Thermal Characteristics of Some Rigid Urethane Foams*

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Synopsis

The thermal stability characteristics of three rigid urethane foams prepared from various formulations, to give a wide range of molecular structure, were investigated by means of TGA, DTA, and long-term heat aging.   Compressive strength values over a temperature range of −73°C to +232°C were also determined for these foams.   Based on all tests performed, a toluene diisocyanate foam displayed the poorest thermal stability characteristics of the three foams studied.   A combination toluene diisocyanate–polymethylene polyphenylisocyanate foam showed intermediate elevated temperature properties, whereas, a foam employing only polymethylene polyphenylisocyanate demonstrated the best over-all high temperature stability.

INTRODUCTION

The use of rigid urethane foams as insulative materials and structural members is rapidly increasing as their unusually low thermal conductivities and good strength-to-weight ratio become better established.   Service temperatures for these applications, as well as others, range from cryogenic to somewhat above normal room conditions.

The utility of rigid urethane foams in higher temperature applications has been limited, to a certain degree, by the lack of significant information concerning the thermal stability of these materials.   However, thermal characteristics of urethanes themselves have long been known, for Hofmann[1] in 1870 showed that an aromatic urethane dissociates into an isocyanate and an alcohol at 170–180°C.   Another investigator[2] has also made an extensive quantitative study of the kinetics of the urethane dissociation, the results of which are in good agreement with this early work. Additional kinetic studies of this decomposition in several solvents indicate that the reaction proceeds at an appreciable rate even at 150°C.[3,4]

Some data on the thermal stability properties of urethane elastomers and low density fluorocarbon blown foams have been published.[5–7]   Compressive strength data at elevated temperatures have also been determined on a rigid urethane foam system at various densities.[8]   Still there exists a considerable absence of detailed information concerning the thermal service limitations for rigid urethane foams.

The work reported in this paper is directed toward both a theoretical and practical aspect for the determination of some of the thermal characteristics for rigid urethane foams. The methods used to measure the parameters include: compressive strength properties at elevated temperatures, thermogravimetric analysis, differential thermal analysis, heat aging (somewhat of a static thermal stability test), and elemental chemical analysis. A possible correlation between physical and thermal properties is suggested as a guide for determining the elevated service temperatures for these materials.

EXPERIMENTAL

Materials

The three rigid urethane foam formulations chosen for this study show a wide range of molecular structure: foam 1: an aromatic dibasic acid-based polyester/toluene diisocyanate (TDI) prepolymer foam; foam 2: an ϵ-caprolactone–pentaerythritol polyester/toluene diisocyanate (TDI) prepolymer (20%)–polymethylene polyphenylisocyanate (PAPI) (80%) material; foam 3: a commercial high-temperature rigid urethane foam based on a polyester and polymethylene polyphenylisocyanate (PAPI).

Formulations from which foam samples were prepared are summarized in Table I. The molded foam test specimens prepared for this work were made from hand (high-speed air stirrer) mixed material. The foam blocks were cured for 10 hr. at 325°F. and had a core density of 20 pcf.

Ultimate Compressive Strength

This test was conducted in accordance with ASTM D-695 over a temperature range of −73°C. to +232°C. The test specimens used were 1-in. cubes machined from the cores of the molded foam blocks. The specimens were conditioned for at least 2 hr. at the test temperature before testing, and compressed parallel to foam rise. A loading rate of 0.050 in./min. was used, with five determinations being made at each test temperature.

Thermogravimetric Analysis (TGA)

All thermogravimetric analyses were made with an Aminco-Therm-Grav No. 4-4430. The material samples used in the analyses were from foam sections taken from five or six different locations on the core of each foam block. The foam sections were then ground into a fine powder with a ball mill. The following parameters were employed on each sample: sample weight, 100 mg.; temperature range, 25–500°C.; heating rate, 6°C./min.; sample atmosphere, air.

TABLE I
Formulations for Rigid Urethane Foams

Raw materials	Formulation, parts by weight[a]		
	Foam 1 (aromatic dibasic acid polyester–TDI prepolymer urethane foam)	Foam 2 (ε-caprolactone polyester–TDI prepolymer/ PAPI urethane foam)	Foam 3 (polyester–PAPI urethane foam)
Aromatic dibasic acid polyester, hydroxyl no. 575	100	—	—
ε-Caprolactone polyester, hydroxyl no. 605	—	100	—
Commercial polyester, hydroxyl no. 600	—	—	100
Toluene diisocyanate (TDI) prepolymer		—	
Foam 1, amine equivalent 129	162		—
Foam 2, amine equivalent 135	—	38	—
Polymethylene polyphenyliso-cyanate (PAPI), amine equivalent 134	—	139	170
Distilled water	1.95	1.50	1.70
Additives (cell stabilizers, amine catalyst, etc.)	3.0	6.0	5.0

[a] TDI = 80/20 toluene diisocyanate. (Mobay Chemical Company); PAPI = polymethylene polyphenylisocyanate (The Upjohn Company).

Differential Thermal Analysis (DTA)

All differential thermal analyses were made with an Aminco-Thermoanalyzer No. 4-4442. Powdered foam samples, prepared by the same method used for the TGA samples, were used in the analyses. The following parameters were employed for each sample: sample weight, 9–12 mg.; temperature range, 25–600°C.; heating rate, 4°C./min.; reference, empty cup of similar weight to sample cup.

Heat Aging

Small cylinders of foam (approximately $1/4$ in. in diameter and $1/4$ in. high) were placed in aluminum pans and then weighed to the nearest 0.1 mg. The initial weights of the samples were 1.03–1.11 g. The pans were then placed into a forced air oven maintained at 175 ± 2°C. The weight loss was determined daily for 4 days and then at longer time intervals, by cooling the samples to room temperature and weighing to the nearest 0.1 mg.

Nitrogen Analysis

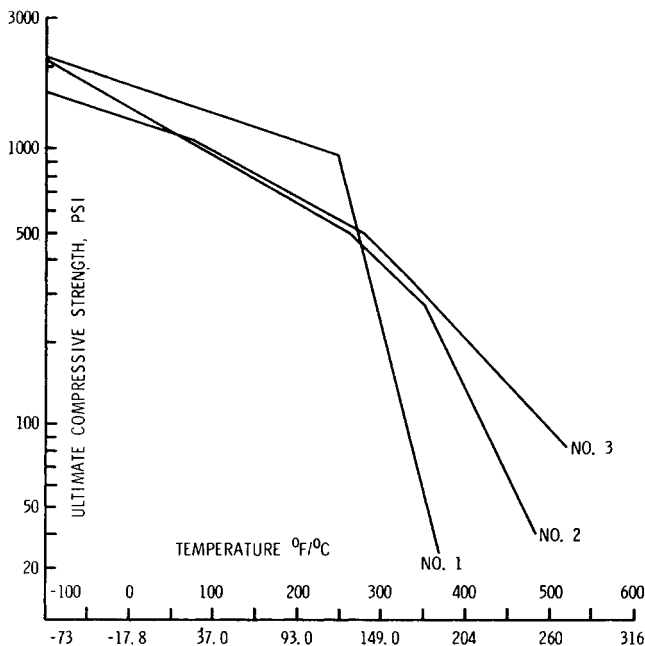Nitrogen analyses (in duplicate) were made on foam powder, with a Coleman nitrogen analyzer.

Fig. 1. Compressive strength curves for rigid urethane foams: (1) TDI foam; (2) TDI/PAPI foam; (3) PAPI foam. Foam density, 20 pcf; specimen size, 1 in. cube; loading rate, 0.050 in./min.

RESULTS AND DISCUSSION

From Figure 1, we note that the compressive strength of the toluene diisocyanate (TDI)-based foam 1 drops off at a considerable rate after 120°C. (250°F.), while both foams 2 and 3, which contain polymethylene polyphenylisocyanate (PAPI), retain reasonable compressive properties up to 175°C. (350°F.). The loss in compressive properties occurs at temperatures somewhat below those reported for the thermal decomposition (150–200°C.) of the chemical linkages usually found in rigid urethane foams.[9] Therefore, it can be surmised that retention of compressive strength of rigid urethane foams at elevated temperatures is not solely dependent upon the various chemical linkages involved in foam formation, and that other parameters must also be considered. These parameters should include: hydrogen bonding, bulkiness of the molecules involved, and stability of the chemical constituents themselves. However, because of the complex nature of the chemical makeup of rigid urethane foams, these additional and important factors do not readily lend themselves to analysis, so one must be content to measure other more tangible parameters.

As a continuation of this practical approach to the determination of thermal characteristics of urethane foams, a TGA determination was made on each of three foam systems. The TGA thermograms (Figs. 2, 3, and 4) all have the same general shape. An initial weight loss is noted between
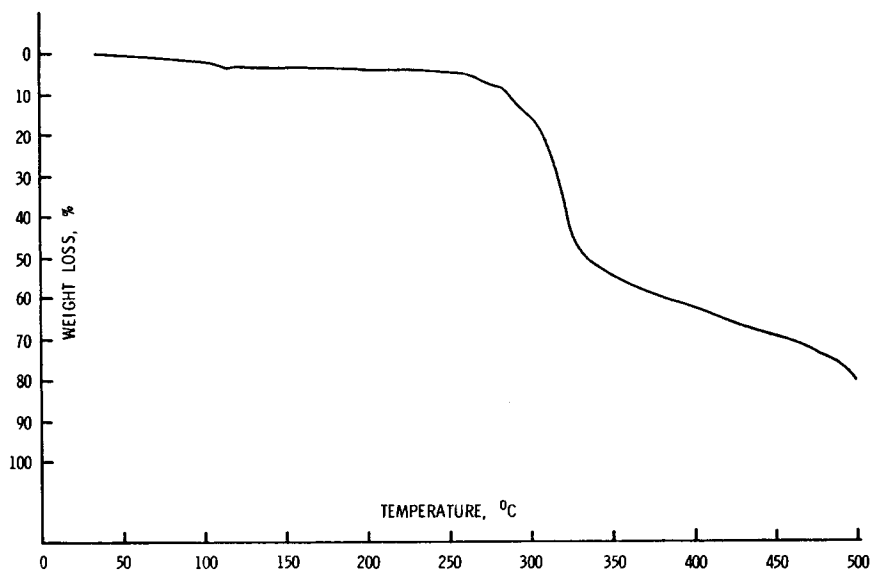
Fig. 2. TGA curve for TDI foam (foam 1). Heating rate, 6°C./min.; sample atmosphere, air; sample weight, 100 mg.
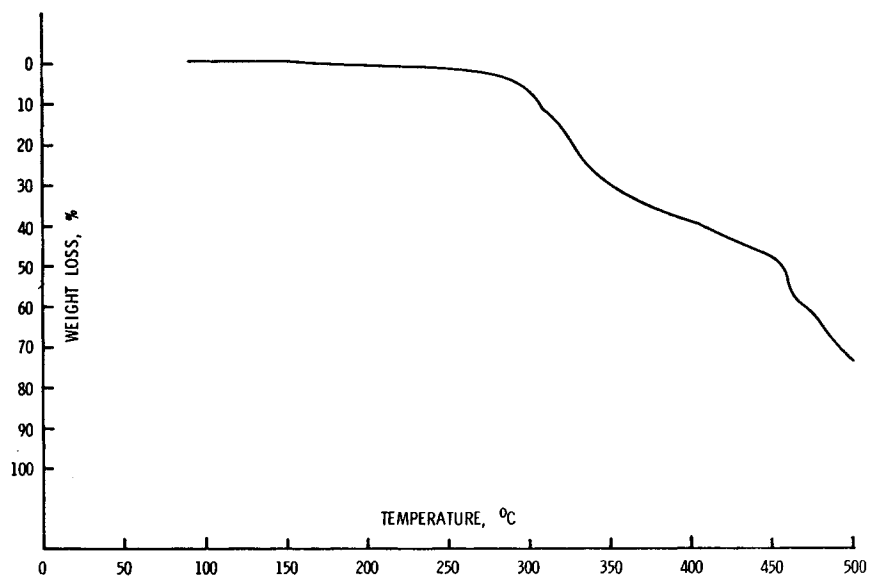

Fig. 3. TGA curve for TDI/PAPI foam (foam 2). Heating rate, 6°C./min.; sample atmosphere, air; sample weight, 100 mg.

150 and 265°C. (depending upon the material), and continues at a similar rate to a temperature of approximately 324–350°C. In this temperature range weight loss continues, but at a slower rate. The change of weight loss rate would indicate a change in the decomposition mechanism.
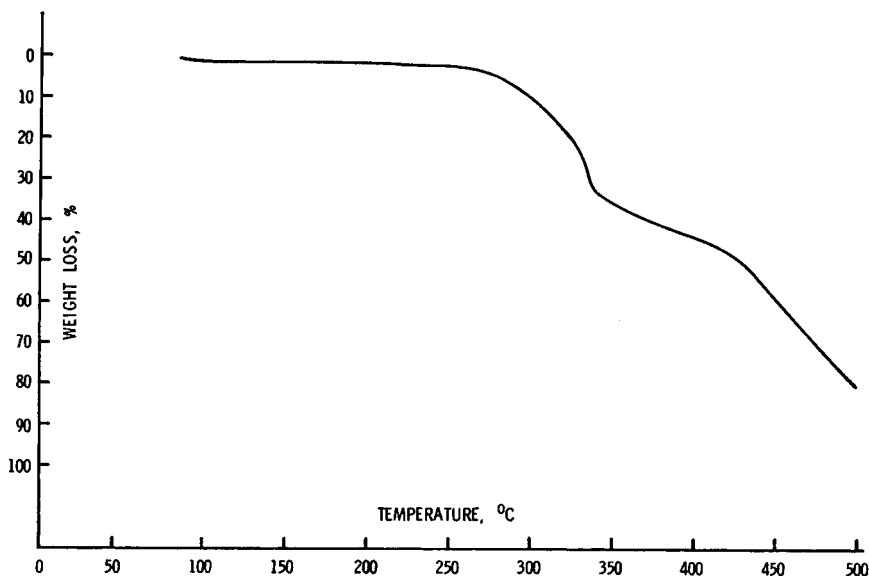
Fig. 4. TGA curve for PAPI foam (foam 3).   Heating rate, 6°C./min.; sample atmosphere, air; sample weight, 100 mg.

The two temperature ranges show that different types of decomposition can occur.   The initial weight loss is thought to be due to oxidation of the urethane linkages and loss of CO_2 and volatile products.   The latter decomposition mechanism is suspected of being a complete depolymerization of the existing polymer fragment.[10]   The temperature of initial weight loss and the approximate temperature of change of weight loss rate from the TGA analyses are shown in Table II.   The corresponding per cent weight loss for the initial decomposition and the total weight loss is also given.   The foams are listed in order of increasing stability according to temperature of initial weight loss.
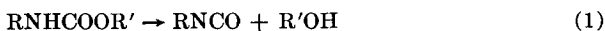
TABLE II
TGA Data for Rigid Urethane Foams

Foam	Initial wt. loss temp., °C.	Initial wt. loss, %	Second wt. loss, temp., °C.	Total wt. loss, %
Foam 1 (TDI)	240–250	52	335	81
Foam 2 (TDI/PAPI)	250	50	350	74
Foam 3 (PAPI)	265	32	345	80

These two decomposition temperatures are in general agreement with other TGA analysis of rigid urethane foams.[5]   The actual chemical products liberated at these temperatures have not, as yet, been clearly defined.   Some studies of the thermal decomposition of substituted urethanes have shown that three general reactions may take place, in the temperature

range (200–300°C.) of the first weight loss found for the TGA analysis[11,12] These reactions are given in eqs. (1)–(3).

Dissociation to isocyanate and alcohol:

$$RNHCOOR' \rightarrow RNCO + R'OH \tag{1}$$

Formation of primary amine and olefin:

$$RNHCOOCH_2CHR' \rightarrow RNH_2 + CO_2 + R'CH = CH_2 \tag{2}$$

Formation of secondary amine:

$$RNHCOOR' \rightarrow RNHR' + CO_2 \tag{3}$$

The actual degradation of rigid urethane foams at elevated temperatures is not as simple as the mechanisms proposed indicate. Several additional factors are present that tend to obscure the overall details of total decomposition: (1) various chemical linkages, other than the urethane, are present in foam; (2) no allowance is made for complete oxidative breakdown of the polymer; (3) the degradation products may further react to form new chemicals, which in turn break down. This complicated picture is just for the initial weight loss temperature range; countless possibilities exist for the second temperature range.

As still another measurement of their thermal stability, a DTA was made for each of the three foams. These DTA thermograms are given in Figure 5. A comparison of the DTA and TGA thermograms of each foam shows
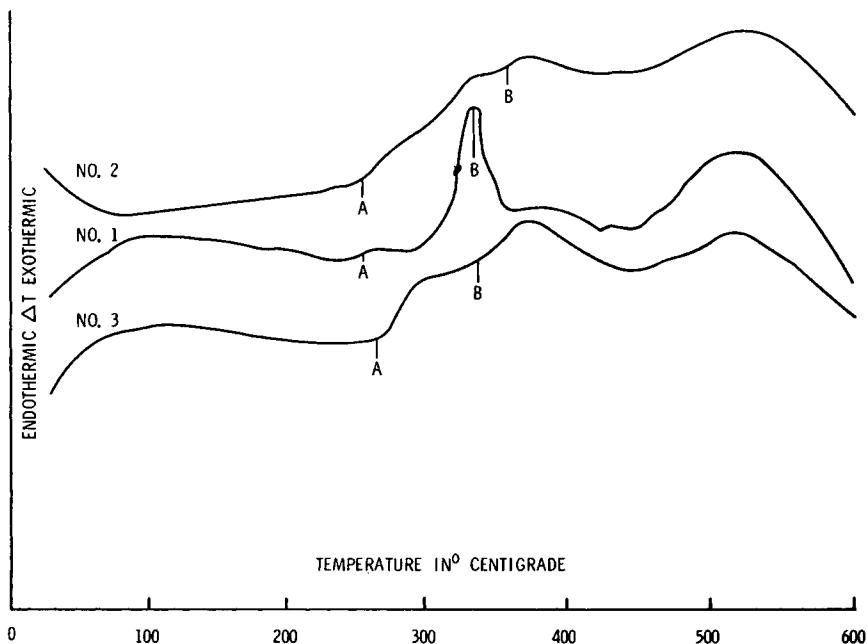

Fig. 5. DTA curves for rigid urethane foams in air: (1) TDI foam; (2) TDI/PAPI foam; (3) PAPI foam. Heating rate, 4°C./min.; sample weight, 9–12 mg.

that in all cases the first DTA exotherm began at approximately the same temperature that initial weight loss started during TGA. The temperature at which the initial weight loss was observed by TGA is marked A on each corresponding DTA curve. Further comparison shows that the termination of the first decomposition mechanism during TGA occurred at temperatures near a maximum of an exothermic reaction by DTA. These points are marked B on the corresponding DTA curves.

The other characteristics of the DTA curves, such as the shoulder observed between points A and B, and other maxima after point B, are yet to be identified. The shoulders between A and B may well represent a change in decomposition mechanism. Such a case was not observed by TGA; however, a change in decomposition mechanism which had no change in rate of weight loss associated with it would not be observed by TGA. Foams 2 and 3, both containing PAPI, showed shoulders between A and B occurring at higher temperatures than foam 1, which was based solely on TDI. It is certainly possible that the diisocyanate component may be responsible for such shoulders. However, complete identification would require extensive additional investigation.

It was also observed that foam 1 gave a very sharp DTA maximum near 330°C, which neither of the other foams exhibited. Both foams 2 and 3 did show maxima, but not nearly of the same intensity and at a considerably higher temperature. This would indicate that the foams containing PAPI had higher thermal stability. That is, the exothermic reaction associated with initial decomposition of the PAPI foams reached a maximum at higher temperatures than did the TDI foam.

The last broad exotherm, shown on the DTA curves in Figure 5, occurred at nearly the same temperature (+525°C.) for all three foams. This exotherm is believed to be due to the final decomposition of the foam. These decomposition products are considered to consist mainly of H_2O, CO_2, and N_2.

Heat aging results are graphically represented in Figure 6 as a plot of per cent weight loss against time at 175°C. Foam 3, containing only PAPI, was the most stable to heat aging, while foam 1, containing only TDI, was the least stable, as indicated by weight loss. Foam 2, containing both TDI and PAPI, was intermediate.

Infrared analysis of the foams, before heat aging, showed that all three foams contained unreacted free isocyanate as determined by the presence of an absorbance at 4.4 μ. The order of increasing amounts of unreacted isocyanate is foam 2 < foam 3 < foam 1. No excess free isocyanate was detectable by infrared analysis after heat aging.

The per cent nitrogen determined for each foam is shown in Table III. The results listed in Table III tend to correlate with the other findings presented throughout this report. The TDI-based foam 1 contained the most nitrogen, yet it was found to be the least thermally stable in the various tests performed. The high nitrogen content found for foam 1 could indicate a high degree of crosslink density. If this is true, the work pre-
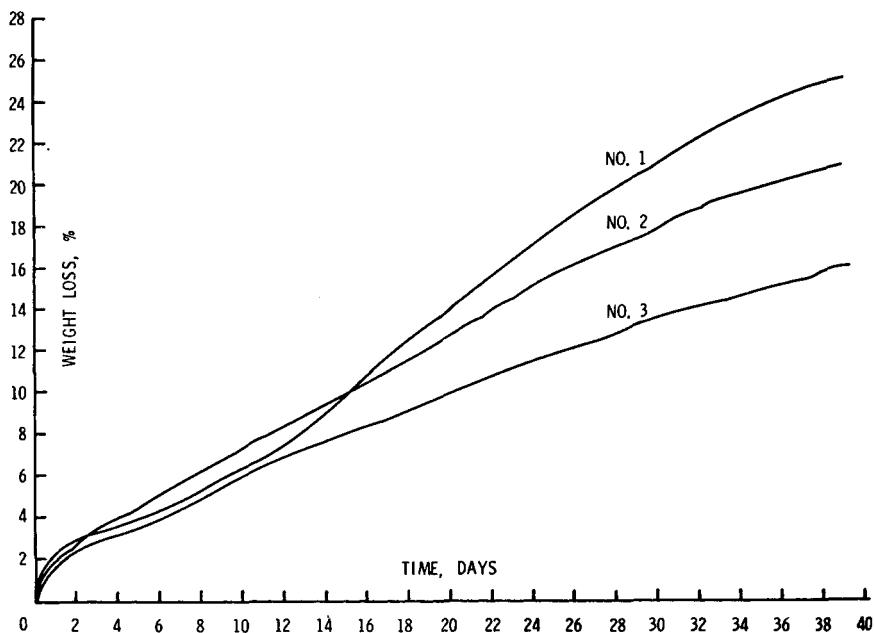
Fig. 6. Heat aging curves for rigid urethane foams: (*1*) TDI foam; (*2*) TDI/PAPI foams; (*3*) PAPI foam.   Aging temperature, 175 ± 2°C.; sample weight, 1.03–11.11 g.

TABLE III
Nitrogen Content for Rigid Urethane Foams

Foam	Nitrogen content, %
Foam 1 (TDI)	8.42
Foam 2 (TDI/PAPI)	7.35
Foam 3 (PAPI)	7.12

sented here would show that thermal stability is more dependent upon the type of crosslink present than on the amount.   The nitrogen content for PAPI containing foams 2 and 3 is in line with the other thermal properties found for these materials.   Foam 2 (TDI/PAPI) has intermediate heat resistance and nitrogen content, while foam 3 (PAPI) has the least nitrogen content, and the greatest thermal stability.

SUMMARY AND CONCLUSIONS

Rigid urethane foams are probably limited in high temperature applications, by the very nature of the thermal stability of the various components of which they are composed.   The experimental data, summarized in Table IV, indicate that the TDI foam (foam 1) has little compressive strength beyond the range of 130–140°C. and loses weight rapidly when

TABLE IV
Thermal Characteristics for Rigid Urethane Foams

Property	Approximate temperature limitation, °C.		
	Foam 1 (TDI)	Foam 2 (TDI/PAPI)	Foam 3 (PAPI)
Compressive strength	130–140	170–180	225–235
Significant weight loss	225	300	300
Heat aging at 175°C.	Poor	Fair	Good

heated above 225°C. The other type foams investigated (PAPI-containing materials) show improved thermal characteristics. A combination TDI/PAPI foam (foam 2) maintains good compressive properties up to 170–180°C., while a foam based solely on PAPI (foam 3) has adequate strength for many applications up to 225–235°C. Neither of the latter two foam systems exhibits significant weight loss below 300°C. Long-term heat-aging characteristics at 175°C. for the foams investigated also indicate that the PAPI materials retain a higher per cent of their original weight than the TDI foam.

The exact reason that the PAPI-based foams show good thermal stability is unknown. The nitrogen analysis of the foams indicates that PAPI-based materials may be slightly less crosslinked than the TDI foam. However, the data presented here shows this is not necessarily the sole criteria for good thermal properties. Many other facets must be taken into consideration, especially in regard to the PAPI foam. The bulkiness of the PAPI molecule, the increased aromatic content provided by its presence, the steric hindrance (protection of linkages) afforded by its size, or even the symmetry of this isocyanate could conceivably contribute to the increased thermal stability properties found for the rigid urethane foams based on this material. However, further investigation would certainly be necessary to verify these speculations.

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Résumé

Les caractéristiques de stabilité thermique de trois mousses d'uréthanes rigides préparées sur la base de diverses formulations en vue d'obtenir une grande variété de structure moléculaire, ont été étudiées par TGA, DTA, et par vieillissement thermique à long terme. Les valeurs de la force à la compression de ces mousses ont été également déterminées sur une gamme de température de −73°C à +232°C. Sur la base des tests exécutés, la mousse à base de toluène-diisocyanate présentait des caractéristiques de stabilité thermique les plus faibles des trois mousses étudiées. Une combinaison de toluène-diisocyanate–polyméthylène-polyphényl-isocyanate présentait des propriétés thermiques intermédiaires, tandis qu'une mousse à base uniquement de polyméthylène-polyphényl-isocyanate était de loin le meilleur du point de vue stabilité à température élevée.

Zusammenfassung

Die thermische Stabilität dreier starrer, nach verschiedenen Rezepten, mit einem weiten Bereich an Molekuülstruktur dargestellter Urethanschaumstoffe wurde mittels TGA, DTA, und Langzeithitzealterung untersucht. Weiters wurden an diesen Schaumstoffen Kompressionsfestigkeitswerte im Temperaturbereich von −73 bis +232°C bestimmt. Auf Grundlage aller durchgeführten Tests zeigte ein Toluoldiisocyanatschaumstoff die schlechteste thermische Stabilität unter dan drei untersuchten Systemen. Ein Kombination eines Toluoldiisocyanat–Polymethylenpolyphenylisocyanatschaumstoffs zeigte mittlere Eigenschaften bei erhöhter Temperatur, wöhrend ein Schaumstoff, der nur aus Polymethylenpolyphenylisocyanat bestand, die beste Gesamtstabilität bei hohen Temperaturen besass.