Optimizing the Properties of Isocyanate-Terminated Polyurethane Prepolymers by Statistically Designed Experiments

T. J. DEARLOVE, G. A. CAMPBELL, and R. P. ATKINS, *Polymers Department, General Motors Research Laboratories, Warren, Michigan 48090*

Synopsis

The properties of isocyanate-terminated polyurethane prepolymers were optimized through the use of statistically designed experiments. A simple 2×2 factorial with centerpoint statistical design was used to determine the effect the diol-to-triol ratio and per cent free isocyanate had on the viscosity of the prepolymer. Combinations of a 1000 or 2000 molecular weight diol with either a 1500 or 4100 molecular weight triol showed that a reasonable range of viscosity could be maintained only with the 4100 molecular weight triol. A nine-point design was then utilized to predict the best levels of free isocyanate and polyol ratio that would yield cured urethane polymers with the highest tensile strengths, moduli, and elongations. With this design, second-order equations were computed that predict the mechanical responses of urethane polymers based on the free isocyanate and polyol ratio used in its formulation.

INTRODUCTION

Polyurethane materials are used in commercial products as a result of the excellent characteristics that these polymers exhibit. By varying the type and level of isocyanate, polyol, plasticizer, and catalyst, an extremely wide range of physical and mechanical properties can be obtained. One method of producing a polyurethane product is to first prepare an isocyanate-terminated prepolymer which is often compounded with fillers, pigments, plasticizers, stabilizers, or catalysts prior to curing with polyols, polyamines, or moisture.

The use of a polyurethane prepolymer is common in the preparation of paints,[1] films,[2,3] lacquers,[4] cast elastomers,[5] sealants,[6] and adhesives.[7] Each of these uses requires a special set of properties that must be incorporated in the polyurethane. In many cases the optimization of the important properties that are reported in the literature are the result of the preparation of many formulations which systematically cover a range of starting materials or additives.[5] Attempts have been made to relate specific variables such as type of isocyanate,[8] isocyanate structure,[9] catalytic aging reactions,[10] and type of polyol[5] to the properties of polyurethane materials.

The use of statistically designed experiments (SDE) has been reported for relating the hardness and toughness of polyurethane coatings with respect to the amounts of toluene diisocyanate and diol used in conjunction with two different triols.[11] In another investigation, SDE were used to determine the relative importance of seven variables on the physical properties of an isocyanate-terminated prepolymer as well as the effect of these variables on the mechanical properties of the polyurethane after moisture curing.[12] However, very little has

0021-8995/78/0022-0927$01.00

been reported on the use of SDE for the systematic investigation of the specific effects that these variables have on the properties of polyurethanes.

This paper discusses the optimization of an isocyanate-terminated prepolymer with respect to its viscosity before curing and its mechanical properties after curing. In this instance, it was desirable to formulate a prepolymer with a low viscosity so that it would be amenable to loading with fillers. The mechanical properties were optimized to give the highest combination of tensile strength, modulus, and elongation.

EXPERIMENTAL

Materials

A list of materials and suppliers is given in Table I. The polyols were rebottled from 18.93-l. containers into smaller glass bottles in order to reduce the absorption of moisture. All other materials were used as received, and any special handling of the materials will be discussed in the appropriate sections below.

Preparation of the Prepolymer

The synthesis of the prepolymers for the statistical analysis was normally accomplished in a 1-liter resin kettle with side indentations, a turbine blade stirrer, nitrogen inlet and outlet, and an iron-Constantan thermocouple. For example, 78.3 g toluene diisocyanate (TDI), 300 g P-1010 diol, 100 g TP-4040 triol, and 59 g HB-40 plasticizer were added to the resin kettle and mixed under nitrogen for at least 5 min while the temperature was brought up to 70°C. A mixture of 0.037 g stannous octoate (T-9) dissolved in 59 g HB-40 plasticizer was added in one portion to the stirred solution in the reactor. The mixture exothermed to 90°C within 15 min after the catalyst was added, and molecular weight determinations on the prepolymer indicated that the reaction was complete. This was shown when subsequent determinations of $\overline{M}_w$ after additional reaction time did not show an increase in molecular weight. The prepolymer was degassed for 10 min under 10 mm mercury and then stored under dry nitrogen in glass containers for testing and evaluation.

TABLE I
Materials and Suppliers

Trade name	Supplier	Description or remarks
Mondur TD-80	Mobay Chemical Co.	toluene diisocyanate (2,4- and 2,6-isomers)
P 1010	BASF-Wyandotte	1000 mol. wt diol
P 2010	BASF-Wyandotte	2000 mol. wt diol
TP 1540	BASF-Wyandotte	1500 mol. wt triol
TP 4040	BASF-Wyandotte	4100 mol. wt triol
HB-40	Monsanto	hydrogenated terphenyl
T-1	M&T Chemical Co.	dibutyltin diacetate
T-9	M&T Chemical Co.	stannous octoate
T-12	M&T Chemical Co.	dibutyltin dilaurate
DABCO	Houdry Chemical Co.	triethylenediamine

Sample Analyses and Testing Procedures

All viscosity measurements are reported in pascal seconds (Pa·sec; 1 mPa·sec = 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 rpm was used for the viscosity measurements.

The percent isocyanate present in the prepolymer was determined in triplicate by a standard analytic technique (ASTM D1638-74). A known amount of prepolymer was reacted with excess dibutylamine, and the amine was back-titrated with hydrochloric acid to a bromphenol blue endpoint.

The weight-average ($\overline{M}_w$) and number-average ($\overline{M}_n$) molecular weights were determined by gel permeation chromatography on a Waters Model GPC-200 using a column standardized against polystyrene. The prepolymer was first capped by treating it with a large excess of absolute methanol which converts the isocyanate functionality into methylurethanes. It was then run as a 0.25% by weight solution in tetrahydrofuran, and the resultant GPC curves were analyzed using the first and second moments of the distribution to give the molecular weights.

The mechanical properties of the prepolymer were tested according to ASTM 412-68. The sample of prepolymer to be tested was cast onto glass plates that were covered with Teflon tape. The films, approximately 2.5 mm in thickness, were cured at ambient temperatures and relative humidity for 14 days. Some bubbles formed in the films during the cure, and when the tensile specimens were die-cut from the films, care was taken to exclude the bubbles from the test samples.

The tensile samples were tested on an Instron testing machine at a cross-head speed of 508 mm/min using an extensometer on the sample. A minimum of three dumbbell specimens were tested to give 100% modulus, ultimate elongation, and ultimate tensile strength. The modulus and tensile strength are reported in kilopascals (kPa, where kPa = 6.9 psi).

RESULTS AND DISCUSSION

Choice of Catalyst

Prior to optimizing the formulation of an isocyanate-terminated polyurethane prepolymer based on TDI, several common polyurethane catalysts were screened with regard to their activity. The four catalysts chosen were triethylenediamine (DABCO), dibutyltin dilaurate (T-12), dibutyltin diacetate (T-1), and stannous octoate (T-9). A formulation of TDI, diol, triol, and a plasticizer was used which yielded a prepolymer with moderate molecular weight and viscosity. The activity of the catalysts was evaluated for time to peak exotherm and rate of molecular weight increase. These molecular weight results are given in Figure 1.

The four catalysts showed a wide range of reactivity in this system. After 1.5 hr, the DABCO, T-1, and T-12 all yielded prepolymers that had attained less than 85% of the expected molecular weight. The T-9 catalyst was found to be much more reactive, with the equilibrium molecular weight being obtained in approximately 15 min. Based on these results, T-9 was chosen as the polymerization catalyst for the TDI prepolymer and was used exclusively for the statistically designed experiments.
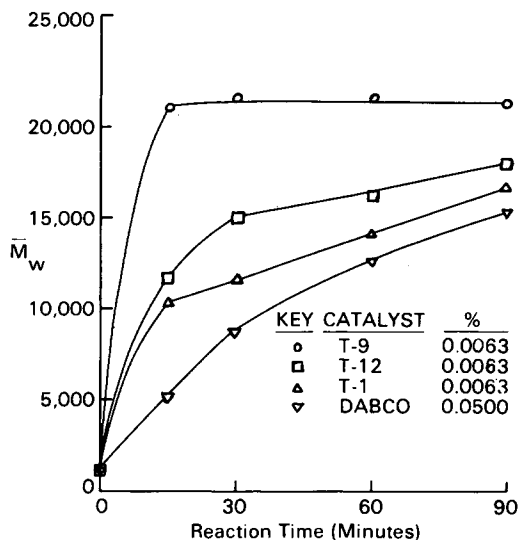
Fig. 1. Weight-average molecular weight ($\overline{M}_w$) vs reaction time for TDI prepolymers formulated with various catalysts.

Preliminary Evaluation of Diols and Triols

Isocyanate-terminated polyurethane prepolymers that are useful in applications such as coatings, films, or sealants are in many cases formulated with fillers. Therefore, reasonably low prepolymer viscosities are often desirable in order to facilitate the use of fillers. The performance of the polyurethane product is strongly dependent on the mechanical properties of the cured prepolymer. Thus, the general characteristics of the prepolymer that were being sought in this investigation were a combination of low viscosity before curing and maximum strength, modulus, and elongation after moisture curing.

Two diols, P1010 (1000 molecular weight) and P2010 (2000 molecular weight), and two triols, TP 1540 (1500 molecular weight) and TP 4040 (4100 molecular weight), were chosen for the preliminary screening. A 2 × 2 with center-point statistical design was employed which would test the four possible combinations of diol and triol. The two control variables were the ratio of diol to triol (1:1, 3:1, and 5:1) and the percent free isocyanate (1.12%, 1.28%, and 1.44%). The formulations based on a combination of these variables are given in Table II. Each combination of diol and triol was given a series number; the first two digits of the series number were the first two numbers of the diol that was used, and the last two digits of the series number were the first two numbers of the triol for that series.

After each prepolymer was synthesized, its isocyanate content, weight-average molecular weight ($\overline{M}_w$), and viscosity at 25°C (after 24 hr at 25°C and after 72 hr of heat aging at 54°C) were determined. The free isocyanate content was found, in most cases, to be very close to the theoretical value. The viscosity after 24 hr at 25°C was found to vary significantly between the four series and, in some instances, within the same series. In the case of the 1015 and 2015 series (both utilizing the 1500 molecular weight triol), the prepolymers with the 1:1 ratio of diol to triol gelled in the reactor. These two series (1015 and 2015) were eliminated from further consideration because of the viscosity data. Even if a viable prepolymer could be formulated in the laboratory from these two series, it is

TABLE II
Preliminary Evaluation of Diols and Triols: Formulations and Physical Properties

Prepolymer	Diol		Triol		HB-40	TDI	Ratio of diol to triol	Percent free isocyanate		Viscosity at 25°C, Pa·sec		$\bar{M}_w \times 10^{-3}$
	P-1010	P-2010	TP 1540	TP 4040				Theory	Actual	24 hr/25°C	72 hr/54°C	
1015-1	333.3	—	66.6	—	120	82.1	5:1	1.12	1.25	176	212	29.9
2	200	—	200	—	120	81.8	1:1	1.12	a	a	a	a
3	300	—	100	—	121	84.1	3:1	1.27	1.22	296	432	27.8
4	333.3	—	66.6	—	122	86.3	5:1	1.44	1.44	120	120	20.0
5	200	—	200	—	121	85.9	1:1	1.44	a	a	a	a
2015-1	—	333.3	66.6	—	114	54.4	5:1	1.12	1.11	56.0	68.0	26.9
2	—	200	200	—	116	65.2	1:1	1.12	a	a	a	a
3	—	300	100	—	115	59.0	3:1	1.27	1.22	69.6	84.0	24.2
4	—	333.3	66.6	—	115	58.3	5:1	1.44	1.50	12.0	12.0	12.0
5	—	200	200	—	117	69.2	1:1	1.44	a	a	a	a
1040-1	333.3	—	—	66.6	119	75.3	5:1	1.12	1.09	108	112	20.1
2	200	—	—	200	115	61.3	1:1	1.12	1.10	64.0	76.0	25.9
3	300	—	—	100	118	73.8	3:1	1.27	1.27	44.0	49.6	15.1
4	333.3	—	—	66.6	120	79.4	5:1	1.44	1.40	44.0	56.0	14.4
5	200	—	—	200	116	65.3	1:1	1.44	1.44	28.8	37.2	15.3
2040-1	—	333.3	—	66.6	112	47.6	5:1	1.12	1.16	16.0	16.0	18.4
2	—	200	—	200	111	44.7	1:1	1.12	1.19	20.0	20.0	24.8
3	—	300	—	100	112	48.8	3:1	1.28	1.32	12.0	12.0	16.8
4	—	333.3	—	66.6	113	51.4	5:1	1.43	1.47	8.8	10.0	14.1
5	—	200	—	200	112	48.5	1:1	1.44	1.52	10.0	10.8	19.5

a Prepolymer gelled in reactor.

obvious that any small errors in formulating the prepolymer under production conditions would lead to a large variance in the final viscosity of the prepolymer.

The two series that were formulated based on the 4100 molecular weight triol yielded prepolymers whose viscosities were in the desired range and did not vary drastically with changes in either the diol-to-triol ratio or free isocyanate content. Therefore, these two series (1040 and 2040) were evaluated further for optimization of their mechanical properties.

Nine-Point Statistical Analysis

The 2 × 2 design described previously was analyzed using a Yates algorithm[13] to determine the first-order equation for the best fit of the data. It was observed that the relationship of the two variables did not appear to be planar, and this was confirmed by the observed values of the center point. This indicated that the observed viscosity was dependent on a more complex interaction of the two variables.

In order to obtain a more accurate estimate of the influence of the two variables on the physical and mechanical properties of the TDI prepolymer, the 2 × 2 design was expanded to an octagonal design with centerpoint. Thus, only four additional experiments were required. With this design, a second-order equation could be generated that would include the interactions of the two variables. In essence, the observed values of viscosity (or any other property of the prepolymer) for the nine prepolymer samples were analyzed through the use of a computer.[14] The mathematical treatment used in the computer program involved regression analysis that is detailed elsewhere;[15,16] its discussion is beyond the scope of this paper.

The computer generates a second-order equation of the type

$$Z = A + BX + CY + DX^2 + EY^2 + FXY$$

where Z is the observed response, X and Y are the variables, and $A, B, C, D, E,$ and F are constants. For the viscosity data obtained from the TDI prepolymer, X is the ratio of diol to triol, Y is the percent free isocyanate, and Z is the expected viscosity. A response surface is generated by the computer for any property of the prepolymer that is measured. For a given value of viscosity (Z), the computer determines all combinations of X and Y that will yield a prepolymer with this desired viscosity. This information is printed in the form of a contour map or surface. Conversely, since the constants are known, any combination of X and Y can be inserted into the equation, and a predicted value of Z can be easily calculated.

The respective response surfaces (where Z is the observed property, representing one of the following: viscosity, molecular weight; tensile strength, ultimate elongation or 100% modulus) were determined for the 1040 and 2040 series of TDI prepolymers. The results of these experiments are given in Table III and are discussed in detail below.

TABLE III
Physical and Mechanical Properties for the 1040 and 2040 Series of TDI Prepolymers used in the Nine-Point Statistical Design

Prepolymer	Ratio of diol to triol	Percent free isocyanate	Viscosity at 25°C, Pa·sec	Ultimate elongation, %	100% modulus, kPa	Ultimate tensile strength, kPa	$\overline{M}_w \times 10^{-3}$
1040-1	5:1	1.12	108.4	1000	315	1015	20.0
2	1:1	1.12	64.0	400	420	1050	25.9
3	3:1	1.27	63.2	975	308	1316	18.0
4	5:1	1.44	44.0	1000	385	1610	14.4
5	1:1	1.44	28.8	255	525	980	15.3
6	5.82:1	1.28	69.2	1010	308	609	16.1
7	3:1	1.50	40.0	935	434	1603	15.0
8	3:1	1.05	96.0	720	371	1169	21.3
9	0.18:1	1.28	24.4	145	700	910	31.7
2040-1	5:1	1.12	8.8	985	245	770	18.4
2	1:1	1.12	20.0	320	511	1120	24.8
3	3:1	1.28	12.0	875	399	1470	17.0
4	5:1	1.43	8.8	1010	455	1680	14.1
5	1:1	1.44	10.0	420	490	1400	19.5
6	5.82:1	1.28	11.6	1010	336	966	15.5
7	3:1	1.50	7.6	940	511	2135	15.3
8	3:1	1.05	21.6	965	343	1610	21.4
9	0.18:1	1.28	20.6	150	455	1085	29.4

Prepolymer Series 1040

The response surface for viscosity of this prepolymer series (Fig. 2) indicates that a low free isocyanate content and high ratio of diol-to-triol yield a high viscosity. The values on this figure that are next to the small crosses are the observed viscosities. The numbers in boxes correspond to the contour lines and are the calculated values of viscosity. The weight-average molecular weight ($\overline{M}_w$) yielded a response surface (Fig. 3) showing that the higher values of $\overline{M}_w$ were obtained for low free isocyanate content and low diol-to-triol ratio. A comparison of Figures 2 and 3 shows that for the 1040 series, the higher viscosities do not correspond to the higher values of $\overline{M}_w$. These unexpected results are difficult to explain without further investigation.

The ultimate elongation and 100% modulus values for this TDI series (Figs. 4 and 5) yielded response surfaces that were shaped, respectively, like a hill and a crater. In both cases, for a given diol-to-triol ratio, the per cent free isocyanate had very little influence on the observed values. The highest elongations and
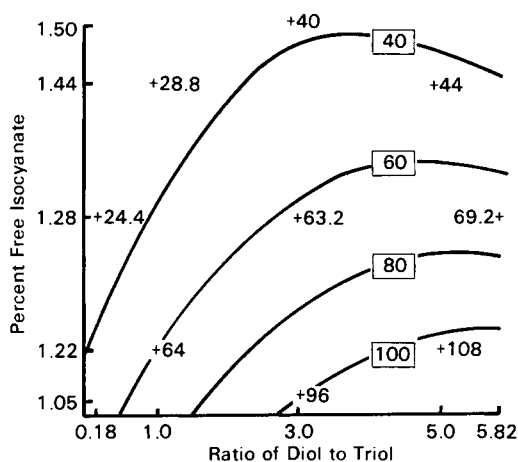
Fig. 2. Response surface for the viscosity (Pa·sec) of the TDI series 1040 prepolymers.
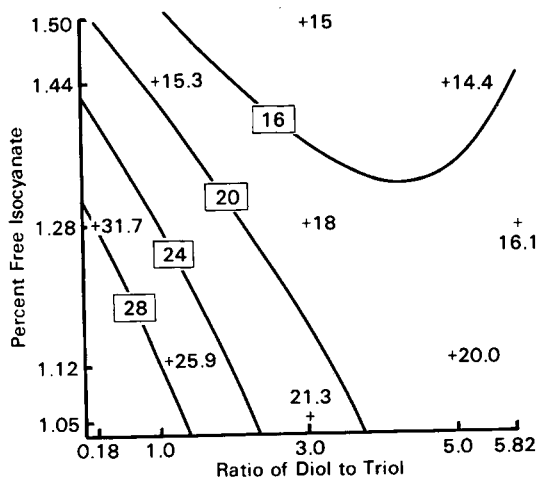
Fig. 3. Response surface for the weight-average molecular weight ($\times 10^{-3}$) of the TDI series 1040 prepolymers.
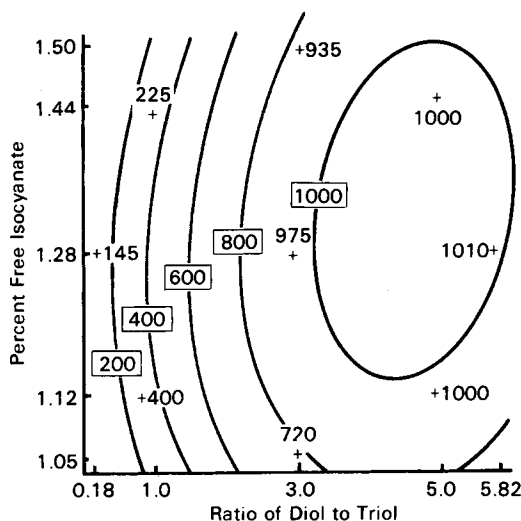
Fig. 4. Response surface for the ultimate elongation (%) of the TDI series 1040 prepolymers.
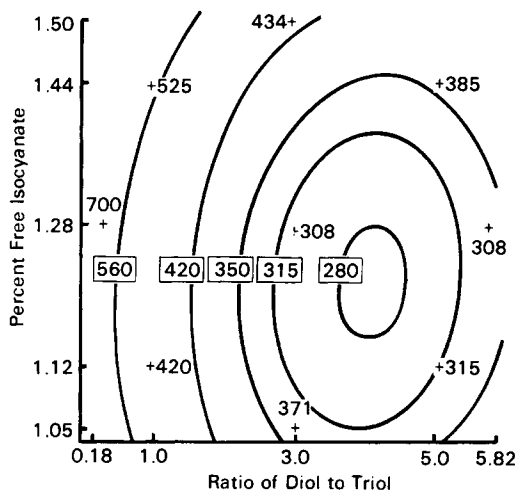

Fig. 5. Response surface for the modulus (kPa) of the TDI series 1040 prepolymers.

lowest modulus values were obtained for polyol ratios in the range of 3:1 to 5:1.

The response surface for ultimate tensile strength (Fig. 6) was the most complex for the 1040 series. The highest strengths were obtained for the intermediate diol-to-triol ratios and for the higher levels of free isocyanate. The strengths did not drop off as rapidly with the lower polyol ratios as they did with the higher polyol ratios.

The purpose of generating the response surfaces was to determine which combination of polyol ratio and free isocyanate content yielded the best combination of physical and mechanical properties. Therefore, the various response surfaces were overlaid on each other and the optimum combination was obtained (Fig. 7). Using this approach, a diol-to-triol ratio in the range of 1.8–2.8 and a free isocyanate content in the range of 1.30%–1.40% gave TDI prepolymers of the 1040 series with ultimate tensile strengths of 1200–1400 kPa, ultimate
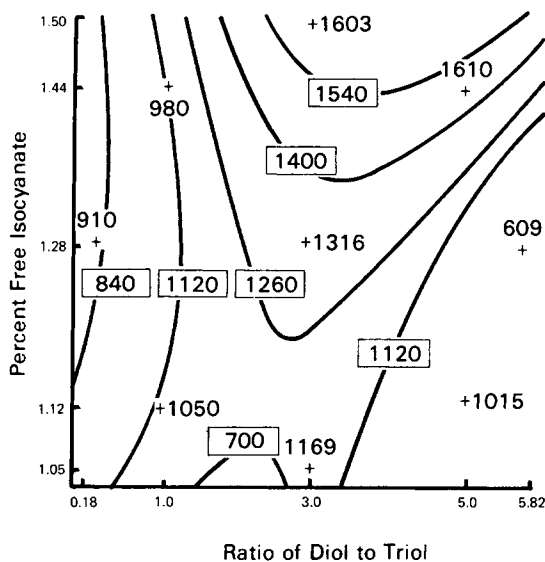
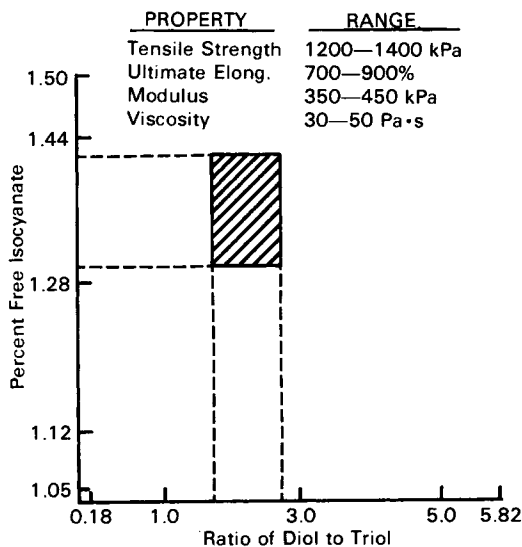Fig. 6. Response surface for the ultimate tensile strength (kPa) of the TDI series 1040 prepolymers.

Fig. 7. Levels of free isocyanate and diol-to-triol ratio that yield the best combination of physical and mechanical properties for the TDI series 1040 prepolymers.

elongations of 700%–900%, 100% modulus values of 350–450 kPa, and viscosities in the area of 30–50 Pa·sec.

Prepolymer Series 2040

The response surfaces for this series of TDI prepolymers are shown in Figures 8–12. With a couple of exceptions, the shapes of the surfaces are similar to those obtained for the 1040 series. The response surface for viscosity (Fig. 8) showed that higher viscosities were obtained with lower values of both polyol ratio and
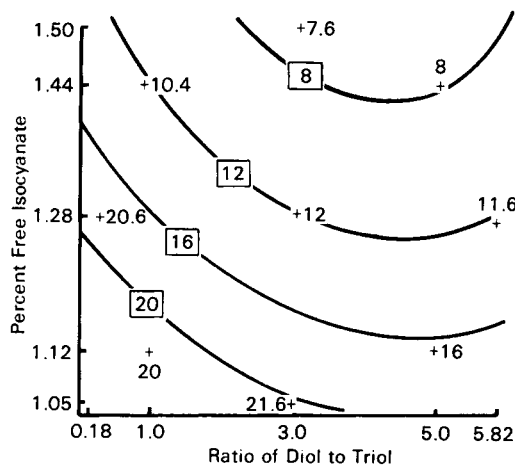
Fig. 8. Response surface for viscosity (Pa·sec) of the TDI series 2040 prepolymers.
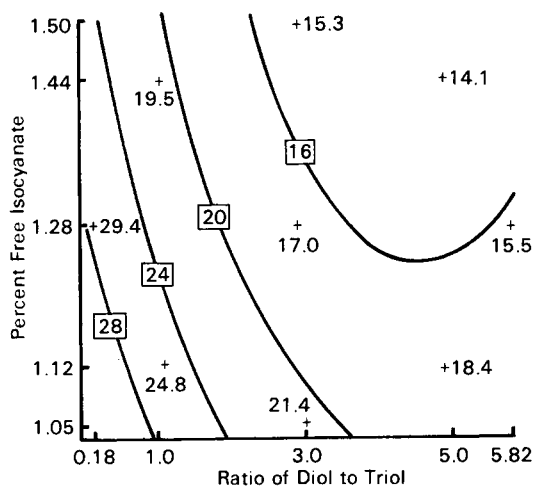

Fig. 9. Response surface for weight-average molecular weight ($\times 10^{-3}$) of the TDI series 2040 prepolymers.

isocyanate content, whereas with the 1040 series, the higher viscosities were found with higher polyol ratios. The reason for this difference is not clear; however, it most likely is a result of different degrees of crosslinking and chain entanglement between the two series of prepolymers as the polyol ratio is varied.

The response surface for $\overline{M}_w$ of the 2040 series (Fig. 9) is virtually identical to that obtained for the 1040 series (Fig. 3). The response surface for the ultimate elongation of the 2040 series (Fig. 10) appears, on the surface, to be different from that of the 1040 series (Fig. 4). However, the contour values are very similar, and the conclusion that, for a given polyol ratio, the percent free isocyanate has little effect on the elongation is the same for both series. The same effect is true for the modulus of the 2040 series (Fig. 11) in comparing it to the 1040 series (Fig. 5) as was observed for the comparison of elongations. The surfaces appear to be different, but in both cases low polyol ratios yielded the highest modulus values.

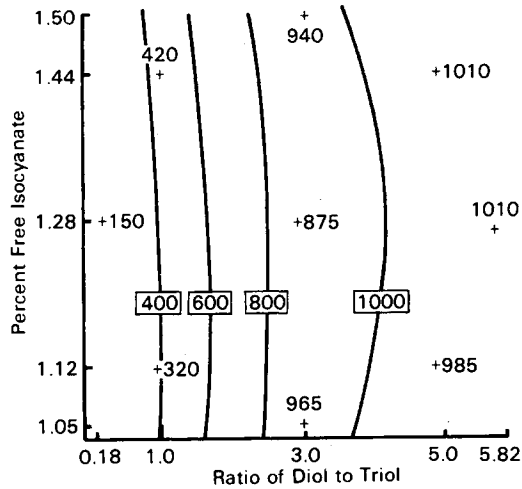The shape of the response surface for ultimate tensile strength for the 2040

Fig. 10. Response surface for the ultimate elongation (%) of the TDI series 2040 prepolymers.
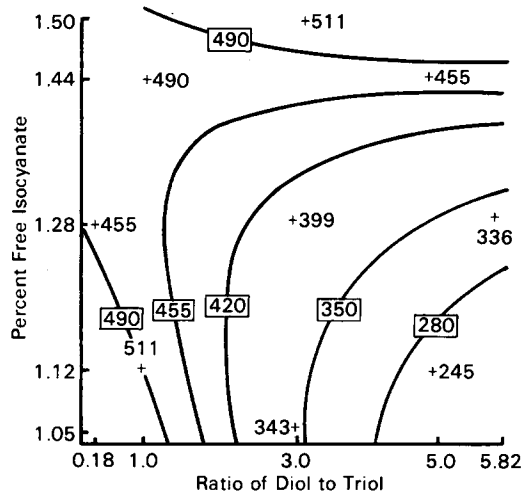

Fig. 11. Response surface for the modulus (kPa) of the TDI series 2040 prepolymers.

series (Fig. 12) was identical to that of the 1040 series (Fig. 6). The 2040 series, when compared to the 1040 series, gave higher tensile values in the intermediate polyol range in conjunction with a high free isocyanate content.

The best combination of properties for the 2040 series (Fig. 13) resulted from a polyol ratio in the 1.4–2.5 range and for a free isocyanate content between 1.08 % and 1.15%. Thus, the 2040 series required low values of free isocyanate while the 1040 series (Fig. 7) required high free isocyanate values. An unexpected correlation was observed between the individual properties of the two series. The magnitude of these properties was similar in the region where the optimum responses were found. The second-order equation that was generated for each observation and that was used to calculate a response surface was discussed previously in the section titled "Nine-Point Statistical Analysis." The computed constants for each set of data have been tabulated in Table IV. As stated earlier, values for X and Y can conveniently be substituted into the general equation,
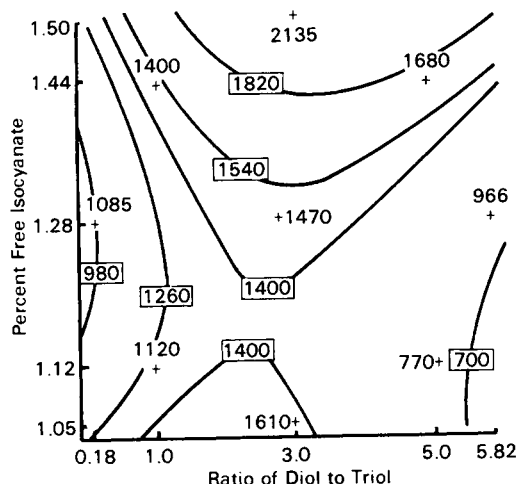
Fig. 12. Response surface for the ultimate tensile strength (kPa) of the TDI series 2040 prepolymers.
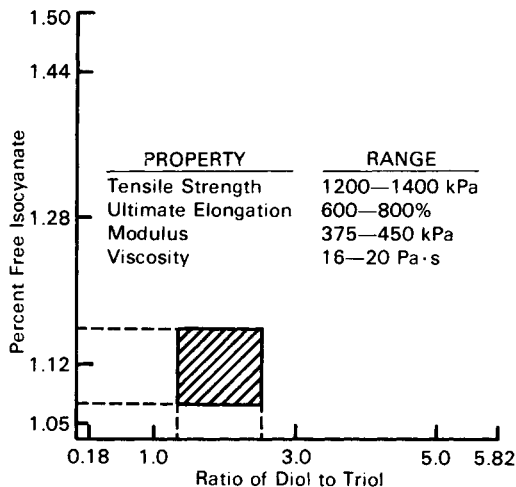

Fig. 13. Levels of free isocyanate and diol-to-triol ratio that yield the best combination of physical and mechanical properties for the TDI series 2040 prepolymers.

along with the appropriate constants, for any desired property (Z), and the expected value of Z can thus be obtained.

Based on our results, this second-order model very closely predicts the actual experimentally observed values for the range of the two variables investigated.

SUMMARY AND CONCLUSIONS

The use of a simple set of SDE showed that prepolymers in series 1040 and 2040 had viscosities in the desired range. Prepolymers in series 1015 and 2015 exhibited a wide range of viscosities which were dependent on the ratio of diol to triol. It was also observed that the relationship of the two variables being investigated was not planar and that a more complex set of SDE was necessary.

TABLE IV

Constants for the Best-Fit Second-Order Equation for the Nine-Point Statistical Design

Series	Property	Constants[a]					
		A	B	C	D	E	F
1040	Viscosity	534.9	39.5	-718.8	-0.6	252.3	-22.5
	Elongation	-5071.9	328.9	8178.4	-52.2	-3278.9	113.3
	Modulus	2612.1	-148.2	-3342.2	21.8	1416.4	-25.5
	Tensile Strength	5211.6	-270.1	-6366.0	-64.1	2225.4	519.5
	$\overline{M}_w$	38.8	-10.4	15.7	0.6	-18.4	3.9
2040	Viscosity	79.1	-4.8	-62.3	0.5	13.3	0.1
	Elongation	843.0	482.4	-1511.3	-42.2	686.3	-58.6
	Modulus	1859.1	-262.54	-1929.9	0.4	672.5	180.5
	Tensile strength	10364.3	-232.7	-14823.9	-68.7	5803.5	492.2
	$\overline{M}_w$	72.3	-6.6	-52.3	0.6	14.1	0.8

[a] General equation: $Z = A + BX + CY + DX^2 + BY^2 + FXY$, where X = ratio of diol to triol, Y = percent free isocyanate, and Z = calculated value of property being determined.

A nine-point design was used in the optimization of viscosity, modulus, ultimate elongation, and ultimate tensile strength for the 1040 and 2040 sets of prepolymers. It was found that for the 1040 series, a 1.30%–1.40% free isocyanate content and a diol-to-triol ratio of 1.8–2.8 were desirable. For the 2040 prepolymer series, a free isocyanate content between 1.08% and 1.15% in conjunction with a diol-to-triol ratio of 1.4 to 2.5 was optimum for the best combination of properties.

It is apparent that through the use of SDE, it is possible to very quickly and efficiently determine what particular formulation will give a product that has the desired properties. If other parameters such as abrasion resistance, tear strength, adhesion, solvent resistance, etc. are important, the use of SDE could easily be employed for investigating these properties.

References

1. F. Blomeyer, *J. Oil Col. Chem. Assoc.*, **54**, 141 (1971).
2. F. D. Shaw (to E. I. du Pont de Nemours and Co.), U.S. Pat. 3,425,973 (1969).
3. H. J. Shearing (to Imperial Chem. Ind. Ltd.), Brit. Pat. 1,126,094 (1968).
4. G. Mennicken, *J. Oil Col. Chem. Assoc.*, **49**, 639 (1966).
5. H. L. Heiss, *Rubber Age*, 89 (October 1960).
6. H. R. Bylsma, *Adhesives Age*, **13**(2), 25 (1970).
7. J. Delmonte, *Adhesives Age*, **18**(12), 29 (1975).
8. K. C. Frisch, L. P. Rumao, and A. J. Mickiewicz, *J. Paint Technol.*, **42**(547), 461 (1970).
9. R. R. Koch, *J. Paint Technol.*, **42**(543), 243 (1970).
10. B. F. Cinadr and E. G. Bobalek, *J. Appl. Polym. Sci.*, **6**, 32 (1962).
11. S. N. Glasbrenner, B. Golding, and L. C. Case, *Offic. Dig. Federation Socs., Paint Technol.*, **32**(421), 203 (1960).
12. T. J. Dearlove and G. A. Campbell, *J. Appl. Polym. Sci.*, **21**, 1499 (1977).
13. J. S. Hunter, *Design of Experiments*, Vol. 4, Factorial Designs, Westinghouse Learning Press, 1968.
14. Program written for the IBM 370 by Drs. S. A. Iobst and R. J. Salloum, Polymers Department, General Motors Research Laboratories.
15. G. E. P. Box and K. B. Wilson, *J. R. Stat. Soc.*, **B13**, 1(1951).
16. G. E. P. Box, *Biometrics*, **10**, 16(1954).