Some Relationships among Strength, Temperature, and Chemical/Physical Structures in Rigid Urethane Foams

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Synopsis

Low density rigid foams, produced by reacting polyether polyols with tolylene diisocyanate in the presence of fluorotrichloromethane, offer mechanical properties at levels which can have commercial utility.   Compressive strength was selected as a representative subject for empirical analysis at temperatures from 25 to 120°C.   The resultant correlation indicates that mechanical performance can be optimized only when foam formulation, manufacturing technology, and conditions of service are considered jointly.   At moderate temperatures, strength is controlled most conveniently through the foam's effective physical structure.   The relative importance of polymer chemistry tends to rise with temperature.   Strengths are generally highest in foams based on highly functional aromatic polyols of low equivalent weight.

INTRODUCTION

Unicellular rigid urethane foams are employed primarily for their superior thermal insulating qualities.   The value of these materials could frequently be enhanced if their load-bearing capabilities were also utilized to eliminate unnecessary structural details from foam-containing products. Before this potential can be realized in practice, mechanical characteristics must be defined so foam formulations and processes can be selected to meet design requirements.

The present analysis constitutes one step toward this goal.   Performance-temperature functions were related empirically to the chemical and physical structures of a variety of foams.   While the approach could be applied to any property, compressive strength was studied for convenience.

It is appropriate to note in passing that factors influencing compressive strength are normally found to have proportional effects on moduli and other strengths.   Since exceptions can be cited, particularly in tension, other mechanical properties should certainly be studied in depth.   The generalization does, however, imply that current results provide a guide for optimizing rigid urethane foam stress–strain responses to other types of loading.

Nomenclature is summarized in Table I.

TABLE I
Nomenclature

Term	Definition	Source
C_x	Foam strength response coefficient for independent variable X, in appropriate units	Multiple regression
d	Foam specimen density, pounds per cubic foot (pcf)	ASTM D1622[1]
e	Average equivalent weight of polyol (blend) foamed	Eq. (4)
e_s	Equivalent weight of polyol starter molecule	Stoichiometry
f	Average functionality of polyol (blend) foamed	Starter f and Eq. (6)
h	Average hydroxyl number of polyol (blend) foamed, mg. KOH/g. polyol	ASTM D1638[1]
m	Molecular weight of polyol	Eq. (1)
m_o	Molecular weight of alkylene oxide	Stoichiometry
m_s	Molecular weight of polyol starter	Stoichiometry
n	Average number of alkylene oxide units per equivalent of polyol (blend) foamed	Eqs. (3), (5)
N	Number of foam samples	—
r	Average number of aromatic rings per molecule of polyol (blend) foamed	Stoichiometry, Eq. (7)
R_s	Foam compressive strength ratio, dimensionless measure of isotropicity	$S_\parallel / S_\perp$
$S_\parallel$	Compressive strength measured parallel to the direction of foam rise, psi	ASTM D1621[1]
$S_\perp$	Compressive strength measured perpendicular to the direction of foam rise, psi	ASTM D1621[1]
S_m	Mean foam compressive strength, psi	Eq. (11)
T	Test temperature, °C.	—

PRELIMINARY CONSIDERATIONS

Cellular plastics are distinguished among load-bearing materials by their high void fraction, normally about 98 vol.-%, which provides unusual dimensions for mechanical variation. The concentration and geometric distribution of solids interact with the base polymer's temperature-sensitive properties to establish foam performance levels.

Polymer

Many criteria have been used to describe chemical structures. Prior work with urethanes based on a single isocyanate successfully employed parameters characterizing the polyol fraction of such polymers.[2] This approach was extended to the current analysis.

Hydroxyl number defines a polyol's stoichiometric isocyanate requirement, thus influencing polymer crosslinking. Higher h builds more phenylene and urethane groups, whose large cohesive energies[3] increase chain stiffness, into the polymer. As a result of these effects, "heat distortion" temperature rises with h in homologous foam series.[4] Analogously, aro-

matic polyols may be expected to yield greater heat resistance than aliphatics.

Average ether chain length influences flexibility and molecular weight per branch point in the crosslinked polymers. Higher n should reduce strength by increasing both factors.[5,6]

The variables h and n jointly define the polyether segment of polyol molecules. The material balances for individual polyols [eqs. (1)–(4)] and for a blend of polyols 1 and 2 [eqs. (5)–(7)] demonstrate that h and n are not entirely independent. Starter molecules constitute a major portion of the final polyol: their equivalent weight, functionality, and aromaticity are therefore expected to have prominent effects on foam performance.

Material balances for individual polyol:

$$m = ef \tag{1}$$

$$m = m_s + fnm_o \tag{2}$$

$$e = e_s + nm_o \tag{3}$$

$$e = 56,100/h \tag{4}$$

Material balances for blend of polyols 1 and 2:

$$n = n_1 \left[\frac{e - e_2}{e_1 - e_2} \right] + n_2 \left[\frac{e_1 - e}{e_1 - e_2} \right] \tag{5}$$

$$f = \frac{f_1 f_2 (e_1 - e_2)}{f_2 (e - e_2) + f_1 (e_1 - e)} \tag{6}$$

$$r = \frac{f_2 r_1 (e - e_2) + f_1 r_2 (e_1 - e)}{f_2 (e - e_2) + f_1 (e_1 - e)} \tag{7}$$

It should be noted that e_s, f, and r do not completely define the starter, so molecular configuration remains subject to change. A pendant phenyl group is not, for example, distinguished from one in a main chain. It was recognized[2] that any effects of starter configuration not accounted for by an empirical model would necessarily be pooled with random errors of measurement.

Differences in urethane structure which might be due to practical variations in catalysis, stoichiometry, and manufacturing processes should be negligible. Extended treatments of this subject appear in the literature.[2,7]

Geometry

Qualitatively, the physical structures of cellular plastics depend on the amount and distribution of polymer in space. The former factor corresponds simply to foam density d, whose general influence on strength is obvious.[6,8] The latter can be redefined in terms of closed cell content, cell size, cross-sectional uniformity of cell walls, and cell shape.
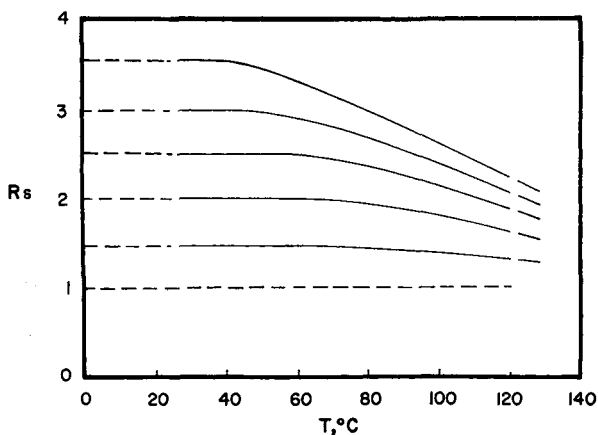
TABLE II
Foam Sample Distribution among Independent Formulation Variables

Polyol h		Polyol n		Polyol f		Polyol r		Foam d	
Range	N	Range	N	Range	N	Range	N	Range	N
200–250	1	0.8–1.0	7	2.0–2.5	1	0	81	1.4–1.6	3
250–300	9	1.0–1.2	21	2.5–3.0	2	0.4–1.0	11	1.6–1.8	25
300–350	48	1.2–1.4	112	3.0–3.5	32	1.0–1.5	94	1.8–2.0	59
350–400	44	1.4–1.6	67	3.5–4.0	100	1.5–2.0	19	2.0–2.2	144
400–450	92	1.6–1.8	51	4.0–4.5	35	2.0–2.5	28	2.2–2.4	48
450–500	76	1.8–2.0	29	4.5–5.0	24	2.5–3.0	29	2.4–2.6	12
500–550	14	2.0–2.2	7	5.0–5.5	17	3.0–3.5	14	2.6–2.8	1
550–600	6			5.5–6.0	56	3.5–4.0	18	2.8–3.0	2
600–650	4			7.5–8.0	27				
	294		294		294		294		294

Fig. 1. Effect of temperature on foam orthotropicity.

Within broad limits, closed cell content and cell size have no direct effect on compressive strength.[9] The large changes possible in cell strut and membrane cross sections could theoretically affect mechanical preformance strongly, although microscopic examination suggests that rigid urethane foams are normally similar in this respect. Since these cellular substructures are not presently subject to quantitative description, empirical analysis must treat any influence they may exert as random data scatter.

The microscope does reveal important relationships between cell shape and oriented strength measurements.[2] For a given formulation, R_s commonly increases from 1 to 3 as average cell elongation rises at ambient temperature. Because foamed structures are theoretically most stable when isotropic, it was anticipated that R_s might become temperature-sensitive as polymer softening points were approached. Figure 1, which reflects the actual behavior of typical rigid urethane foams, confirms this hypothesis.

EXPERIMENTAL

The products studied were urethanes based on conventional polyether polyols and their blends, reacted with 5–10% excess tolylene diisocyanate in the presence of various catalyst–surfactant systems, and blown to densities near 2 pcf using fluorotrichloromethane. Approximately 300 unicellular one-shot and quasi-prepolymer foams were supported by the desired minimum of chemical and physical measurements. The $S_\parallel$ and $S_\perp$ of each were available at 25, 85, 100, and 120°C. Distributions of raw data are summarized in Tables II and III.

Test descriptions can be minimized since laboratory procedures were either standards (Table I) or of a nature such that data would be available only to polyol manufacturers. Foam sample size and test specimen size and location were fixed to eliminate these potential sources of variation.

TABLE III
Foam Strength Distribution among Test Environments

Strength tested	Range, psi	25°C.	N measured at		
			85°C.	100°C.	120°C.
$S_{\parallel}$	0–5	—	—	—	65
	5–10	—	—	6	49
	10–15	—	1	15	54
	15–20	—	7	43	62
	20–25	5	29	84	34
	25–30	13	79	64	18
	30–35	36	73	59	11
	35–40	75	71	19	1
	40–45	62	29	2	—
	45–50	71	5	2	—
	50–55	23	—	—	—
	55–60	6	—	—	—
	60–65	2	—	—	—
	65–70	1	—	—	—
		294	294	294	294
$S_{\perp}$	0–5	—	—	3	124
	5–10	6	11	50	91
	10–15	70	116	160	62
	15–20	120	144	73	16
	20–25	80	21	8	1
	25–30	15	2	—	—
	30–35	3	—	—	—
		294	294	294	294

Total number of strength measurements = 2352

Specimens were 2-in. cubes removed 1 in. from the polymer skins which form naturally at foam surfaces.

Data were analyzed in multiple regression equations relating compressive strength, the dependent variable, to polymer chemistry (h, n, f, r), physical structure (d, R_s) and temperature (T). The original model incorporated each independent factor in the first and second orders (e.g., h and h^2). Since it was noted that h and n may be related, a term was inserted to allow this interaction. Least-square moments were taken about a base at $h = 400, n = 1.5, f = 4, r = 1.5, d = 2$, and $R_s = 1$.

A preliminary objective centered on finding the simplest adequate expression of mean strength, since correlations based on S_m might involve fewer terms and should be relatively free of cell shape effects. It was concurrently recognized that the "best" mean need not be the simplest. For example, among the three mutually perpendicular directions in which a foam might be compressed, $S_{\parallel}$ could be measured only once, and it was not clear whether $S_{\parallel}$ and $S_{\perp}$ should combine arithmetically or geometrically.

Four reasonable definitions of mean strength emerged from these considerations:

$$S_m = (S_\parallel + S_\perp)/2 = S_\perp(1 + R_s)/2 \qquad (8)$$

$$S_m = [S_\parallel + 2(S_\perp)]/3 = S_\perp(2 + R_s)/3 \qquad (9)$$

$$S_m = [(S_\parallel)(S_\perp)]^{1/2} = S_\perp(R_s)^{1/2} \qquad (10)$$

$$S_m = [(S_\parallel)(S_\perp)^2]^{1/3} = S_\perp(R_s)^{1/3} \qquad (11)$$

Regressions utilizing the last expression generally produced the lowest standard estimates of error and highest multiple regression coefficients obtained. Because R_s simultaneously vanished as an independent variable, this geometric mean was selected for continued study.

It was also observed at this point that the second-order d term was superfluous.

Independent chemical factors were studied in the simplified model. Variance checks on response coefficients for individual factors showed that second-order h and r terms, and the $h–n$ interaction, did not contribute significantly to regression quality.

Both orders were needed to describe n and f effects: decreasing n or increasing f caused S_m to rise at diminishing rates. For convenience in application, new functions were sought to present this behavior more simply with no loss of precision. Suitable functions were obtained when $(n - 1.5)$ and $(n - 1.5)^2$ were replaced by $(n - 1.5)/n$, and when $(f - 4)$ and $(f - 4)^2$ were replaced by $(f - 4)/f$.

RESULTS

A separate regression was developed for each test temperature. The final general model reduced to

$$S_m = C_0 + C_h(h) + C_n/n + C_f/f + C_r(r) + C_d(d) \qquad (12)$$
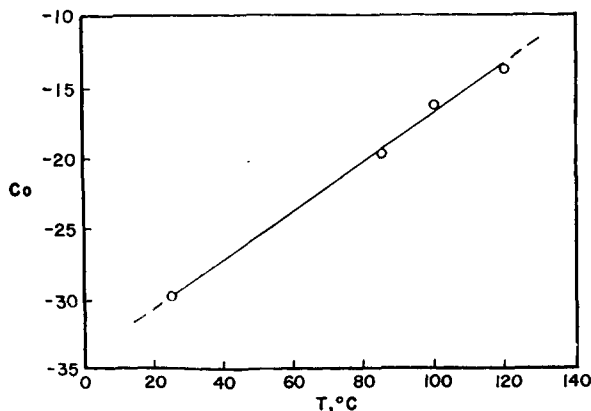
Fig. 2. Zero-level multiple regression coefficient for mean foam strength.
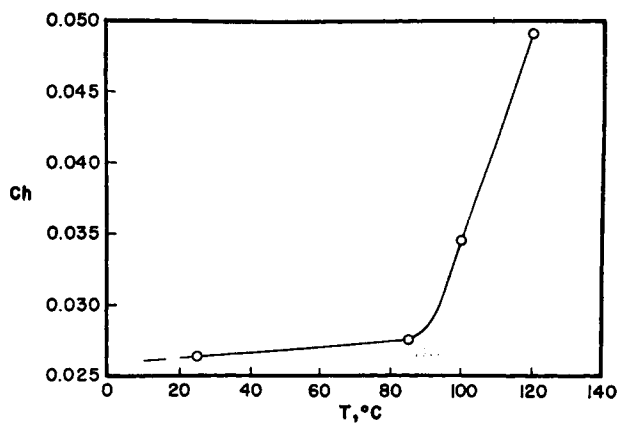
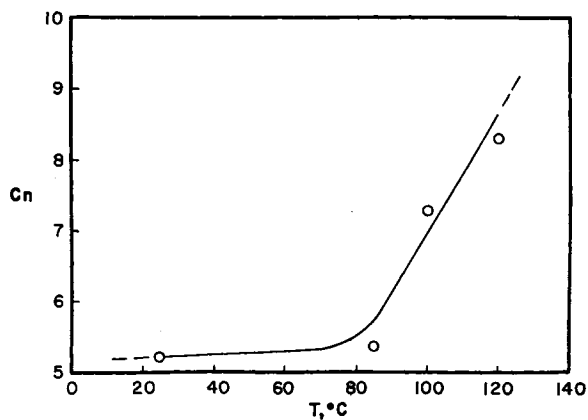Fig. 3. Coefficient for mean foam strength response to polyol hydroxyl number.

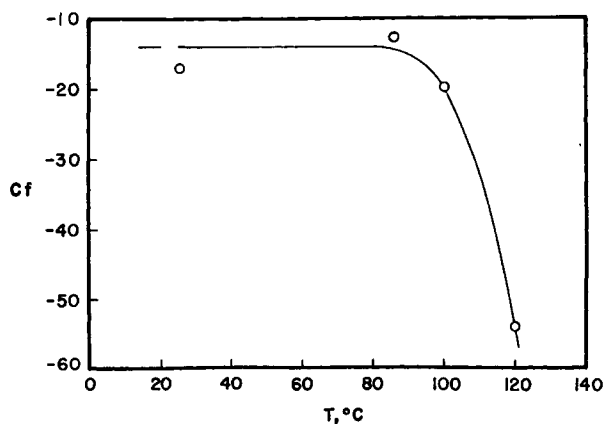Fig. 4. Coefficient for mean foam strength response to polyether chain length.

Fig. 5. Coefficient for mean foam strength response to polyol functionality.
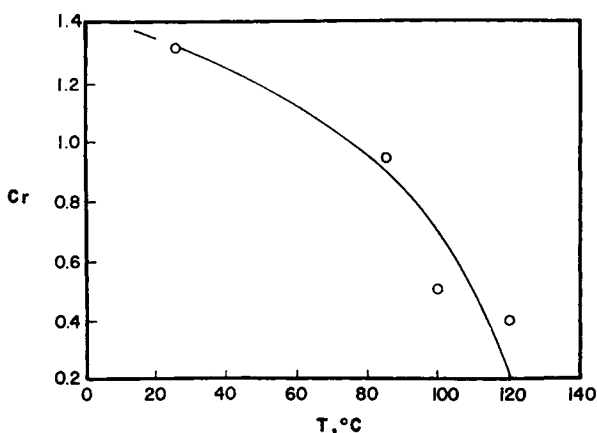
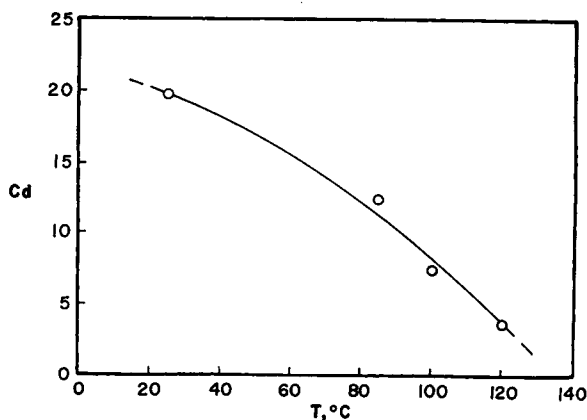Fig. 6. Coefficient for mean foam strength response to polyol aromaticity.

Fig. 7. Coefficient for mean foam strength response to density.

when decoded. The empirical response coefficients, C_x, are plotted as temperature functions in Figures 2–7.

Within the factor levels studied, the multiple correlation coefficient approximates 0.85, and 90% confidence limits on a predicted S_m are ±4.2 psi. These limits combine random errors of measurement for all variables and therefore apply strictly only to the laboratory methods actually used.

Independent reproducibility studies showed that local between-sample confidence limits on individual compressive strength measurements average ±2.5 psi at the 90% level. The significant difference between precision of prediction and of direct measurement reveals a potential for further improvement in regression quality, which could doubtless be accomplished by appropriate description of starter configuration and foam microstructure. Since these factors have not been reduced to terms suitable for numerical analysis, the model will not completely satisfy polymer chemists. Its

precision is nevertheless adequate for judicious application by foam technologists.

DISCUSSION

Figures 3–7 indicate that mean foam strength rises at constant temperature as h, f, r, or d increase and as n decreases. These qualitative observations were anticipated, and their predicted magnitudes are now of major interest. A series of examples, calculated to simulate realistic foam systems, helps interpret eq. (12) in a practical sense.

Chemical Effects

Figures 8 to 10 show some results achieved by polyol modification. It is immediately apparent that h provides the maximum potential for adjusting
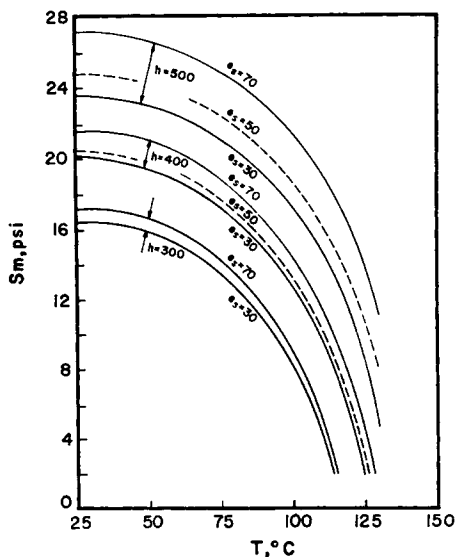
Fig. 8. Effects of polyol chain length on mean foam compressive strength; $n = (996/h) - (e_s/58.1)$, $f = 4$, $r = 0$, $d = 2$, $R_s = 1$.

S_m chemically to a desired level. Corresponding changes in n, related to h on Figure 8 through equivalent starter weight, reveal that the flexibilizing effect of polyether chains increases with T. Reducing n from 2.7 to 0.7 units increases S_m from 17 to 27 psi at 25°C. and from 0 to 17 psi at 115°C. (2 pcf foam based on aliphatic tetrols).

Figure 9 indicates that polyol functionality becomes important mainly at higher T. Increasing f from 3 to 8 causes S_m to rise only from 19 to 22 psi at 25°C., but from 0 to 12 psi at 120°C. (2 pcf foam based on aliphatic polyols of constant equivalent weights).
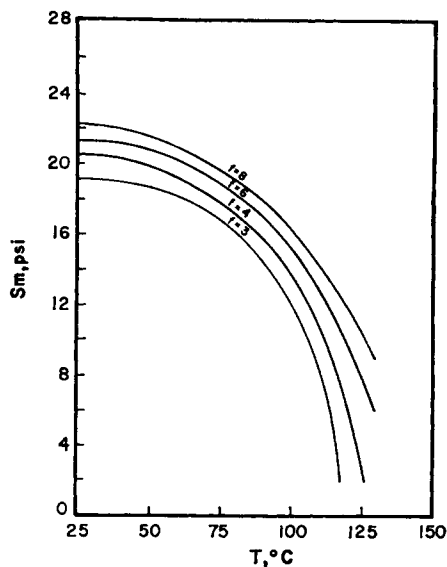
Fig. 9. Effect of polyol functionality on mean foam compressive strength; $h = 400$, $n = 1.56$, $r = 0$, $d = 2$, $R_s = 1$.
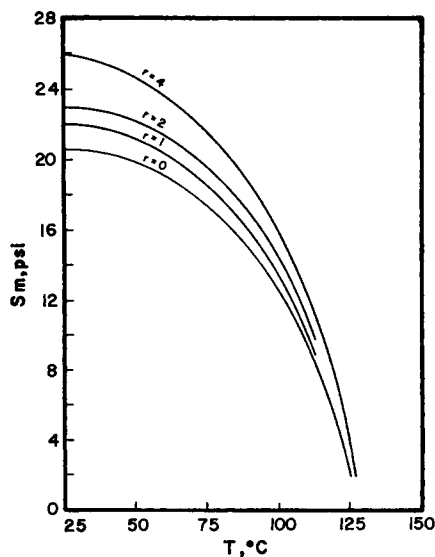

Fig. 10. Effect of polyol aromaticity on mean foam compressive strength; $h = 400$, $n = 1.56$, $f = 4$, $d = 2$, $R_s = 1$.

The benefits conferred by aromatic polyols appear on Figure 10, and contrast with the preceding effects by decreasing in magnitude as T rises. Incorporating one ring into each "leg" of a tetrol (fixed equivalent weights) increases S_m from 21 to 26 psi at 25°C., but only from 2 to 4 psi at 125°C. (2 pcf foam).

Ideally, these factors can be superimposed in combinations too numerous to illustrate. A variety of polyols could therefore provide comparable foam performance at specified T. The technical challenge of achieving desired S_m economically will be considered briefly in a later section.

Physical Effects

Figures 11 and 12 reveal that foam structure can reasonably have much larger effects on S_m than polymer structure. Physical factors are strongest at ambient T, however, and become less significant as T approaches the urethane softening point.
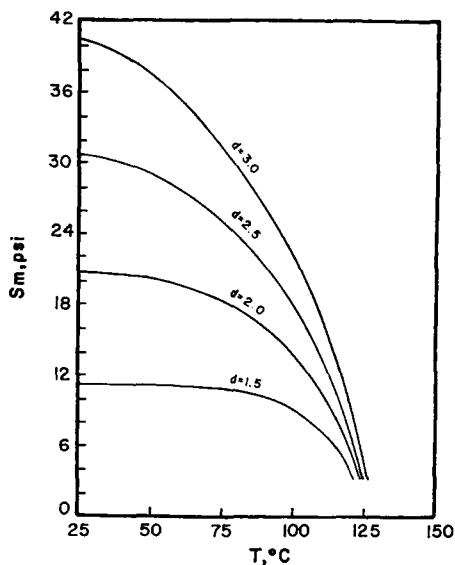

Fig. 11. Effect of foam density on mean compressive strength; $h = 400, n = 1.56, f = 4$, $r = 0, R_s = 1$.

Figure 11 is the source of a second pertinent observation. Doubling foam density might be expected to double S_m since twice as much polymer is present: S_m actually increased 360% at 25°C. (250% at 120°C.) as d rose from 1.5 to 3.0 pcf.

Figure 12 was constructed by translating S_m into the $S_{\parallel}$ and $S_{\perp}$ from which it was originally derived. Appropriate inversions of eq. (11) are

$$S_{\parallel} = S_m(R_s)^{2/3} \tag{13}$$

$$S_{\perp} = S_m(R_s)^{-1/3} \tag{14}$$

Since a foam becomes more isotropic when heated sufficiently, Figure 1 was used to modify the 25°C. R_s selected for presentation. Figure 12 then demonstrates that effective strength is a function of both load orien-
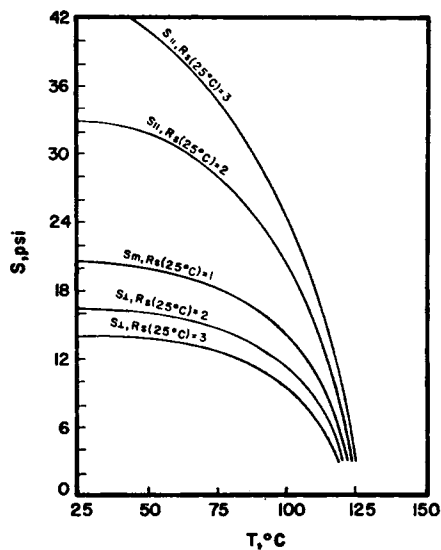
Fig. 12. Effect of foam orthotropicity on compressive strength; $h = 400, n = 1.56, f = 4,$
$r = 0, d = 2.$

tation and cell shape: while lower R_s increases $S_\perp$ when other factors are constant at moderate T, it reduces $S_\parallel$ more rapidly. Naturally, interest tends to center on one or the other of these strengths (not both) in a given situation.

Application

Relative costs per pound of urethane foam ingredients are generally: catalysts and surfactants > isocyanate > polyether polyols> fluorocarbon. Since the first components are present in minor amount, and since iso-cyanate/polyol ratios vary with stoichiometry, material cost per volume of foam increases mainly with h and d. Figure 13 thus provides a comparison among equal-cost foams based on aliphatic ($n = 1.89$) and aromatic ($n = 1.21$) tetrols and hexols. The curves reflect the fact that e_s tends to rise with r and reveal some effects of polymer changes taken jointly, rather than singly as was the case earlier.

It should be noted that cost–performance analysis is seldom this straight-forward in practice. Most polyol h are actually above 450 when $r = 0$ and below 400 when $r > 0$. At equivalent d and f, product S_m would there-fore be more nearly similar than indicated while material costs would be higher for systems based on aliphatic polyols.

Foam d is adjusted primarily through blowing agent content, but also by catalyst-surfactant systems and the exotherm from urethane formation. The minimum d produced when a formulation is free-blown (e.g., commer-cial slabstock) will not be realized during foam-in-place operations. Ex-pansion is restricted in the latter case by manufacturing limitations (e.g.,
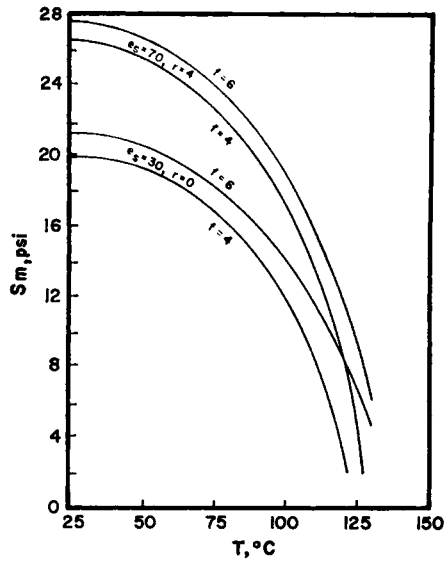
Fig. 13. Compressive strengths of isotropic foams based on various polyols; $h = 400$,
$n = 2.41 - (e_s/58.1)$, $d = 2$, $R_s = 1$.

mold configuration and fill technique, thermal environment, effective viscosity of foaming material, etc.) beyond the scope of these comments. Although foam technologists must evaluate such factors in specific products, it can be noted that minimum and optimum d are not necessarily synonymous because cost per unit S_m falls as d rises (Fig. 11).

The above considerations apply to R_s, but in varying degree. It is generally found that R_s ranges from 1 to 2 in slabstock and 2 to 3 in the foamed-in-place cores of thin panels. Within limits set by formulation and processing requirements, the direction of compression should coincide with that of foaming to maintain $S_{\parallel}$ as the pertinent strength, and R_s should then be maximized. For example, horizontal decking should be manufactured so the foam rise is skin-to-skin whether obtained by laminating cut board or by direct molding.

Product acceptance specifications requiring a minimum compressive strength at some temperature will include other performance criteria as well. This discussion has considered strength exclusively. Since other properties respond quite differently to chemical and physical variables,[2] cost–performance relationships must ultimately be optimized on an overall basis.

CONCLUSIONS

Probably the most effective means for increasing foam strength chemically is to employ polyols of low equivalent weight. Unfortunately, this approach is not desirable commercially because it tends to increase system

cost and handling problems (viscosity). Alternate solutions require modification of the polyol's starter molecule. High aromaticity and functionality maximize strength mainly at ambient and elevated temperatures, respectively. High equivalent weight also improves strength by minimizing the polyether chain length needed to provide attractive polyol hydroxyl numbers.

Physical variables actually have larger effects on foam strength, particularly at ambient temperature, than do practical changes in urethane structure. Density adjustment is very effective, although economic considerations normally dictate that this factor should be minimized. Control of cell shape and of load orientation relative to cell elongation provides appreciable design latitude with no inherent financial complication.

A broad range of strengths results as these chemical and physical effects cumulate. In general, however, the optimum formulation and process for a given application will be determined by using minimum strength as one of several performance criteria.

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Résumé

Les mousses rigides de faible densité, produites par réaction de polyéthers polyols avec le diisocyanate de tolylène en présence de fluorotrichlorométhane, présentent des propriétés mécaniques susceptibles d'avoir une utilité commerciale. La longueur de compression a été choisie comme un sujet de représentation pour l'analyse empirique à des températures de 25 à 120°C. Il en résulte une corrélation indiquant qu'on peut améliorer des performances mécaniques uniquement si la formulation de la mousse, la technique de fabrication, et les conditions d'utilisation sont considérées en même temps. Pour des températures modérées, la force est controlée d'une façon plus convenable au moyen de la structure physique effective de la mousse. L'importance relative de la chimie des polymères tend à augmenter avec la température. Les forces sont généralement plus élevées pour des mousses contenant des polyalcools aromatiques hautement fonctionnels de poids équivalent peu élevé.

Zusammenfassung

Starre Schaumstoffe von niedriger Dichte, erzeugt durch Reaktion von Polyätherpolyolen mit Toluylendiisocyanat in Anwesenheit von Fluortrichlormethan, besitzen mechanische Eigenschaften von möglicherweise technischer Bedeutung. Die Kompres-

sionsfestigkeit wurde als repräsentative Eigenschaft für die empirische Untersuchung bei Temperaturen von 25 bis 120°C ausgewählt. Die resultierende Beziehung deutet an, dass die mechanischen Eigenschaften optimal werden, wenn Schaumstoffzusammensetzung, Erzeugungstechnologie und Verwendungsbedingungen im Zusammenhang betrachtet werden. Bei mässigen Temperaturen kann man die Festigkeit am bequemsten durch die effektive physikalische Schaumstoffstruktur kontrollieren. Die relative Bedeutung der Polymerchemie scheint mit der Temperatur zu wachsen. Die grösste Festigkeit wird im allgemeinen in auf hochfunktionellen aromatischen Polyolen von niedrigem Äquivalentgewicht basierenden Schaumstoffen erreicht.