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POLYURETHANE/IMIDE MODIFIED FOAM

PDO 6989176, Final Report

J. Salary, Project Leader

Project Team:
O. A. Krueger
E. T. Walsh

August 1974

Prepared for the
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**Kansas City
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Project Leader:
J. Salary
Department 814

Project Team:
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Final Report

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POLYURETHANE/IMIDE MODIFIED FOAM

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Prepared by J. Salary, D/814, under PDO 6989176

A rigid polyurethane/imide foam was developed for high temperature applications. A study of model compounds was conducted to gain knowledge about the chemistry of the reaction between isocyanates and carboxylic anhydrides. The results indicated that the reaction proceeds through an active intermediate which decomposes into an imide and carbon dioxide. The addition of imide linkages into the polymer network of polyurethane foams significantly improves thermal stability. The material has potential use for structural applications.

THE BENDIX CORPORATION

KANSAS CITY DIVISION

KANSAS CITY, MISSOURI

A prime contractor for the

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SUMMARY

A study of the reaction between isocyanates and anhydrides was made to develop a polyurethane/imide-modified foam. The procedure consisted of preparing and characterizing model compounds prepared by reacting isocyanates with various anhydrides, preparing isocyanate prepolymers containing various percentages of anhydrides, and preparing foam formulations and testing thermal stability and compressive strength of foam samples based on these prepolymers. For the kinetics study, infrared analysis was used to determine the rate of reaction. Thermogravimetric analysis (TGA), differential scanning calorimeter analysis (DSC), thermomechanical analysis (TMA), isothermal heat aging, and compressive strength tests were performed on foam samples containing up to 10 percent by weight of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) in the prepolymer.

The results show that the reaction of isocyanates with anhydrides proceeds through an active intermediate to give an imide and carbon dioxide. The compressive strength of foams containing polymeric isocyanate (PAPI)/BTDA prepolymers increased as the reaction time of the prepolymer was increased.

Catalysts such as phenylmercuric hydroxide have no effect on the reaction between PAPI and BTDA at 400°F (204°C) after 2 hours. Long cure cycles and reaction times at high temperatures appear to promote the formation of imide linkages in the polymer network of polyurethane foams containing BTDA in the prepolymer, resulting in improved thermal stability.

DISCUSSION

SCOPE AND PURPOSE

This investigation was undertaken to study the chemistry of the reaction between isocyanates and anhydrides in order to develop a usable rigid polyurethane/imide-modified foam having high temperature capabilities.

ACTIVITY

Aromatic polyimide polymers are being developed and used in increasing amounts because of the thermal stability and resistance to fire inherent to the imide structure.¹ The common method of polyimide synthesis requires the dehydration of an amide acid formed from a diamine and an anhydride.^{2,3} An alternate approach to polyimide synthesis is reacting isocyanates with anhydrides to form imides and carbon dioxide.^{4,5} Despite the implied utility of this reaction for making polyimides, relatively little is known about it. The first report of an aromatic imide (N-phenylphthalimide) was recorded by Dains⁶ as the reaction product of phthalic anhydride (PA) and phenyl isothiocyanate. Hurd and Prapas⁷ prepared the same product from the reaction of phenyl isocyanate and phthalic anhydride. Using similar techniques Meyers⁸ synthesized polyimide polymers from the reaction of pyromellitic dianhydride (PMDA) with diphenylmethane diisocyanate (MDI) and suggested that the mechanism of the reaction involved a seven-membered ring.

Three steps were used to develop a rigid polyurethane/imide foam. The first step was the synthesis and analysis of model compounds. The second step was determining the rates and possibly the mechanisms of the reactions between isocyanates and various anhydrides. A third step consisted of preparing and testing rigid foams formulated from prepolymers, made from a polymeric isocyanate and carboxylic dianhydride, and an R-component (polyol component).

Materials

The following isocyanates were used in this investigation:

Phenyl Isocyanate (PI) 99.9 percent pure from Matheson Coleman & Bell;

4,4'-Diphenylmethane Diisocyanate (MDI) 99.9 percent pure;

Polymeric Isocyanate (PAPI) commercial grade from The Upjohn Company.

The following solvents were used in this investigation:

Dimethylacetamide (DMAc) Analyzed Reagent Grade from Fisher Scientific Company,

Dimethylformamide (DMF) Analyzed Reagent Grade from J. T. Baker Chemical Company.

The following anhydrides were used in this investigation:

Phthalic Anhydride (PA) high purity from Aldrich Chemical Company,

3,3',4,4'-Benzophenonetetracarboxylic Dianhydride (BTDA) practical grade from Fisher Scientific Company.

Apparatus and Procedures for Making Model Compounds

The apparatus consisted of a 250-cm³, three-necked Instatherm flask fitted with a thermometer, magnetic stirrer, and a carbon dioxide exhaust tube. The required amount of isocyanate was dissolved in 50 cm³ of DMac. A stoichiometric amount of anhydride was also dissolved in 50 cm³ of the same solvent. The dissolved constituents were added to the Instatherm flask. The mixture was heated at 40°C for 2.5 hours. The temperature of the mixture was increased to 100°C and held for 4 hours. The material was allowed to cool to approximately 50°C and the contents of the flask were transferred to a 400-cm³ beaker. A precipitate was formed and filtered from the cooled solvent. The filtrate was reduced to one-half of its original volume and a second precipitate was obtained. This precipitate was combined with the first yielding approximately 12.6 g of total product designated as Product A. The clear solution was added to excess water giving approximately 2.3 g of a second precipitate. This was washed with cold methanol and dried in a vacuum oven at 40°C. The second precipitate was designated as Product B. Infrared spectra were determined on each of the products using a Perkin-Elmer Model 457 grating spectrophotometer with potassium bromide pellets.

The solubility of each model compound was determined by placing approximately 10 mg of the compound in a test tube containing approximately 10 cm³ of one of the following solvents: water, ether, DMac, acetone, ethanol, DMF, dimethylsulfoxide, and toluene. Product A was insoluble in all of the solvents and Product B was soluble in all.

Infrared Method for Determining Isocyanate Concentration

A method was established by which infrared techniques could be used to follow the rate of consumption of isocyanate groups. The isocyanate group has a very intense and distinct peak absorption

at approximately 4.4 μm . The isocyanate peak height is proportional to the concentration of isocyanate groups. Solutions of PI and MDI in DMAc of known concentrations varying from 0.005 g/cm³ to 0.036 g/cm³ were prepared. The infrared spectrum of each solution was plotted for wavelengths of 2.5 to 15 μm . The peak height of each absorption as a function of its concentration was also plotted. These plots (Figures 1 and 2) are linear and served as calibration curves for determining the concentrations of isocyanate groups during the kinetic study.

Kinetic Study

The procedure used for this study was the same as for the preparation of the model compounds, with the exception that the reactions were carried out at 25°C. The Instatherm flask was equipped with a glass tube for withdrawing samples. An amount of sample was withdrawn from the reaction mixture necessary to make the concentration of the isocyanate groups equal to 0.024 g/cm³. The sample was then placed into a 25-cm³ volumetric flask and diluted to the mark with DMAc.

The first sample was taken as soon as the solutions of anhydride and isocyanate were mixed in the flask. The amount to be diluted was based on the equivalent weight of the isocyanate. For example, using PI, 6 cm³ was pipetted into a 25-cm³ flask and diluted to the mark with DMAc. The material was thoroughly mixed in the flask and a 1-cm³ aliquot was quickly withdrawn and placed into a 0.025-millimeter-thick infrared cell and the spectrum was recorded. The calibration curve was used to determine the concentration of isocyanate at a designated zero time. Other samples were taken at 1-hour intervals for 4 hours.

Plots of the reciprocal concentration of isocyanate groups against the reaction time were made for each kinetic run and are shown in Figures 3 and 4. The rate constants were taken as slopes of straight lines. The rate constants (cm³ min⁻¹eq⁻¹) were found to be 0.016 for PI and 0.031 for MDI, at 25°C.

Prepolymer Preparation

The apparatus used to prepare isocyanate prepolymers consisted of a 4-dm³ resin flask fitted with a Barret distilling receiver, stirrer, water cooled condenser, thermocouple, and a dry nitrogen inlet. PAPI was added to the reaction flask. The isocyanate was then heated to 300°F (149°C) with a heating mantle. When the temperature of the isocyanate had stabilized, the anhydride was slowly added to the PAPI. After all of the anhydride was added, the temperature of the reaction mixture was raised to 400°F (204°C) and held for time intervals of from 2 to 12 hours. The material was then allowed to cool slowly. After the material had cooled to 125°F (52°C), it was placed in a glass jar. The contents of

Figure 1. Calibration Curve for PI Concentration Versus Infrared Absorbance at 4.4 μm

Figure 2. Calibration Curve for MDI Concentration Versus Infrared Absorbance at 4.4 μm

Figure 3. Second Order Kinetic Plot for the Reaction of PI With PA

Figure 4. Second Order Kinetic Plot for the Reaction of MDI With PA

the jar were purged with dry nitrogen, and the jar was sealed. Table 1 is a listing of the amine equivalents and viscosities of the various prepolymers made from PAPI and BTDA.

Table 1. Amine Equivalent and Viscosity of Prepolymers Prepared From the Reaction of PAPI With BTDA

Prepolymer (Percent BTDA)		Reaction Time (Hours)	Amine Equivalent (Equivalent Grams)	Viscosity at 25°C (Centipoise)
PAPI/BTDA	5	2	140.0	16,000
PAPI/BTDA	5	4	144.1	1,920
PAPI/BTDA	5	8	147.0	3,840
PAPI/BTDA	5	12	151.3	7,040
PAPI/BTDA	7.5	2	140.7	1,856
PAPI/BTDA	7.5	4	143.6	2,560
PAPI/BTDA	7.5	8	149.2	17,920
PAPI/BTDA	7.5	12	153.9	19,840
PAPI/BTDA	10	2	143.1	3,392
PAPI/BTDA	10	4	143.6	4,480
PAPI/BTDA	10	8	146.5	12,640
PAPI/BTDA	10	12	148.5	120,320
Heat-Treated PAPI		8	144.0	2,304
Heat-Treated PAPI		12	148.5	4,480
Heat-Treated PAPI		15	152.0	6,720
PAPI/BTDA/ Phenylmercuric Hydroxide	7.5 0.1	2	144.2	6,560
PAPI/BTDA/ Phenylmercuric Hydroxide	7.5 1.0	2	152.3	7,040

Foam Block Preparation

All foam blocks were prepared by mixing polyol resin and isocyanate prepolymers together for approximately 2 minutes using a Conn-type impeller fitted to a high speed air-driven stirrer. Quantities of material adequate for the desired density were weighed

into a 6 by 6 by 1 inch (152 by 152 by 25 mm) metal mold. Foam rise was in the 6 inch (152 mm) direction. Table 2 gives the basic formulation for the foams made from various prepolymers listed in Table 1.

The mold preheat temperatures ranged from 120 to 125°F (48 to 52°C). The foam blocks were cured stepwise using a cure cycle of 325°F (156°C) for 8 hours, 400°F (204°C) for one hour, and 500°F (260°C) for another hour.

Table 2. Formulation for Rigid Polyurethane/Imide Modified Foams

Material	Foam Formulation (Grams)
E-Caprolactone/Pentaerythritol Polyester Polyol (OH Number $\approx$ 605)	100.0
Distilled Water	1.8
R-150 Cell Stabilizer*	6.0
Tris (Dimethylaminomethyl) Phenol (DMP-30)**	1.0
PAPI/BTDA Prepolymer	***
<p>*Houdry Air Products Company, Philadelphia, Pa. **Rohm and Haas, Philadelphia, Pa. ***The amount of material used in each foam formulation was based on the amine equivalent of the prepolymer listed in Table 1 calculated to provide an excess of 0.20 equivalents.</p>	

Physical and Thermal Testing

Compressive Strength

The compressive strength tests were conducted in accordance with American Society for Testing Materials Standard D-695 over a temperature range of 77 to 500°F (25 to 260°C). The test samples were cylinders 1.129 inches (28.7 mm) in diameter and 1.000 inch (25.4 mm) thick machined from a 6 by 6 by 1 inch (152.0 by 152.0 by 25.4 mm) molded foam block. The samples were conditioned for 1 hour at each test temperature and compressed perpendicular to the direction of foam rise at a loading rate of 0.050 inch (1.3 mm) per minute. Five determinations were made at each test temperature.

Thermogravimetric Analysis (TGA)

All TGA analyses were made with a duPont Thermogravimetric Analyzer Model 950. The samples were powdered, placed into a platinum pan, and weighed. The tests were performed in a dry nitrogen atmosphere and employed the following parameters: a sample weight of approximately 12 mg, a temperature range of 25 to 700°C, and a heating rate of 10°C per minute.

Differential Scanning Calorimeter (DSC)

The DSC curves were determined using a duPont Model 900 Differential Scanning Calorimeter operating at the following parameters.

Heating rate	10°C/min
Heating range	25 to 500°C
ΔT sensitivity	0.5°C/min
Reference	Empty pans
Dynamic atmosphere	Nitrogen
Gas flow rate	50 cm ³ /min
Sample weight	10 mg

Thermomechanical Analysis (TMA)

The softening points of all samples were determined using a duPont Model 940 Thermomechanical Analyzer. This apparatus uses a quartz probe coupled to a movable core differential transformer to sense displacement changes as small as 100 microinches (2.5 μ m). The softening points were obtained using an expansion probe which has a small, flat tip (0.025 inch diameter [0.63 mm]), at a loading of 5 grams. The samples were approximately 0.161 inch (4.09 mm) sections of foam blocks. The temperature range was from 25 to 500°C at a heating rate of 10°C per minute.

Isothermal Heat Aging

Foam blocks 1.129 inches (28.8 mm) in diameter and 1 inch (25.4 mm) thick were placed in aluminum pans and weighed to the nearest 0.1 mg. The samples were heated at 175°C in an air atmosphere for approximately 50 days. The weight of each sample was recorded at various time intervals.

Results of Model Compound Investigation

The reaction of isocyanates with anhydrides in a DMAc solution gives the corresponding imide (Product A), an active intermediate (Product B), and carbon dioxide. A possible reaction based on PI and PA is shown in the following equation.

Infrared spectra of Products A and B from the reaction of phthalic anhydride and phenylisocyanate are shown in Figures 5, 6, and 7. The spectra show no anhydride or isocyanate absorption and have the usual pair of imide bands at approximately 5.6 μ m and 5.8 μ m. The infrared spectrum of Product B is similar to that of Product A with the exception that the band at approximately 6.2 μ m is relatively strong in the spectrum of Product B while this band is very weak in Product A. It is this relatively intense band, at approximately 6.2 μ m which is indicative of a cyclic intermediate seven-membered ring that is assumed to be a constituent of the structure of Product B. The spectrum also indicates that part of the cyclic units of Product B have been converted to imide units. The seven-membered ring shown in Figure 8 has three carbonyl groups, two of which are accounted for by bands at approximately 5.5 μ m and 5.8 μ m. The band at approximately 6.2 μ m may be assigned to the amide carbonyl. It is this band which disappears as Product B is converted to Product A.

This can be seen in the spectrum of B (Figure 7) where the product was heated at 168°C for 24 hours. This seven-membered ring intermediate as postulated by Meyers⁸ is a plausible explanation of the mechanism by which this reaction proceeds. Farrissey and others¹ performed this reaction similarly and suggested that trace amounts of water present in the solvents and starting compounds hydrolyze the isocyanate into a diphenyl urea. The diphenylureas then react with carboxylic anhydrides to form the corresponding imide plus carbon dioxide and water. This is a possibility but from the evidence shown in this study, it is reasonable to assume a postulation similar to that of Meyers.

Figure 5. Infrared Spectrum of Product A From the Reaction of PI With PA

Figure 6. Infrared Spectrum of Product B From the Reaction of PI With PA

Figure 7. Infrared Spectrum of Product B From the Reaction of PI With PA After Heating at 168°C for 24 Hours

Figure 8. Proposed Structure of the Cyclic Intermediate Seven-Membered Ring Constituent of Product B

Results of Physical and Thermal Testing

Compressive Strength

The compressive strength of a rigid polyurethane foam is proportional to the density raised to a power. Since there is a density gradient in most foam samples, the compressive strengths of all samples studied were normalized to a density of 21 lb/ft³ (336 kg/m³). Table 3 shows the compressive strength and modulus of foam at the 10 percent deflection. These foam samples were based on prepolymers prepared from PAPI and different percentages of BTDA using various reaction times. The foam described by Smith and DeGisi (BKC Thermalthane 4003) was used as a standard.⁹

Referring to Table 3, the foam samples containing 7.5 percent BTDA in the prepolymer showed the highest compressive strength when tested at 400°F (204°C). This prepolymer was reacted for 12 hours. The samples containing 5 percent BTDA in the prepolymer and reacted for two hours showed the lowest compressive strength at this same temperature.

The data suggest that as the reaction time of the prepolymer is increased, the compressive strength is increased, indicating that longer reaction time generates more imide groups in the polymer chain and, thereby, improves thermal stability. At the lower test temperatures, -65°F (-53.9°C) and room temperature (25°C), there was little correlation between prepolymer reaction time and compressive strengths of the foam sample.

Table 3. Physical Properties* (Average) of Foam** at 10 Percent Deflection Using Different Percentages of Anhydride and Reaction Times

Prepolymer (Percent BTDA)	Reaction Time (Hours)	-65°F (-54°C)		77°F (25°C)		275°F (135°C)		325°F (163°C)		400°F (204°C)	
		Compressive Strength PSI (MPa)	Modulus PSI (MPa)	Compressive Strength PSI (MPa)	Modulus PSI (MPa)	Compressive Strength PSI (MPa)	Modulus PSI (MPa)	Compressive Strength PSI (MPa)	Modulus PSI (MPa)	Compressive Strength PSI (MPa)	Modulus PSI (MPa)
BKC Thermalthane 4003		1018.8 (70.2)	28,755 (198.4)	751.8 (5.18)	21,722 (149.7)	462.8 (3.19)	12,174 (83.9)	363.0 (2.50)	9,636 (66.4)	156.8 (1.08)	3064 (21.1)
BTDA/PAPI 5	2	630.8 (4.35)	22,542 (155.4)	542.7 (3.74)	18,731 (129.1)	255.8 (1.76)	6,105 (42.1)	138.2 (0.95)	2,862 (19.7)	104.5 (0.72)	2342 (16.1)
BTDA/PAPI 5	4	588.1 (4.05)	20,682 (142.6)	657.0 (3.77)	21,011 (144.8)	317.6 (2.19)	10,912 (75.2)	215.3 (1.48)	5,177 (35.7)	135.1 (0.93)	3135 (21.6)
BTDA/PAPI 5	8	836.7 (5.77)	29,039 (200.2)	633.5 (4.37)	22,821 (157.3)	384.1 (2.65)	15,604 (107.6)	320.6 (2.21)	11,924 (82.2)	173.5 (1.19)	4614 (31.8)
BTDA/PAPI 5	12	840.5 (5.79)	34,387 (207.1)	617.5 (4.26)	24,939 (171.9)	422.9 (2.92)	16,404 (133.1)	344.1 (2.37)	13,896 (95.8)	206.6 (1.42)	6915 (47.7)
BTDA/PAPI 7.5	2	663.4 (4.57)	26,440 (182.3)	558.8 (4.06)	20,775 (143.2)	266.8 (1.76)	6,870 (47.4)	272.8 (1.88)	9,664 (66.6)	109.7 (0.76)	2504 (17.26)
BTDA/PAPI 7.5	4	764.2 (5.27)	25,489 (175.7)	572.7 (3.95)	22,013 (151.8)	296.9 (2.05)	9,686 (66.8)	198.7 (1.37)	4,242 (29.2)	125.9 (0.87)	2859 (19.7)
BTDA/PAPI 7.5	8	812.5 (5.60)	28,381 (195.6)	626.4 (4.32)	25,957 (179.1)	391.12 (2.69)	14,295 (98.5)	326.3 (2.25)	10,604 (73.1)	144.8 (0.99)	3791 (26.1)
BTDA/PAPI 7.5	12	773.2 (5.33)	32,222 (222.1)	636.3 (4.39)	23,516 (162.1)	422.7 (2.91)	14,938 (102.9)	419.7 (2.89)	14,269 (98.4)	233.3 (1.61)	8000 (55.2)
BTDA/PAPI 10	2	620.4 (4.28)	21,069 (145.2)	564.2 (3.89)	20,413 (140.7)	276.9 (1.91)	9,859 (67.9)	212.2 (1.46)	4,907 (33.8)	114.3 (0.79)	2514 (17.3)
BTDA/PAPI 10	4	915.2 (6.31)	33,379 (230.1)	656.8 (4.53)	25,086 (172.9)	279.6 (2.62)	15,009 (103.5)	279.2 (1.92)	7,722 (53.2)	155.3 (1.07)	3335 (22.9)
BTDA/PAPI 10	8	716.9 (4.94)	27,785 (191.5)	706.5 (4.87)	27,397 (188.9)	434.6 (2.99)	16,997 (117.2)	352.3 (2.43)	13,775 (94.9)	208.7 (1.44)	5942 (40.9)
BTDA/PAPI 10	12	866.6 (5.97)	27,712 (191.0)	764.0 (5.27)	20,782 (143.3)	472.0 (3.25)	15,176 (104.6)	413.4 (2.85)	12,495 (86.1)	224.7 (1.55)	6683 (46.1)

*Compressive strengths were normalized to a density of 21 lb/ft³ (336 Kg/m³). The data were derived from five samples at each test temperature. The samples were machined from 6 by 6 by 1 inch (152.2 by 152.2 by 25.4 mm) molded foam blocks.

**E-Caprolactone/Pentaerythritol Polyester Polyol-PAPI/BTDA Prepolymer

Carleton and others¹⁰ reported results of catalyst on the reaction between polyisocyanates and carboxylic anhydrides. They suggested that catalysts such as phenylmercuric hydroxide (PhHgOH) give markedly improved reaction rates. Table 4 shows the average compressive strength and modulus at the 10 percent deflection of foam samples based on prepolymers containing different percentages of BTDA. In this group of samples, PhHgOH was used as a catalyst in the preparation of one of the prepolymers. The results in Table 4 show however the foam samples containing heat-treated PAPI (15 hours) gave the highest compressive strength when tested at 500°F (260°C). The strength retention exhibited by the heat-treated PAPI based foam sample at this temperature could be caused by the formation of trimers in the prepolymer. Trimerization generally proceeds most readily in the presence of trace amounts of some active hydrogens. A possible mechanism is shown in the following equation.

Isocyanate trimers are known to be stable to at least 200°C.⁵ The samples containing 10 percent BTDA in the prepolymer also show high compressive strength at this temperature. However, the foam samples containing PhHgOH as a catalyst for the prepolymer reaction show inferior compressive strength, indicating the catalyst had little effect on the formation of imide linkages. In addition, longer reaction times used for the preparation of PAPI/BTDA prepolymer formed more imide linkages and appear to improve the stability of the foam samples at elevated temperatures.

Table 4. Physical Properties* (Average) of Foam** at 10 Percent Deflection Using Different Percentages of Anhydride, Reaction Times, and Catalyst

Prepolymer (Percent BTDA)	Reaction Time, (Hours)	-65°F (-54°C)		77°F (25°C)		275°F (135°C)		325°F (163°C)		400°F (204°C)		500°F (260°C)	
		Compressive Strength PSI (MPa)	Modulus PSI (MPa)	Compressive Strength PSI (MPa)	Modulus PSI (MPa)	Compressive Strength PSI (MPa)	Modulus PSI (MPa)	Compressive Strength PSI (MPa)	Modulus PSI (MPa)	Compressive Strength PSI (MPa)	Modulus PSI (MPa)	Compressive Strength PSI (MPa)	Modulus PSI (MPa)
Heat-Treated PAPI	8	752.8 (5.19)	37,885 (261.2)	662.5 (4.29)	27,852 (192.0)	442.0 (3.05)	16,572 (114.2)	409.9 (2.82)	15,539 (107.1)	245.8 (1.69)	6002 (41.4)		
BTDA/PAPI 7.5 PhHgOH 1.0	2	943.7 (6.51)	30,766 (212.1)	703.7 (4.85)	27,053 (186.5)	439.5 (3.03)	15,704 (108.3)	363.6 (2.51)	12,368 (82.3)	213.3 (1.47)	4465 (30.8)		
BTDA/PAPI 7.5	2	866.9 (6.11)	23,760 (163.8)	632.4 (4.36)	22,020 (151.8)	385.2 (2.66)	13,689 (94.4)	328.0 (2.26)	9,212 (63.5)	175.6 (1.21)	3656 (25.2)	60.0 (0.42)	1241 (8.55)
BTDA/PAPI 7.5	8	831.4 (5.75)	29,746 (205.1)	750.3 (5.17)	25,080 (172.9)	464.3 (3.20)	14,249 (98.2)	393.0 (2.71)	12,773 (88.1)	226.4 (1.56)	5932 (40.9)	21.3 (0.15)	345 (2.38)
BTDA/PAPI 10	4	1014.0 (6.99)	33,872 (233.5)	816.4 (5.63)	28,083 (193.6)	483.3 (3.33)	13,133 (90.5)	416.2 (2.87)	13,457 (92.8)	219.5 (1.51)	5100 (35.2)	41.4 (0.28)	766 (5.28)
BTDA/PAPI 10	8	1024.0 (7.06)	29,564 (203.8)	768.1 (5.29)	24,187 (166.7)	521.9 (3.59)	15,652 (107.9)	402.9 (2.78)	12,423 (85.6)	250.8 (1.73)	5125 (35.3)	239.8 (1.65)	3143 (21.7)
Heat-Treated PAPI	15	1051.4 (7.27)	36,030 (248.4)	839.1 (5.78)	28,258 (194.8)	436.2 (3.01)	14,327 (98.8)	341.3 (2.35)	9,875 (68.1)	214.7 (1.48)	4163 (28.7)	345.8 (2.38)	5977 (41.2)

*The compressive strengths were normalized to a density of 21 lb/ft³ (336 kg/m³). The data were derived from five samples at each temperature. The samples were machined from 6 by 6 by 1 inch (152 by 152 by 25.4 mm) molded foam blocks.

**E-Caprolactone/Pentaerythritol Polyester Polyol-PAPI/BTDA Prepolymer

Table 5. Physical Properties* (Average) of Foam** at 10 Percent Deflection Using Longer Cure Cycles

Prepolymer (Percent BTDA)	Reaction Time (Hours)	-65°F (-54°C)		77°F (25°C)		275°F (135°C)		325°F (163°C)		400°F (204°C)		500°F (260°C)	
		Compressive Strength PSI (MPa)	Modulus PSI (MPa)	Compressive Strength PSI (MPa)	Modulus PSI (MPa)	Compressive Strength PSI (MPa)	Modulus PSI (MPa)	Compressive Strength PSI (MPa)	Modulus PSI (MPa)	Compressive Strength PSI (MPa)	Modulus PSI (MPa)	Compressive Strength PSI (MPa)	Modulus PSI (MPa)
BTDA/PAPI 5	12	725.0 (5.18)	24,270 (167.3)	543.6 (3.75)	14,895 (102.7)	459.1 (3.16)	16,316 (112.5)	347.5 (2.39)	11,351 (78.2)	214.9 (1.48)	5970 (41.2)	107.2 (7.39)	1958 (13.5)
BTDA/PAPI 7.5	12	788.1 (5.44)	26,898 (185.4)	692.9 (4.78)	21,518 (148.3)	445.6 (3.07)	15,161 (104.5)	296.3 (2.04)	9,532 (65.7)	161.3 (1.11)	3942 (27.2)	45.6 (0.31)	817 (5.63)
BTDA/PAPI 10	12	768.9 (5.30)	29,952 (206.5)	649.5 (4.78)	20,825 (143.6)	449.2 (3.09)	17,983 (123.9)	303.3 (2.09)	9,529 (65.7)	165.6 (1.14)	3766 (25.9)	26.9 (0.18)	457 (3.15)
Heat-Treated PAPI	12	1003.2 (6.92)	32,124 (221.5)	982.1 (6.77)	25,441 (175.4)	611.4 (4.21)	15,092 (104.0)	425.9 (2.94)	9,898 (68.2)	203.7 (1.40)	3995 (27.5)	28.9 (0.19)	455 (3.14)
BKC Thermalhane 4003		723.0 (4.98)	24,980 (172.2)	654.3 (4.51)	21,753 (149.9)	370.5 (2.55)	14,117 (97.3)	281.0 (1.94)	10,530 (72.6)	143.0 (0.98)	2893 (19.9)	40.7 (0.28)	893 (6.16)

*The compressive strengths were normalized to a density of 21 lb/ft³ (336 kg/m³). The data were derived from five samples at each temperature.

**E-Caprolactone/Pentaerythritol Polyester Polyol-PAPI/BTDA Prepolymer

Cure cycles also appear to affect the compressive strength retention of the foam samples based on PAPI/BTDA prepolymers. Longer cure cycles drive the reaction between isocyanate groups and anhydride groups further toward completion. This would cause more imide groups to be formed in the polymer network thereby improving thermal stability. Several 6 by 6 by 1 inch (152 by 152 by 25.4 mm) foam blocks based on PAPI/BTDA prepolymers with identical reaction times were prepared using the following cure cycle: 325°F (135°C) for 8 hours, 400°F (204°C) for 2 hours, and 500°F (260°C) for an additional 2 hours. The compressive strength results of these foam samples are given in Table 5.

The results show the foam samples containing 5 percent BTDA in the prepolymer had the highest compressive strength retention at 400°F (204°C) and 500°F (260°C). At temperatures ranging from -65 to 325°F (-54 to 163°C), the samples that contained heat treated PAPI showed the highest strengths. The reaction between the isocyanate groups and anhydride groups seems to have gone further toward completion in the samples containing 5 percent BTDA in the prepolymer than in the other samples. It appears that more imide groups were formed in these samples, promoting better thermal stability.

Thermal Analyses

Table 6 shows the thermogravimetric analysis (TGA) data of foams containing different percentages of BTDA in the prepolymer. Figure 9 gives a typical TGA curve for foam samples. The onset of weight loss ranges from approximately 285 to 312°C. Most of the foam samples containing BTDA retain higher percentages of weight than did the samples without BTDA, indicating the stability of the samples was improved by the imide groups.

Table 7 shows differential scanning calorimeter analysis (DSC) data of foams containing BTDA. Figure 10 gives a typical DSC curve of such samples. There are two transitions seen in the DSC profiles of the foam samples studied. One is an endothermic transition occurring at approximately 300°C. The other is an exothermic transition occurring at approximately 360°C. The data in the table show both the endothermic and exothermic transitions are shifted to higher temperature in the samples containing BTDA than in those without the anhydride.

Thermomechanical analysis (TMA) data for these foam samples are given in Table 8 and a typical TMA curve is shown in Figure 11. With the exception of the sample containing heat treated PAPI, the TMA results in good agreement with TGA and DSC results in that the foam samples with imide groups show better thermal properties.

Table 6. Thermogravimetric Analysis Data of Foams Made From E-Caprolactone/Pentaerythritol Polyester Polyol and PAPI/BTDA Prepolymers Using Different Reaction Times and Percentages of the Anhydride

Prepolymer (Percent BTDA)	Reaction Time (Hours)	Onset of Weight (°C)	Weight Retained at 650°C (Percent)
PAPI/BTDA 5	2	310	27.75
PAPI/BTDA 5	4	311	25.00
PAPI/BTDA 5	8	305	25.00
PAPI/BTDA 5	12	300	25.45
PAPI/BTDA 7.5	2	304	27.50
PAPI/BTDA 7.5	4	304	30.75
PAPI/BTDA 7.5	8	306	28.75
PAPI/BTDA 7.5	12	287	33.25
PAPI/BTDA 10	2	312	34.75
PAPI/BTDA 10	4	302	33.25
PAPI/BTDA 10	8	305	27.50
PAPI/BTDA 10	12	295	26.85
Heated-Treated PAPI	15	285	21.00
BKC Thermalthane 4003		305	20.00

The results of thermal analyses of foam samples based on BTDA prepolymer with the same reaction times using longer cure cycles are shown in Table 9. The TGA results showed the foam samples containing 5 percent and 7.5 percent BTDA in the prepolymer had identical percentages of weight retention at 650°C. The samples containing heat treated PAPI and 10 percent BTDA in the prepolymer

Figure 9. Thermogravimetric Analysis of Foam Containing 10 Percent BTDA in the Prepolymer

Table 7. Differential Scanning Calorimeter Analysis Data of Foams Made From E-Caprolactone/Pentaerythritol Polyester Polyol and PAPI/BTDA Prepolymers Using Different Reaction Times and Percentages of the Anhydride

Prepolymer (Percent BTDA)	Reaction Time (Hours)	Endothermic Transition (°C)	Exothermic Transition (°C)
PAPI/BTDA 5	2	324	360
PAPI/BTDA 5	4	335	360
PAPI/BTDA 5	8	325	362
PAPI/BTDA 5	12	337	368
PAPI/BTDA 7.5	2	312	365
PAPI/BTDA 7.5	4	320	366
PAPI/BTDA 7.5	8	335	365
PAPI/BTDA 7.5	12	335	366
PAPI/BTDA 10	2	330	363
PAPI/BTDA 10	4	326	368
PAPI/BTDA 10	8	336	365
PAPI/BTDA 10	12	336	370
Heat-Treated PAPI	15	325	360
BKC Thermalthane 4003		315	352

also retained about the same percent of weight at this temperature. The samples without BTDA or heat treated PAPI retained the lowest percent of weight. The DSC results of the samples containing 5 percent BTDA show that both the endothermic and exothermic transitions are shifted to higher temperatures than for the others. The foams without BTDA show the lowest endothermic and exothermic transitions. The TMA results are in good agreement with the TGA and DSC results in that the foam samples containing 5 percent BTDA also show the highest softening temperature while the samples without BTDA show the lowest.

Figure 10. Differential Scanning Calorimeter Analysis of Foam Containing 5 Percent BTDA in the Prepolymer

Table 8. Thermomechanical Analysis Data of Foams Made From E-Caprolactone/Pentaerythritol Polyester Polyol and PAPI/BTDA Prepolymers Using Different Reaction Times and Percentages of the Anhydride

Prepolymer (Percent BTDA)	Reaction Time (Hours)	Softening Point (°C)
PAPI/BTDA 5	2	235
PAPI/BTDA 5	4	244
PAPI/BTDA 5	8	244
PAPI/BTDA 5	12	249
PAPI/BTDA 7.5	2	222
PAPI/BTDA 7.5	4	232
PAPI/BTDA 7.5	8	246
PAPI/BTDA 7.5	12	229
PAPI/BTDA 10	2	228
PAPI/BTDA 10	4	236
PAPI/BTDA 10	8	246
PAPI/BTDA 10	12	215
Heat-Treated PAPI	15	260
BKC Thermalthane 4003		221

Table 9: Thermal Analysis of Foams* Made From Prepolymers Using Longer Cure Cycles**

Test Method	Prepolymers				
	PAPI/BTDA (5 Percent Anhydride)***	PAPI/BTDA (7.5 Percent Anhydride)***	PAPI/BTDA (10 Percent Anhydride)***	Heated PAPI	BKC Thermalthane 4003
TGA Onset of Weight Loss (°C)	290	290	280	285	285
TGA Weight Retained at 650°C (Percent)	26.4	26.4	30	31	14.5
TMA Softening Point (°C)	251	231	231	236	212
DSC Endothermic Transition (°C)	330	325	326	325	315
Exothermic Transition (°C)	370	370	360	365	360
<p>*E-Caprolactone/Pentaerythritol Polyester Polyol - PAPI/BTDA Prepolymer **Cure Cycle: 325°F (135°C) for 8 hours, 400°F (204°C) for 2 hours, and 500°F (260°C) for an additional 2 hours. ***Reaction time 12 hours at 400°F (204°C).</p>

Figure 11. Thermomechanical Analysis of Foam Containing 5 Percent BTDA in the Prepolymer

Isothermal Heat Aging

Isothermal heat aging is another measure of thermal stability. The foam samples in this study were placed in a forced-air laboratory oven and heated at 347°F (175°C) for approximately 50 days. The sample weights were recorded periodically. The data were derived from an average of two samples from a test block. Figure 12 compares plots of percent weight loss versus days.

These results are also in good agreement with the TGA, DSC, TMA, and compressive strength results in that the foams containing 5 percent BTDA in the prepolymer showed better thermal stability than the other materials investigated.

- 1 PAPI/BTDA 5 PERCENT REACTED FOR 2 HOURS AT 400°F (204°C)
- 2 PAPI/BTDA 5 PERCENT REACTED FOR 12 HOURS AT 400°F (204°C)
- 3 PAPI/BTDA 10 PERCENT REACTED FOR 12 HOURS AT 400°F (204°C)
- 4 BKC THERMALTHANE 4003
- 5 PAPI/BTDA 5 PERCENT REACTED FOR 8 HOURS AT 400°F (204°C)

Figure 12. Isothermal Heat Aging of Foam
Based on PAPI/BTDA Prepolymers

ACCOMPLISHMENTS

A series of isocyanate prepolymers based on PAPI and BTDA, suitable for the incorporation of imide linkages into rigid urethane foam systems, has been developed. A foam system based on one of the prepolymers containing 5 percent BTDA shows thermal stability superior to a high temperature foam system currently used in production. This material, when cured using a programmed schedule up to 500°F (260°C), could be satisfactorily utilized at a service temperature of 400°F (204°C). The foam system can be processed in a conventional manner and is capable of being used in the manufacture of molded-to-size parts.

REFERENCES

- ¹William J. Farrissey, Jr., James S. Rose and Peter S. Carleton, "Preparation of a Polyimide Foam," *Journal of Applied Polymer Science*, Volume 14, 1970, p 1093.
- ²R. A. Dine-Hart and W. W. Wright, "Preparation and Fabrication of Aromatic Polyimides," *Journal of Applied Polymer Science*, Volume 11, Number 5, May 1965, p 609.
- ³C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Oliver, "Aromatic Polypyromellitimides From Aromatic Polyamic Acids," *Journal of Polymer Science*, Volume 3, Part A, 1965, p 1373.
- ⁴A. Wurtz, "Mémoire Sur les Éthers Cyaniques et Cyaniques, et Sur la Constitution des Amides," *Annales DE Chimie ET DE Physique*, Volume 42, Number 3, 1854, p 54.
- ⁵J. A. Saunders and D. C. Frisch, *Polyurethanes; Chemistry and Technology*, Part 1, Interscience Publishers, New York, 1963, p 81, *Ibid*, 1963, p 96.
- ⁶F. B. Dains, "Action of Certain Acid Reagents" *Journal of American Chemical Society*, Volume 22, 1900, p 186.
- ⁷C. D. Hurd and A. G. Prapas, Preparation of "Acyclic Imides" *Journal of Organic Chemistry*, Volume 24, 1969, p 338.
- ⁸R. A. Meyers, "The Polymerization of Pyromellitic Dianhydride With Diphenylmethane Diisocyanate" *Journal of Polymer Science*, Volume 7, Number 10, Part A-1, 1969 p 2757.
- ⁹C. H. Smith and S. L. DeGisi, "Structural Application Characteristics of a Rigid Urethane Foam System," *Journal of Cellular Plastics*, Volume 4, Number 10, October, 1968, p 386.
- ¹⁰Peter S. Carleton, North Branford, William J. Farrissey Jr. and James S. Rose, U. S. Patent 3,701,756 (October 31, 1973) to Upjohn Company.

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