Synthesis and Characterization of Isocyanate-Terminated Polyurethane Prepolymers

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Synopsis

Using statistically designed experiments, seven variables were investigated to determine their effect on the physical and mechanical properties of isocyanate-terminated polyurethane prepolymers. The choice of catalyst (dibutyltin diacetate, T-1, or stannous octoate, T-9) along with the ratio of diol to triol were found to most significantly control the prepolymer properties. Other variables such as reaction temperature, reaction time, and order of polyol addition did not affect the system. In comparing the two catalysts, T-9 was found to be concentration sensitive, yielding low-viscosity prepolymers at the lower catalyst level and higher viscosity, unstable materials at the higher catalyst level. No evidence was found to show concentration sensitivity of T-1. A series of prepolymers based on varying ratios of diol to triol were synthesized, and their physical and mechanical properties are reported.

INTRODUCTION

Urethane-based materials are of commercial interest in many applications because of their excellent properties such as abrasion resistance, low-temperature flexibility, high strength, and environmental and chemical resistance. There are various ways of combining polyols and isocyanates in order to produce a polyurethane product. One of the methods involves the preparation of an isocyanate-terminated polyurethane prepolymer intermediate. This active prepolymer may or may not be compounded with fillers, solvents, plasticizers, or catalysts before it is reacted with water, polyols, or polyamines to yield the final product.

While there is a modest number of literature references concerned with the preparation of isocyanate-terminated polyurethane prepolymers as product intermediates, there is a lack of information relating to the optimization of reaction variables for manufacturing this material. In general, even when catalysts are employed, fairly lengthy cook times at relatively high cook temperatures are utilized. For example, when the prepolymer was prepared in the presence of a catalyst but without the use of a solvent, the synthesis is reported as being accomplished either by a one-step method[1,2] or a two-step method where the catalyst was added after a certain prereaction was completed.[3,4] Again, fairly lengthy reaction times are cited, even in the instances where reaction temperatures in excess of 90°C are used. In instances where the prepolymer was to be used as a coating,[5] for films[6,7] or in a varnish,[8] the prepolymer was reported as

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being prepared in a solvent and in the absence of a catalyst. Various times from several hours at 90°C to three days at room temperature were employed in carrying out the reaction.

The object of the work reported in this paper was the optimization of the reaction which yields isocyanate-terminated polyurethane prepolymers. More specifically, a preparation procedure was being sought that would, for a given formulation, yield prepolymers under the mildest reaction conditions which would have the lowest viscosities and the best mechanical properties.

EXPERIMENTAL

Materials. Diphenylmethane diisocyanate (The Upjohn Company), P-2010 (2000 mol. weight diol) and TP-4040 (4100 mol. weight triol) polyols (BASF-Wyandotte), HB-40 hydrogenated terphenyl plasticizer (Monsanto), stannous octoate, and dibutyltin diacetate catalysts (M&T Chemical, Inc.) were all used without further purification.

Preparation of Prepolymer. In all cases, diphenylmethane diisocyanate (MDI, 12 parts by weight), plasticizer (20 parts), and catalyst (0.025 or 0.0063 parts) were placed in a glass resin kettle that was fitted with a stirring motor, thermometer, and nitrogen inlet and outlet. The desired temperature was maintained using a Glas-Col heating mantle. Additions of the polyols (67 parts) were made either with a wide-bore dropping funnel or, when required, with direct addition, in portions, from a beaker. A constant level of plasticizer (20% by weight) was utilized in all the prepolymers in order to maintain a workable viscosity range at the low free isocyanate content of these prepolymers.

Testing Procedures. The per cent free isocyanate was determined using standard analytical techniques involving the reaction of dibutylamine with the isocyanate and back titrating the excess amine with hydrochloric acid to a bromphenol blue endpoint.

All viscosity measurements are reported in pascal-seconds (Pa·s; 1 mPa·s = 1 cp) and were made on prepolymer samples that had been equilibrated in a 180-ml-wide-mouth bottle for 24 hr at 25° ± 0.1°C. A Brookfield viscometer using a #6 spindle at 10 revolutions per minute was used for the viscosity measurements. Stability during storage was maintained by blanketing the prepolymer with dry nitrogen prior to sealing the bottles.

Samples for gel permeation chromatography (GPC) were prepared by capping the active prepolymer with methanol. The samples were run on a Waters Model GPC-200 in tetrahydrofuran solution (0.25% by weight) on a column standardized against polystyrene. The resultant GPC curves were then analyzed using the first and second moment of the distribution to give the number- ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights of the polymer samples.

The mechanical properties of the moisture-cured prepolymer were tested according to ASTM 412. Films approximately 2.5-mm thick were cast on Teflon and allowed to cure for 14 days at ambient conditions. A minimum of three dumbbell specimens were cut from each film and tested to give 100% modulus, ultimate elongation, and ultimate tensile strength. The 100% modulus and ultimate tensile strengths are reported in kilopascals [kPa; (psi) (6.9) = kPa]. Care was taken to exclude any obvious flaw, such as a bubble, from the narrow portion of the sample.

TABLE I
Viscosity and Isocyanate Content of Polyurethane Prepolymers

Series	Addition time, hr	Cook time, hr	Addition method[a]	Cook temperature, °C	% NCO	Viscosity at 25° ± 0.1°C, Pa·s	Remarks
A1	1.0	0.5	dropwise	68–73	—	gelled	gelled
A2	1.0	0.5	dropwise	68–73	1.50	44.0	microgel
A3	1.0	0.5	dropwise	68–73	1.25	72.0	microgel
A4	1.0	0.5	dropwise	68–73	1.36	44.0	microgel
B1	1.0	0.5	portions	69–73	1.35	56.0	microgel
B2	1.0	0.5	portions	69–73	1.23	112.0	microgel
B3	1.0	0.5	portions	69–73	1.30	84.0	microgel
C1	1.0	0.6	portions	69–71	1.32	48.0	no gel
C2	1.0	0.5	portions	69–71	1.33	46.0	no gel
C3	1.0	0.5	portions	69–71	1.32	46.4	no gel
C4	1.0	0.5	portions	69–71	1.45	44.0	no gel
C5	1.0	0.5	portions	69–71	1.45	38.0	no gel
D1	1.0	1.0	portions	69–71	1.32	40.0	no gel
D2	1.0	1.0	portions	69–71	1.32	40.0	no gel

[a] Diol was added first, followed by the triol for series A-C. In series D, the diol and triol were premixed, then added in small portions over a 1.0 hour period.

DISCUSSION OF EXPERIMENTAL RESULTS

Reactor Design

The optimization of the reaction to yield an isocyanate-terminated polyurethane prepolymer was investigated using statistically designed experiments. However, in order for this approach to be valid, batch-to-batch variability in the properties of prepolymers prepared under identical conditions had to be minimized. Under the conditions stated in Table I, prepolymers of series A and B were synthesized in straight-walled resin kettles using a paddle stirrer. A wide range of viscosities was observed, and the prepolymers were found to contain small lumps of microgel. In series C and D, a glass resin kettle with four indentations was used in conjunction with a turbine blade stirrer. This reactor gave better agitation and much more reproducible viscosities. In addition to the consistent viscosities, no gel particles were found in the prepolymers.

Statistical Analysis

A total of seven variables was chosen as having a possible effect on the properties of the prepolymers. With such a large number of controlled variables, it was decided that a fractional factorial design[9] of the experiments would give the maximum indication as to which variables were the most important with a minimum number of experiments.

A 2^{7-4} design with foldover was initially set up using ABD, ACE, BCF, and ABCG as one set of generators and −ABD, −ACE, −BCF, and ABCG as the other set of generators. These two designs were then combined into a 2^{7-3} design with BCD, ACD, and ABC as generators. Table II (a and b) lists the study variables, the levels for these variables, and the 2^{7-3} statistical design. Two separate sta-

TABLE II
Statistical Analyses

a. Control Variables

Designation	Variable	+	−
A	Cook time	1.5 hr	0.5 hr
B	Cook Temperature	71°C	49°C
C	Addition rate	portions	dropwise
D	Addition time	1.0 hr	0.5 hr
E	Ratio of diol to triol	2.85:1 (w/w)	4.0:1 (w/w)
F	Addition	premix polyols	separate (diol then triol)
G	Catalyst	stannous octoate (T-9)	dibutyltin diacetate (T-1)

b. 2^{7-3} Design

Series	A	B	C	D	E	F	G
E1	−	−	−	−	−	−	−
E2	+	−	−	−	−	+	+
E3	−	+	−	−	+	−	+
E4	+	+	−	−	+	+	−
E5	−	−	+	−	+	+	+
E6	+	−	+	−	+	−	−
E7	−	+	+	−	−	+	−
E8	+	+	+	−	−	−	+
E9	−	−	−	+	+	+	−
E10	+	−	−	+	+	−	+
E11	−	+	−	+	−	+	+
E12	+	+	−	+	−	−	−
E13	−	−	+	+	−	−	+
E14	+	−	+	+	−	+	−
E15	−	+	+	+	+	−	−
E16	+	+	+	+	+	+	+

tistical analyses were run, one using 0.025% catalyst (high concentration) and one using 0.0063% catalyst (low concentration).

Observations for use in the statistical analyses were made on both the physical and mechanical properties of the prepolymers. Specific physical property measurements were made on % free NCO, viscosity at 25°C after 24 and 72 hr, and the viscosity at 25°C after a 72-hr heat aging test at 54°C. Weight-average molecular weight ($\bar{M}_w$) determinations were made using GPC on samples of prepolymer at various time intervals. The effect of the variables on the mechanical properties of the prepolymer was followed by determining the 100% modulus, ultimate elongation, and ultimate tensile strength of the cured prepolymers. The statistical analysis experiments were performed in random order. However, the data in Tables III, IV, and V have been reordered to coincide with the design in Table IIb.

The viscosity data for the prepolymers synthesized with either a high or low catalyst concentration are given in Table IIIa. These data were then analyzed using the Yates algorithm,[10] and the relative effect of each variable on viscosity was determined. Table IIIb lists the variables that appeared to affect the viscosities of the prepolymers. No data are given for the measurement of the per cent free isocyanate because none of the variables under study significantly

TABLE III
Results and Conclusions on Analyses Based on Physical Properties

a. Viscosity and % NCO

Series[a]	% NCO	Viscosity at 25° ± 0.1°C, Pa·s			Series[d]	Viscosity at 25° ± 0.1°C, Pa·s		
		24 hr[b]	72 hr[b]	72 hr[c]		24 hr[b]	72 hr[b]	72 hr[c]
E1	1.40	36.8	35.2	36.0	F1	40.0	41.6	44.0
E2	1.37	40.0	40.0	64.0	F2	30.4	30.4	30.4
E3	1.28	41.6	40.0	183.0	F3	33.6	36.0	36.0
E4	1.36	38.4	36.8	43.2	F4	36.0	40.0	40.0
E5	1.30	32.8	31.2	43.2	F5	28.0	28.0	29.6
E6	1.32	38.4	37.6	44.0	F6	40.0	40.0	42.4
E7	1.41	33.6	32.8	36.0	F7	34.4	36.8	36.8
E8	1.42	36.0	36.8	114.0	F8	32.0	32.0	32.0
E9	1.43	38.0	41.6	44.0	F9	37.6	36.8	38.4
E10	1.26	56.0	52.8	78.4	F10	33.6	35.2	39.2
E11	1.40	32.0	32.8	46.4	F11	32.0	33.6	33.6
E12	1.41	38.4	40.8	40.8	F12	40.0	44.0	44.0
E13	1.37	32.8	36.0	95.2	F13	26.4	28.8	29.6
E14	1.39	36.0	35.2	35.2	F14	36.8	38.4	38.4
E15	1.45	35.2	33.6	33.6	F15	40.0	42.4	42.4
E16	1.38	44.0	40.8	176.0	F16	31.2	32.0	32.0

b. Conclusions—Reaction Conditions that Tended to Yield Prepolymers with Lower Viscosities

Catalyst concentration	Viscosity, (24 hr)	Viscosity (72 hr)	Viscosity (72 hr at 54°C)
High tin (0.025%)	0.5 hr cook time 4.0:1 polyol ratio	0.5 hr cook time 4.0:1 polyol ratio portion additions	T-1
Low tin (0.0063%)	4.0:1 polyol ratio T-9	4.0:1 polyol ratio T-9	4.0:1 polyol ratio T-9

[a] Catalyst concentration 0.025%. [b] Aged at 25°C. [c] Aged at 54°C. [d] Catalyst concen-
[b] Aged at 25° C.
[c] Aged at 54° C.
[d] Catalyst concentration 0.0063%.

controlled this parameter. For the high catalyst concentration (series E), the prepolymers with the lowest viscosities, after being stored at ambient conditions, were those prepared with the high ratio of diol to triol and with the short cook time. With heat aging, any effect of cook time is masked by the large viscosity increases that are observed with some of the T-9 systems. It is because of the instability to heat aging of the T-9 prepolymers that T-1 is reported as being significant in yielding lower viscosities under the aging conditions.

For prepolymers synthesized with low catalyst concentrations (series F), two variables were significant in yielding materials with lower viscosities. They were the high ratio of diol to triol and T-9. The reason T-9 was found to be an important variable in this case can be seen in Figure 1. Varying the concentration of T-1 did not change the range of prepolymer viscosities. However, with the lowering of the concentration of T-9, a decided decrease in prepolymer viscosity

TABLE IV
Results and Conclusions of Analyses Based on Weight-Average Molecular Weight ($\overline{M}_w$)

a. Results

| Series[a] | $\overline{M}_w \times 10^{-3}$ | | | |
	0 hr[b]	24 hr[c]	72 hr[c]	72 hr[d]
F-1	23.0	23.3	22.6	23.9
F-2	19.2	18.1	19.6	18.4
F-3	21.6	21.4	21.6	22.1
F-4	19.5	20.9	21.2	21.5
F-5	9.8	19.2	18.9	19.0
F-6	23.2	23.2	22.2	22.9
F-7	19.9	21.2	20.7	20.9
F-8	21.0	21.1	20.6	20.6
F-9	20.3	21.2	21.0	22.5
F-10	20.9	20.7	22.5	22.1
F-11	14.1	19.2	19.9	19.1
F-12	23.0	23.2	22.2	22.9
F-13	6.9	19.5	20.0	20.2
F-14	21.6	20.7	21.9	20.7
F-15	22.4	23.4	23.1	22.9
F-16	18.8	19.4	19.3	19.2

b. Conclusions—Reaction Conditions that Tended
to Yield Prepolymers with Lowest $\overline{M}_w$

	0 hr	24 hr	72 hr	72 hr at 54°C
0.5 hr cook time	X	—	—	—
4.0:1 polyol ratio	X	X	X	X
T-9	X	X	X	X

[a] Obtained from prepolymers prepared using low tin (0.0063%).
[b] Sample obtained directly from reaction mixture.
[c] Aged at 25°C.
[d] Aged at 54°C.

was found. The prepolymers containing low concentrations of either T-1 or T-9 showed only slight increases in viscosity on heat aging, indicating stability.

A series of GPC samples were taken on the prepolymers synthesized for the statistical analysis (series F) using the low catalyst concentration. The GPC curves were analyzed for the weight-($\overline{M}_w$) and number-average ($\overline{M}_n$) molecular weights, and the values of $\overline{M}_w$ were analyzed using Yates algorithm. These results are given in Table IV. Samples were obtained immediately upon completion of the reaction (0 hr) and at the specific intervals listed in the table. The statistical analysis shows that the high ratio of diol to triol as well as the T-9 catalyst are significant in yielding low values of $\overline{M}_w$. At 0 hr, the short cook time was also found to be important. This indicates that the short cook time, coupled with low catalyst levels and low temperatures, will yield incomplete reactions with some systems. However, 24 hr later, the prepolymers all had reached an equilibrium state and the cook time was no longer significant.

Samples of the prepolymer (series E and F) were cast into films, and their mechanical properties were examined after a 14-day cure at ambient conditions. The results of 100% modulus, ultimate elongation, and ultimate tensile strength

TABLE V
Results and Conclusions of Analyses Based on Mechanical Properties

a. Results[a]

Series[b]	100% Modulus, kPa	Ultimate elonga- tion, %	Ultimate tensile strength, kPa	Series[c]	100% Modulus, kPa	Ultimate elonga- tion, %	Ultimate tensile strength, kPa
E1	455	760	2030	F1	406	885	2275
E2	371	930	1960	F2	350	910	1925
E3	469	465	1015	F3	385	605	1400
E4	441	660	1785	F4	385	675	1610
E5	476	600	1715	F5	434	625	1680
E6	420	635	1470	F6	350	595	1330
E7	420	940	2555	F7	336	810	1785
E8	399	770	1750	F8	385	905	2205
E9	441	565	1505	F9	385	550	1295
E10	420	575	1365	F10	441	595	1540
E11	490	610	1505	F11	385	930	1855
E12	371	920	1960	F12	350	855	1960
E13	385	970	2030	F13	364	840	1995
E14	406	870	2240	F14	420	895	2275
E15	525	630	1995	F15	420	710	1890
E16	385	430	1120	F16	420	570	1400

b. Conclusions—Reaction Conditions that Tended to Yield the Highest Values of Modulus, Elongation, and Tensile Strength

Catalyst concentration	100% Modulus	Ultimate elongation	Ultimate tensile strength
High tin (0.025%)	2.85:1 polyol ratio 0.5 hr cook time	4.0:1 polyol ratio T-1	4.0:1 polyol ratio T-1
Low tin (0.0063%)	2.85:1 polyol ratio 1.0 hr addition time T-1	4.0:1 polyol ratio	4.0:1 polyol ratio

[a] Results are an average of at least three samples.
[b] High catalyst concentration (0.025%).
[c] Low catalyst concentration (0.0063%).

are given in Table Va. Analysis by Yates algorithm indicates that the higher ratio of diol to triol and T-1 catalyst yields high elongations and tensile strengths for polymer films containing the higher catalyst level (Table Vb). With the lower catalyst level, only the higher ratio of diol to triol was significant in increasing the elongation and tensile strength of the films.

Diol-to-Triol Ratio

The physical and mechanical properties of the isocyanate-terminated poly-urethane were investigated with respect to varying ratios of diol to triol. These experiments were designed to expand on the information obtained from the statistical analyses.

The compositions of prepolymers with the various diol-to-triol ratios were calculated using the general formula given in Table VI. Calculations were based on maintaining an excess of 1.8% free NCO (1.4% with the plasticizer included

TABLE VI
Calculations for Determining Composition of Diol:Triol Ratios

	Ratio of Diol to Triol					
	2.5:1	2.85:1	3.64:1	4.0:1	4.5:1	5.0:1
Equivalents of diol[a]	0.972	0.999	1.045	1.061	1.079	1.095
Grams of diol	970.1	997.5	1043.1	1059.1	1077.5	1092.5
Equivalents of triol[b]	0.281	0.254	0.208	0.192	0.173	0.158
Grams of triol	388.0	350.0	286.6	264.8	239.4	218.5
Equivalents of water	0.070	0.070	0.070	0.070	0.070	0.070
Grams of water	0.63	0.63	0.63	0.63	0.63	0.63
Total equivalents	1.253	1.253	1.253	1.253	1.253	1.253
A	1.8	1.8	1.8	1.8	1.8	1.8
B	4200	4200	4200	4200	4200	4200
C	1358.1	1347.5	1330.0	1323.9	1316.9	1311.0
D	125	125	125	125	125	125
E	1.323	1.323	1.323	1.323	1.323	1.323
X[c]	251.6	251.0	250.0	249.7	249.3	249.1

[a] Hydroxyl number = 56.2, water content = 0.05%.
[b] Hydroxyl number = 40.6, water content = 0.04%.

[c] $X = \dfrac{BE + AC}{(B/D) - A}$, where A = per cent free isocyanate desired; B = equivalent weight of NCO $\times$ 100; C = total weight of polyols; D = equivalent weight of isocyanate; E = equivalents of polyol and equivalents of water; X = grams of isocyanate (to be calculated).

in the calculations) and the same total number of hydroxy equivalents for each ratio. The amount of water was assumed constant and was based on information from the supplier.

These prepolymers were prepared at 60°C by premixing the polyols, adding
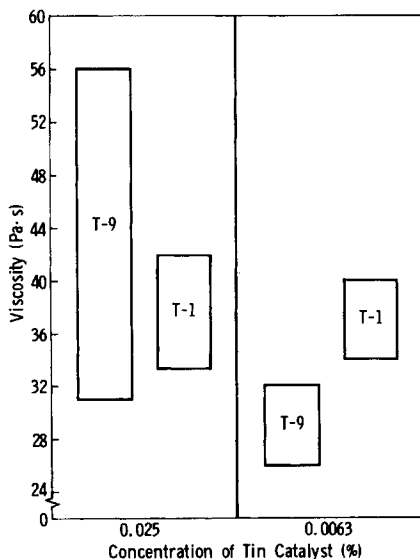

Fig. 1. Comparison of viscosity ranges at 25°C (after 24 hr) for prepolymers synthesized at two concentrations of stannous octoate (T-9) and dibutyltin diacetate (T-1).
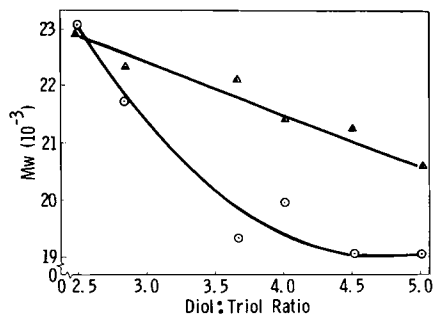
Fig. 2. Weight-average molecular weight ($\bar{M}_w$) vs. diol:triol ratio at 0 hr and 24 hr for dibutyltin diacetate (T-1)-Catalyzed Prepolymers: (⊙) 0 hr; (△) 24 hr.
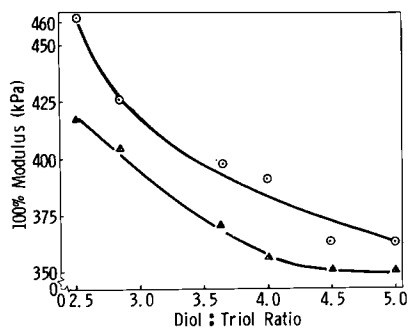

Fig. 3. Modulus (100%) vs. diol:triol ratio. Catalyst (0.0063%): (⊙) dibutyltin diacetate (T-1); (△) stannous octoate (T-9).
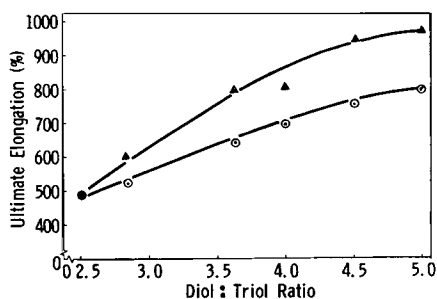

Fig. 4. Ultimate elongation vs. diol:triol ratio. Catalyst (0.0063%): (⊙) dibutyltin diacetate (T-1); (△) stannous octoate (T-9).

them in portions to the isocyanate–plasticizer–catalyst mixture over a 0.5-hr period, and cooking for 1.0 hr. Two series of prepolymers were synthesized in this manner using the low concentration of either T-1 or T-9.

The measurement of viscosity, after allowing the prepolymers to equilibrate for 24 hr at 25°C, showed that as the diol-to-triol ratio increased from 2.5 to 5.0, the viscosity decreased from approximately 40 to 34 Pa·s for both T-1- and T-9-catalyzed prepolymers. GPC samples were obtained at the termination of the reaction (0 hr) and 24 hr later when the viscosity measurements were being taken.
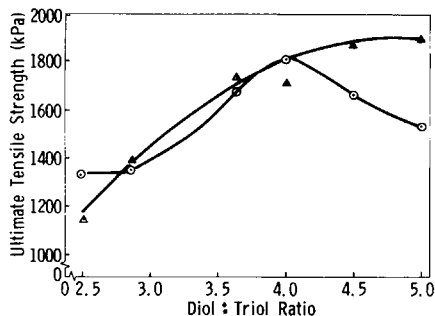
Fig. 5. Ultimate tensile strength vs. diol:triol ratio. Catalyst (0.0063%): (⊙) dibutyltin diacetate (T-1); (△) stannous octoate (T-9).

The results for the T-1-catalyzed prepolymers are shown in Figure 2 and indicate that at the higher ratios, a greater change in $\bar{M}_w$ occurs between 0 and 24 hr. No further increases in $\bar{M}_w$ were observed when the samples were checked at 72 hr.

The prepolymers were cast into films, allowed to cure for 14 days, and the 100% modulus (Fig. 3), ultimate elongation (Fig. 4), and ultimate tensile strength (Fig. 5) were measured. As expected, with increasing diol-to-triol ratio, the modulus decreases and elongation increases. Comparison of the two catalysts indicates that T-1 yields prepolymers with generally higher modulus and lower elongation. It was also observed that the T-1 films cured faster to yield tack-free surfaces than did T-9 films. These results indicate that T-1 is a faster catalyst for the water reaction, and it also gives more crosslinking from side reactions accounting for the higher modulus and lower elongation. Comparison of the tensile strengths for T-1 and T-9 catalyzed prepolymers shows that with T-1, a maximum strength is recorded at a 4.0:1 ratio while the T-9 prepolymers do not have a peak strength.

SUMMARY AND CONCLUSIONS

The results of a designed set of fractional factorial experiments investigating seven variables at two levels with regard to the physical and mechanical properties of the prepolymers showed that the polyol ratio and the catalyst are the most significant variables. The reaction temperature and addition sequence were found not to play a dominant role in the prepolymer properties.

The desirable physical properties of the prepolymer, low viscosity, and heat age stability, were found to be dependent mainly on the concentration of T-9 catalyst. At higher levels of T-9, the prepolymers became unstable during heat aging, whereas the T-1-catalyzed prepolymers showed no instability. The ultimate tensile strength was found to be superior with prepolymers catalyzed with higher concentrations of T-1 (Table V).

Varying the ratio of diol to triol for prepolymers synthesized with a low concentration of T-1 or T-9 showed that the best balance of properties resulted when ratios in the range of 3.5–4.0 were used.

Stable isocyanate-terminated polyurethane prepolymers were synthesized under relatively mild conditions to yield a uniform product with reproducible

properties. The choices of catalyst and ratio of diol to triol allow the production of a reactive polyurethane with a range of physical and mechanical properties.

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