Volume Change on Humid Aging. The volume of a sample, $4 \times 4 \times 1$ in., was measured before and after humid aging for 7 days at 70°C. and 100% R.H. The volume of each sample was determined by measuring the volume of rape seed "fluid" displaced by the sample from a standard rectangular container. For the volume measurement before humid aging, each sample was conditioned for 24 hr. at 73°F. and 50% R.H. This test is similar to the one used by several members of the Cellular Plastics Division of the SPI.

Shear Strength (ASTM C273-53). Shear strength was determined by pulling apart a sample to which special aluminum fittings had been adhered. The Universal Tester was employed to pull

the fittings apart at a constant rate of 0.05 in./min. Each aluminum shear plate measured $2 \times 8^1/_2 \times 1/_2$ in., while the dimensions of each sample were $6 \times 2 \times 1/_2$ in. The samples were so cut that the testing load was applied in the direction of foam rise. Prior to testing the samples were conditioned at 73°F. and 50% R.H.

Tack-Free Time. Tack-free time was defined as the length of time in minutes before the freshly poured foam became tack-free to the touch. It was used as an indication of relative cure time in the statistical study.

Thermal Conductivity (K-Factor). The K factor was expressed in the B.T.U. conducted per hour through one square foot of surface perpendicular to the direction of flow at a temperature gradient of 1°F./in. in the direction of flow. In the statistical

study the Pittsburgh Corning thermal conductivity probe was used. The probe itself was a long, needlelike instrument which contained both a heating element and thermocouple. In measuring thermal conductivity, the heater was fed with a predetermined wattage and the increase in temperature of the probe was plotted as a function of time. From the resulting curve it was possible to compute the value of K. In carrying out the test, the probe was placed between two blocks of foam, each of which measured 2 × 4 × 12 in. The values shown in Table X were obtained after aging the newly poured foams for 67 ± 3 days at room temperature.

Water Absorption. Foam blocks, 4 × 4 × 1 in., were immersed in water at a 10-ft. head of pressure for 48 hr. Each block was weighed to determine the amount of water absorbed, and the volume per cent of water absorbed was reported. This is not a standard test, but it has been employed by several number of the Cellular Plastics Division of the SPI.

Percentage of Open Cells. This property was measured by placing a small foam sample in the closed air chamber of a suitable apparatus. The following principle was employed. An increase in volume of a closed air chamber results in a pressure drop. If the same operation is performed when a cellular material is in the sample chamber, the pressure drop is greater than for the empty chamber. From the pressure drop and the known volume of the sample it is possible to compute the per cent open cells in the sample. (The remainder of the sample is made up of closed cells and cell walls). This is not a standard test, but it has been employed in identical form by a number of members of the Cellular Plastics Division of the SPI

Moisture Vapor Transmission. A 2 × 2 × 1-in. foam block was cemented to a 4-oz. wide-mouthed jar lid having a $1^1/_2$ in. hole. Epon 820 (Shell) adhesive was used to adhere the block to the lid. Sufficient alumina gel was placed in the jar to absorb about 5 g. of water. The jar and lid assembly were placed in an oven maintained at 100% R.H. and 100°F. The permeability of the block in perms per in. was computed from the weight gain of the assembly less the weight gain of the lid and block.

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Synopsis

Each rigid urethane foam formulation must be carefully designed to meet the key requirements of its specific end use. For example, refrigerator insulation is an application which requires low thermal conductivity, low density, and excellent resistance to humid aging. The present investigation was carried out to determine variations in foam properties caused by changes in catalyst concentration, isocyanate/hydroxyl ratio in the quasi-prepolymer, quasi-prepolymer cooking time, dispersing agent concentration, and isocyanate/hydroxyl ratio in the total foam. The basic foam formulation contained sorbitol polyether (Hydroxyl Number 490), toluene diisocyanate, trichlorofluoromethane blowing agent, catalyst, and dispersing agent. The results showed that the tensile strength decreased as the isocyanate/hydroxyl ratio in the total foam increased. Shear strength was affected strongly by catalyst concentration, and by isocyanate/hydroxyl ratio in the prepolymer and in the total foam. Cure time (at room temperature) was strongly affected by catalyst concentration and technique of prepolymer preparation. The only factors having a significant effect on humid aging resistance were isocyanate/hydroxyl ratio in the prepolymer and in the total foam. The effects on thermal conductivity were complex, and included an interaction between dispersing agent concentration and catalyst concentration, and also between prepolymer preparation technique and isocyanate/hydroxyl ratio in the prepolymer. The compressive strength increased with catalyst concentration, and was strongly affected by prepolymer preparation techniques. Key effects and interactions were plotted in graphical form.

Résumé

Chaque type de mousse d'uréthanne rigide doit être étudiée avec soin pour connaître les conditions critiques de son usage final spécifique. Par exemple, l'isolement de réfrigérateur est une application qui exige une basse conductivité thermique, une basse densité et une excellente résistance à l'humidité. La présente recherche fut effectuée pour déterminer les variations dans les propriétés de l'écume causées par des variations dans les concentration du catalyseur, dans le rapport isocyanante/hydroxyle dans le quasi-prépolymère, dans le temps de cuisson du quasi-prépolymère, dans la concentration de l'agent dispersant et dans le

rapport isocyanate/hydroxyle dans la mousse. Le récipé de base pour une mousse contenait du polyéther de sorbitol, du diisocyanate de toluène, du trichlorofluorométhane comme agent de gonflement, du catalyseur et de l'agent de dispersion. Les résultats ont montré que la résistance à la traction décroissait quand le rapport isocyanate/hydroxyle augmentait. La résistance au cisaillement était affectée fortement par la concentration en catalyseur et par le rapport isocyanate/hydroxyle dans le prépolymère et dans le mousse totale. Les seuls facteurs ayant un effet significatif sur la résistance à l'humidité est le rapport isocyanate/hydroxyle dans le prépolymère et dans la mousse finale. Les effets sur la conductivité thermique sont complexes et comprennent une interaction entre la concentration de l'agent dispersant et la concentration du catalyseur et aussi entre le technique de préparation du prépolymère et le rapport isocyanate/hydroxyle dans le prépolymère. La résistance à la compression augmente avec la concentration en catalyseur et se trouve fortement affectée par les techniques de préparation du prépolymère. Les effets les plus caractéristiques et les interactions ont été mises en graphiques.

Zusammenfassung

Ein jedes Rezept für starre Urethanschäume muss sorgfältig auf die Hauptanforderungen abgestimmt werden, die die endgültige Verwendung mit sich bringt. So ist zum Beispiel die Isolierung von Kühlschränken eine Verwendung, die eine niedrige Wärmeleitfähigkeit, eine niedrige Dichte sowie eine ausgezeichnete Alterungsbeständigkeit in feuchtem Milieu erfordert. Die vorliegende Untersuchung wurde zur Ermittlung der Abhängigkeit der Schaumeigenschaften von der Katalysatorkonzentration, dem Verhältnis Isocyanat zu Hydroxyl im Quasi-Vorpolymerisat, der Kochdauer des Quasi-Vorpolymerisats, der Konzentration an Dispersionsmittel und dem Verhältnis Isocyanat zu Hydroxyl im Gesamtschaum ausgeführt. Das Grundrezept für den Schaum enthielt Sorbitolpolyäther (Hydroxylzahl 490), Toluoldiisocyanat, Trichlorfluormethan als Treibmittel, Katalysator und Dispersionsmittel. Die Ergebnisse zeigten, dass die Zugfestigkeit mit steigendem Verhältnis Isocyanat zu Hydroxyl im Gesamtschaum abnahm. Die Scherfestigkeit wurde stark durch die Katalysatorkonzentration und durch das Verhältnis Isocyanat zu Hydroxyl im Vorpolymerisat und im Gesamtschaum beeinflusst. Die Härtungsdauer (bei Rautemperatur) hing stark von der Katalysatorkonzentration und dem Darstellungsverfahren für das Vorpolymerisat ab. Die einzigen Faktoren mit einem erkennbaren Einfluss auf die Alterungsbeständigkeit in feuchtem Milieu waren das Verhältnis Isocyanat zu Hydroxyl im Vorpolymerisat und im Gesamtschaum. Die Einflüsse auf die Wärmeleitfähigkeit waren komplexer Natur, wobei der der Dispersionsmittelkonzentration von der Katalysatorkonzentration und der des Verfahrens zur Herstellung des Vorpolymerisats vom Verhältnis Isocyanat zu Hydroxyl im Vorpolymerisat abhängig war. Die Kompressionsfestigkeit nahm mit der Katalysatorkonzentration zu und zeigt eine starke Abhängigkeit vom Verfahren zur Herstellung des Vorpolymerisates. Die Haupteffekte und -abhängigkeiten wurden graphisch dargestellt.