

Speciality Polyurethane Soft Segments. II. Mixing Studies in Micro-RIM Using Polyether Diamine Oligomers Containing Backbone Urea Moieties

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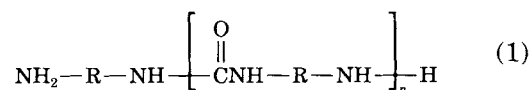
SYNOPSIS

Polyether polyamines containing preformed urea moieties in their backbone, prepared by the reaction of aminated polyglycols with urea, were used to fabricate high modulus urea polymers by reaction injection molding (RIM) on micro-RIM equipment. A formulation was studied based on a 2000 g/mol molecular weight polyether diamine containing about 4 internal urea moieties/molecule as the soft segment and Isonate 143L and diethyltoluenediamine (DETDA) as the hard segment (60 vol %). Mixing was measured by the temperature rise produced by injection of the components into an adiabatic cup as a function of the B-side Reynolds number at the mixhead. B-Side Reynolds numbers of about 300 or above were required for adequate mixing in this system. Plaques were made and compared to the corresponding polyether diamine without urea moieties. The formulation containing preformed urea moieties in the soft segment produced urea polymers with superior properties such as higher modulus, greater strength, increased hardness, superior organic solvent resistance, and improved green strength at demold. Impact properties were reduced. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

The (AB)_n block copolymers are a major structural class of urethane/urea polymer systems, where A and B represent hard segment and soft segment blocks. Hydrogen bonding has a strong influence on the properties of these block copolymers, forming physical crosslinks between the hard segment blocks. If hydrogen bonding sites are also present in the backbone of the soft segment, then additional interactions are possible. These soft segment to soft segment and soft segment to hard segment interactions can lead to different polymer morphologies and properties.

We are studying polyether polyamine materials containing preformed urea moieties in their backbone as hydrogen bonding sites.¹ The general structure for a representative diamine is depicted by



where R represents the polyether segments. The incorporation of these urea moieties into the backbone of polyether polyamines greatly increases the viscosity of these materials. However, since the viscosity is due in large part to intermolecular hydrogen bonding as a consequence of the added hydrogen bonding moieties, the viscosity can be reduced considerably by increasing the temperature. In addition, when parts are fabricated by reaction injection molding (RIM), a chain extender is added to the polyamine side with a resultant decrease in viscosity.

Since a program was initiated to evaluate a number of highly viscous polyether polyamines and polyols in polyurea and polyurethane formulations by fabrication in micro-RIM equipment,² it was necessary to carry out a short mixing study early in the program. Adiabatic temperature rise measurements were used to determine the extent of mixing.

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This paper defines the required B-side (polyamine formulation) temperature and Reynolds number for adequate mixing and presents preliminary property data on the resultant polyureas. Prior to this work, polyureas containing preformed urea moieties in a polyether soft segment had not been reported.³

EXPERIMENTAL

Starting Materials

Jeffamine D-400 and D-2000 are aminated poly(propylene glycol)s, manufactured by Texaco, of approximately 400 and 2000 g/mol molecular weight, respectively. Diethyltoluene diamine (DETDA) was obtained from Ethyl Corp. Urea was purchased from Aldrich Chemical Co. Isonate 143L is a liquid polyisocyanate manufactured by The Dow Chemical Company.

Preparation of a Diamine Containing about Four Urea Moieties per Average Molecule (MW = 1912; 4-Urea Diamine)

Jeffamine D-400 (3775.7 g, 8.64 mol) and urea (432.0 g, 7.20 mol) were mixed in a D-400 : urea molar ratio of 1.30 : 1 in a 5-L, three-necked flask equipped with an overhead stirrer, condenser, thermometer, nitrogen purge, and temperature controller. The exit from the condenser was attached to an aqueous scrubber to absorb the byproduct ammonia. Nitrogen was slowly purged through the system, and the mixture was heated at 150°C for 24 h. The resultant viscous liquid was transferred to a rotary evaporator operating at 90°C under a 20 mm Hg vacuum to remove residual ammonia. The product was a clear, viscous liquid having an amine content of 1.046 meq/g (determined by titration of a methanolic solution with 0.1N aqueous HCl), which corresponds to a diamine molecular weight of 1912 g/mol. Carbon-13 NMR showed internal urea carbonyl moieties (158.0 ppm), the methine carbon attached to urea [$-\text{CH}(\text{CH}_3)\text{NHC}(\text{O})\text{NH}-$, 45.7 ppm] and the methine carbon attached to the amino end groups [$-\text{CH}(\text{CH}_3)\text{NH}_2$, 46.8 ppm].¹

Preparation of a Diamine Containing about One Urea Moiety per Average Molecule (MW = 2562; 1-Urea Diamine)

A diamine containing about one urea moiety per average molecule was prepared by the same procedure used above by reacting an aminated poly(propylene

glycol) with a number average molecular weight of 1207 g/mol (2704.8 g, 2.16 mol) with urea (64.8 g, 1.08 mol) for 18 h at 150°C. The product was a light amber, viscous liquid with the following properties: basicity, 0.781 meq/g; molecular weight by end group titration, 2562; Brookfield viscosity, 1,138 cps at 24°C. Carbon-13 NMR showed internal urea carbonyl moieties (158.0 ppm), the methine carbon attached to urea [$-\text{CH}(\text{CH}_3)\text{NHC}(\text{O})\text{NH}-$, 45.7 ppm] and the methine carbon attached to the amino end groups [$-\text{CH}(\text{CH}_3)\text{NH}_2$, 46.8 ppm].

Micro-RIM Equipment and Conditions; Adiabatic Cup Shots

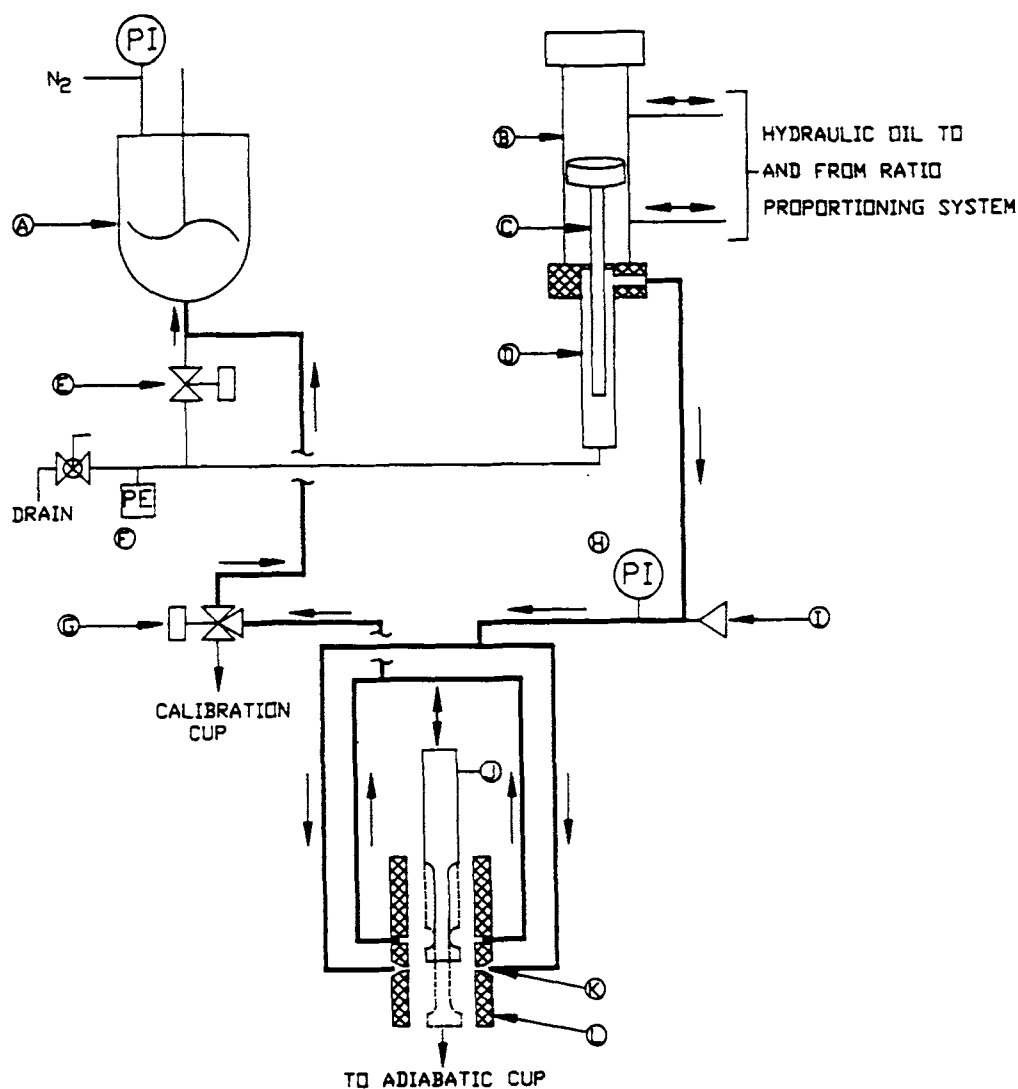
A small scale reaction injection molding (RIM) machine was used to obtain adiabatic cup data.² The machine consisted of two chemical tanks (1.5-L volume each) and a pumping system capable of dispensing precise quantities of each component into a four-port mixhead where the components were rapidly mixed by impingement mixing and delivered into an adiabatic cup. Component temperatures were controlled by heating tapes, in series, on the chemical tanks, mixhead, and connecting lines; rapid response thermocouples just upstream from the mixhead monitored the temperatures of each stream. Pressure was monitored by transducers at the lance cylinders and by gauges just upstream from the mixhead. A diagram of half of the chemical system is given in Figure 1.

Description of Adiabatic Cup

A 5-in. section of 1.5 in. ID Tygon tubing was used to fabricate the adiabatic cup. One end of the tube was clamped to the mixhead and the other end of the tube was closed with a rubber stopper and clamped (cup length was 4.0 in.). Two rapid response time thermocouples (exposed junction, 40 gauge, type E) were placed on the center line in the direction of flow at 1.5 in. (TC-1) and 2.5 in. (TC-2) downstream from the mixhead. The thermocouples were previously calibrated at 0°C and 180°C. A diagram is given in Figure 2. The adiabatic cup was insulated with polystyrene foam.

Data Acquisition System

The data acquisition system consisted of a CAMILE 2000 interfaced to an IBM PC/AT computer. This system was used to collect A-side and B-side component temperatures prior to and during each adiabatic cup shot (20 points per second for 75 s) as



- | | |
|-----------------------------------|----------------------|
| A. Component Storage Tank | G. Calibration Valve |
| B. Hydraulic Lance Drive Cylinder | H. Pressure Gage |
| C. Lance Piston | I. Thermocouple |
| D. Component Delivery Cylinder | J. Wipe Piston |
| E. Component Block Valve | K. Orifices |
| F. Pressure Transducer | L. Mixing Head |

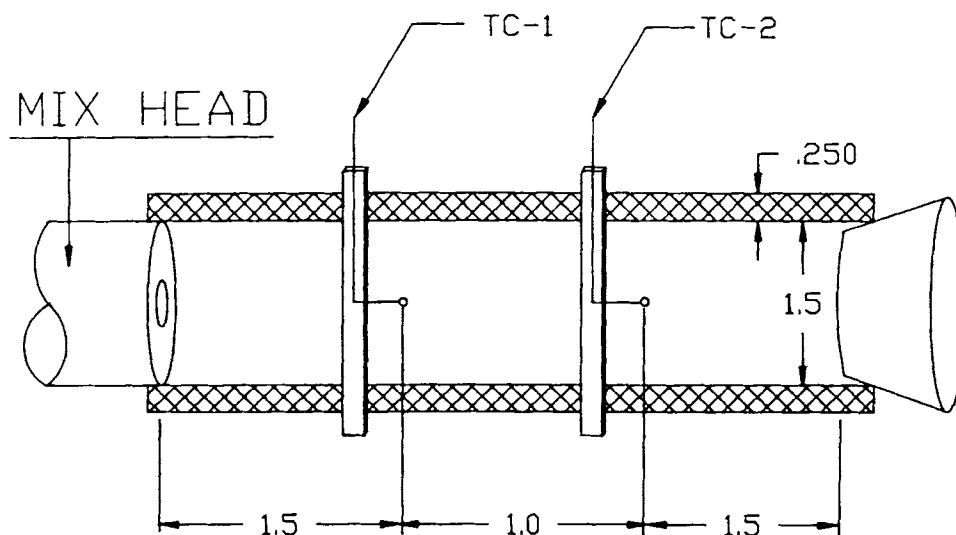
Figure 1 RIM machine configuration.

well as to collect temperature data from TC-1 and TC-2 (20 points per second for 250 s). In addition, the A-side and B-side pressure transducer readouts were collected on a Nicolet 3091 oscilloscope during each cup shot, transferred to the computer through the RS-232 port and analyzed using Waveform Basic (Blue Feather Software). Data obtained on both the Camile 2000 and within Waveform Basic were

transferred to a VAX computer using Crosstalk/Kermit for further data manipulation within RSE.

Micro-RIM Equipment and Conditions; Fabricated Plaques

The same small scale RIM machine described above was used to fabricate parts suitable for physical



< NOTE: DIMENSIONS ARE IN INCHES >

Figure 2 Configuration of adiabatic cup.

property testing. The heated components were delivered to the mixhead, rapidly mixed by impingement mixing and forced into a heated mold ($4 \times 8 \times 0.125$ in.) at 165°C . The mold was held in a horizontal position within a hydraulic press. Demold times were not critical; 60 s were used for convenience; however, demold times as short as 10 s were usable. FluoroGlide CP mold release agent was used. The following machine conditions were employed:

A-side:	Isonate 143L
B-side:	Given in Table I
Recycle pressure:	2000 psi (A- and B-sides)
Throughput:	~ 37 lb/min
Shot time:	~ 500 ms
Hard segment:	60.0 vol % (64.7 wt %)
Index:	1.03
Mold temperature:	165°C
Demold time:	60 s

All plaques were either aged for 2 weeks at ambient temperatures or post-cured for 1 h at 175°C prior to property testing. The parts made are summarized in Table I.

Viscosity Measurements

Viscosity measurements were made on a Brookfield Synchro-Lectric Digital Viscometer with a Brookfield Thermosel Heater using a HBTD #21 spindle. Temperature was controlled with a Model 84 Brookfield programmable temperature controller.

Physical Property Measurements

Physical properties were measured using standard procedures: Shore D hardness, ASTM E-140; flexural modulus, ASTM D-790; tensile properties, ASTM D-638; notched Izod, ASTM D-256. Flexural and tensile measurements (Type I bars) were taken from four different plaques at four bars per plaque (16 test specimens). Dynamic mechanical testing was carried out on a Rheometrics spectrometer in torsion rectangular geometry in temperature sweep mode at a frequency of 1 rad/s, with a thermal soak time of 2 min and measurements taken every 7°C . Impact tests were made on three different plaques using four specimens per plaque (12 tests). Two ad-

Table I Description of Plaques Used in This Study

Plaque No.	B-Side Composition (wt %)	Density of Plaque (g/cm^3)
I	61.5% D-2000 ($\bar{M}_n = 2038$) 38.5% DETDA	1.10
II	61.0% 1-urea diamine ($\bar{M}_n = 2562$) 39.0% DETDA	1.08
III	30.8% 4-urea diamine ($\bar{M}_n = 1912$) 30.8% D-2000 ($\bar{M}_n = 2038$) 38.6% DETDA	1.12
IV	61.6% 4-urea diamine ($\bar{M}_n = 1912$) 38.4% DETDA	1.11

jacent plaques were never used in the same property measurement in order for the results to be representative over a large number of samples. Results are reported as average values.

RESULTS AND DISCUSSION

Formulation Viscosity

A-side temperatures were 35–40°C. B-side temperatures were somewhat higher, depending on the particular diamine employed. The introduction of urea moieties into the backbone of diamines greatly increased their viscosity. However, since this increased viscosity was due largely to intermolecular hydrogen bonding between urea moieties and/or amino end groups, it was significantly reduced by increased temperatures. Table II shows how the viscosity of the diamine containing four urea moieties per average molecule (4-urea diamine) is reduced (1) by increasing the B-side component temperature, (2) by the presence of the chain extender, DETDA, and (3) by using Jeffamine D-2000/4-urea diamine mixtures. The presence of DETDA in the 4-urea diamine formulation reduces the temperature required to obtain a viscosity of 500 cps from about 95 to about 65°C. If a 50/50 wt % mixture of D-2000/4-urea diamine is used in the formulation, the temperature required to obtain a viscosity of 500 cps is further reduced to about 45°C.

System Parameters for Adiabatic Cup Shots

The system parameters used for adiabatic cup shots are given in Table III. The A-side delivery pressure

was approximately 2000 psi in all cases. The B-side delivery pressure varies substantially depending on component viscosity (recirculation temperatures), mass throughput, and mixhead orifice adjustment. The high B-side component viscosity results in lower orifice ΔP due to the overall pressure limitations of the RIM machine and the fact that the more viscous the material, the more of the available pressure drop that must be taken through the recirculation loop leaving less available for the orifice. However, this observation is qualified by variations in mass flow rate and mixhead orifice adjustments which also influence the pressure drop across the orifices.

Temperature Control for Adiabatic Cup Shots

Temperature variations exist throughout the circulating chemical component streams due to differences in local line heating. These temperature variations are evident by examination of the traces in Figure 3. Component temperatures are plotted as a function of time in seconds. Each curve has three components:

1. The temperature of the chemical component with the mixhead in the recirculation position (0 s).
2. The instantaneous temperature reached due to component flow when the mixhead is opened to the adiabatic cup (~ 2 s), and
3. Thermal equilibrium back to the initial chemical component temperature with the mixhead back in the recirculation position.

Various curve shapes were obtained depending on the magnitude and direction of the thermal gradients

Table II Effect of Temperature on the Viscosity of a 4-Urea Diamine; Both Neat and Formulated at 60 Vol % Hard Segment

Temperature (°C)	Viscosity (cps)		
	100% 4-Urea Diamine	61.2% 4-Urea Diamine, 38.8% DETDA	30.6% D-2000, 30.6% 4-Urea Diamine, 38.8% DETDA
30	72,800	14,400	1440
40	25,600	2840	540
50	7600	1160	272
60	3640	560	
70	1960	300	
80	1080	180	
90	660		
100	420		
110	280		

Table III System Parameters during Adiabatic Cup Experiments

Run No.	Delivery Pressure (psi)		Stream Temperature Range (°C)		Average Stream Temperature (°C)		Shot Time (ms)	Shot Weight (g)	Combined Total Throughput (lb/min)
	A-Side	B-Side	A-Side	B-Side	A-Side	B-Side			
1	1948	1982	33.0–36.0	68.0–72.0	34.5	70.0	479	115.1	31.8
2	1980	1932	34.5–37.5	68.5–71.0	36.0	70.0	491	118.5	31.9
3	2151	1777	29.0–34.0	84.0–88.5	31.5	86.0	503	119.6	31.5
4	1925	1854	31.0–34.0	77.0–83.0	32.5	80.0	463	111.1	31.7
5	1851	1025	32.0–35.0	50.5–55.0	33.5	53.0	473	117.4	32.8
6	1988	741	28.0–31.0	36.5–39.5	34.0	38.0	1322	129.0	12.9
7	1991	957	29.5–32.0	51.5–53.5	31.0	52.5	489	113.9	30.8
8	1906	1664	40.0–48.0	76.0–83.0	44.0	79.5	459	111.1	32.0
9	1930	1913	36.0–41.5	59.0–62.0	39.0	60.5	420	103.7	32.7
10	1949	1592	36.5–41.5	70.5–74.5	39.0	72.5	471	114.4	32.1

that existed at a given time. Temperature changes (ΔT) ranged from 2 to 5°C, except for run 8, where the temperature change was about 8°C. All subsequent adiabatic temperature rise calculations were based on the average ΔT , since this represents the average component temperature delivered to the mixing chamber.

Adiabatic Temperature Rise Results

The average temperature of the two chemical components in the mixing chamber prior to any chemical reaction was calculated from the average temperature of each component as it entered the mixing chamber, the relative proportion of each component, and its heat capacity (polyisocyanate, $C_p = 0.43$ cal/g °C; polyamine, $C_p = 0.547$ cal/g °C by DSC). These initial average mix temperatures are listed in Table IV.

Temperatures were recorded versus time in the adiabatic cup to follow the adiabatic temperature changes. The maximum temperature recorded minus the initial mix temperature was called the adiabatic temperature change. In a system with good mixing, the level of component segregation in the mixture was reduced to a level which allowed complete reaction and the maximum adiabatic temperature change. In more poorly mixed systems, component segregation was greater leading to less heat output (less reaction). Mixing quality was a function of the Reynolds number at the mixhead. The adiabatic temperature changes are listed in Table IV. Run numbers which had good mixing had adiabatic temperature changes in the range of 146–150°C.

Selected adiabatic temperature changes are plotted versus time for different B-side Reynolds num-

bers in Figure 4. The maximum adiabatic temperature changes occurred as the B-side Reynolds number was increased to 200–300. Further increases in Reynolds number produced essentially the same adiabatic temperature change.

The adiabatic temperature change data of selected samples are replotted in Figure 5. Only the first 3 s of temperature rise data are plotted to ascertain what information was available at a very early time into the reaction. The very poor mixing of run 6 was evident by data variations; this was also true, but to a much lesser extent for run 7.

Reynolds Number Calculations

In an attempt to correlate processing conditions and material properties with mixing performance, mix-head orifice Reynolds numbers were calculated for both the polyisocyanate and polyamine. The Reynolds number for fluid flow across an orifice is described by

$$Re = 4M/\pi\mu d \quad (2)$$

where Re is the Reynolds number, M is the mass throughput, μ is the viscosity, and d is the orifice diameter. Previous workers studying the efficiency of RIM impingement mixing have demonstrated a correlation between the observed total adiabatic temperature rise and the orifice jet Reynolds number of the more viscous component.⁴ A minimum orifice Reynolds number in the range of 200–500 for the more viscous component has been shown to be necessary in order for the adiabatic temperature rise to reach its maximum value. The maximum adiabatic

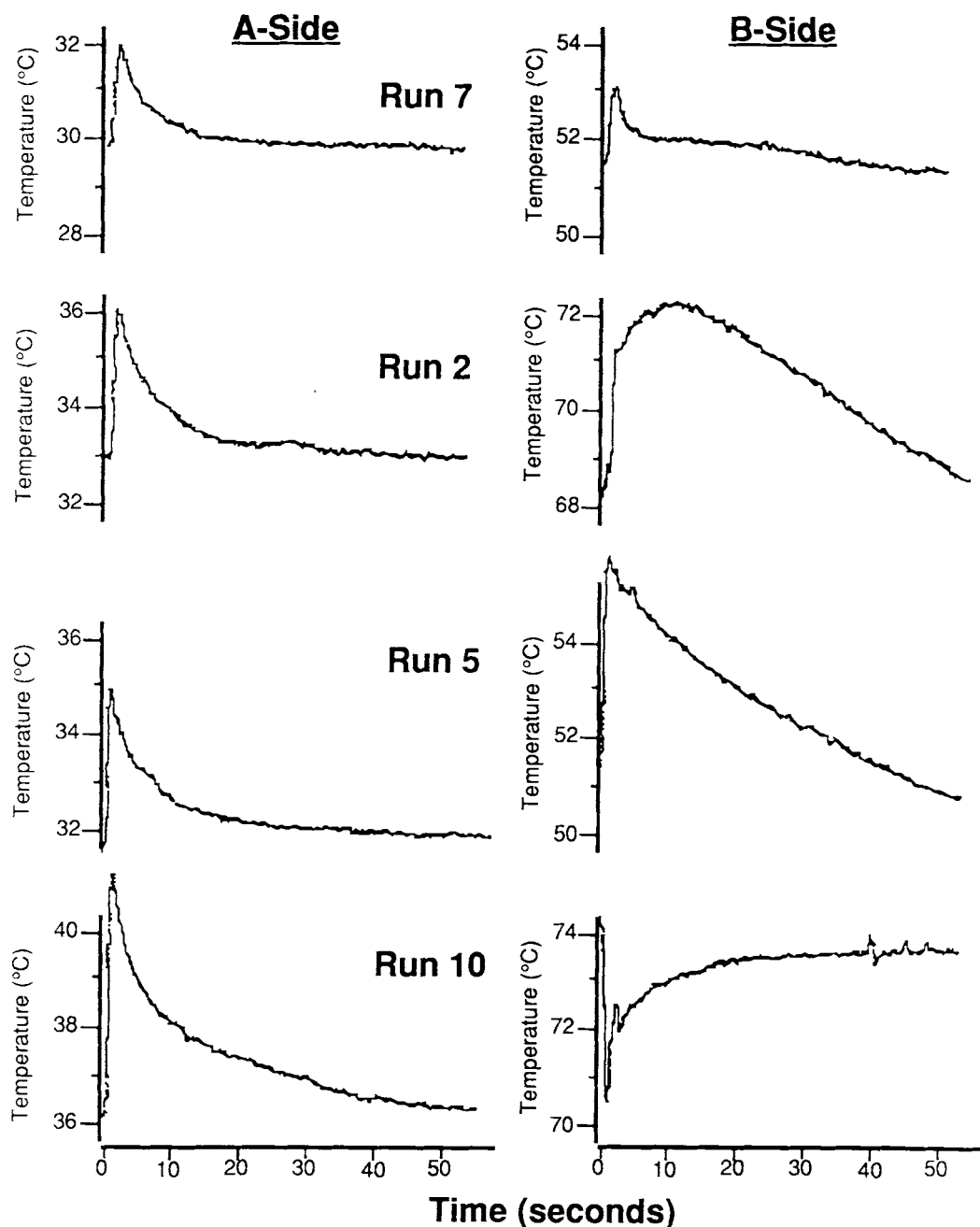


Figure 3 Representative A-side and B-side temperature curves.

temperature rise corresponds to essentially complete reaction and is thus an indication that "good" mixing had occurred.

The results of the calculations for the polyamine component used in this study are shown in Figure 6, where the orifice jet Reynolds number is plotted against the adiabatic temperature rise (Table IV). At low polyamine Reynolds numbers, the adiabatic temperature rise is low. As polyamine Reynolds

number increased to a value of about 200–300, the adiabatic temperature rise also increased. At polyamine Reynolds numbers about 300, no further increase in the adiabatic temperature rise was apparent. Thus, with adiabatic temperature rise as the criterion for mixing quality, it appeared that good mixing was achieved for this system at a polyamine Reynolds number of about 200 or greater. When the same adiabatic temperature rise results were plotted

Table IV Adiabatic Temperature Changes and Effective Reynolds Numbers during Adiabatic Cup Experiments

Run No.	Average Component Temperature at Mixhead Inlet (°C)		Initial Mix Average Temperature (°C)	Maximum Temperature (°C)	Adiabatic Temperature Change (°C)	Effective Reynolds Number	
	A-Side	B-Side				A-Side	B-Side
1	34.5	70.0	57.2	207	149.8	4454	369
2	36.0	70.0	57.5	207	149.5	4482	380
3	31.5	86.0	66.0	215	149.0	3731	851
4	32.5	80.0	62.6	206	143.4	3780	624
5	33.5	53.0	45.9	181	135.1	3953	107
6	34.0	38.0	34.9	153	118.1	2151	15
7	31.0	52.5	44.6	188	143.4	3497	98
8	44.0	79.5	66.5	213	146.5	5680	594
9	39.0	60.5	52.6	199	146.4	5053	197
10	39.0	72.5	60.2	205	144.8	5024	406

against the corresponding polyisocyanate Reynolds number (Table IV), the data appear more scattered, suggesting a weaker influence on mixing efficiency.

The dominant component in the Reynolds number calculation in this study was the B-side component viscosity. Adiabatic temperature rise as a function of the B-side viscosity is plotted in Figure 7. This data is system dependent and indicates that a B-side temperature of about 65°C is the lowest

temperature at which sufficient mixing occurred in this system. A larger machine with higher throughput could run at even lower B-side temperatures.

Plaque Fabrication

Jeffamine D-2000 was used as the standard polyether diamine. It is an aminated poly(propylene glycol) of about 2000 g/mol number average mo-

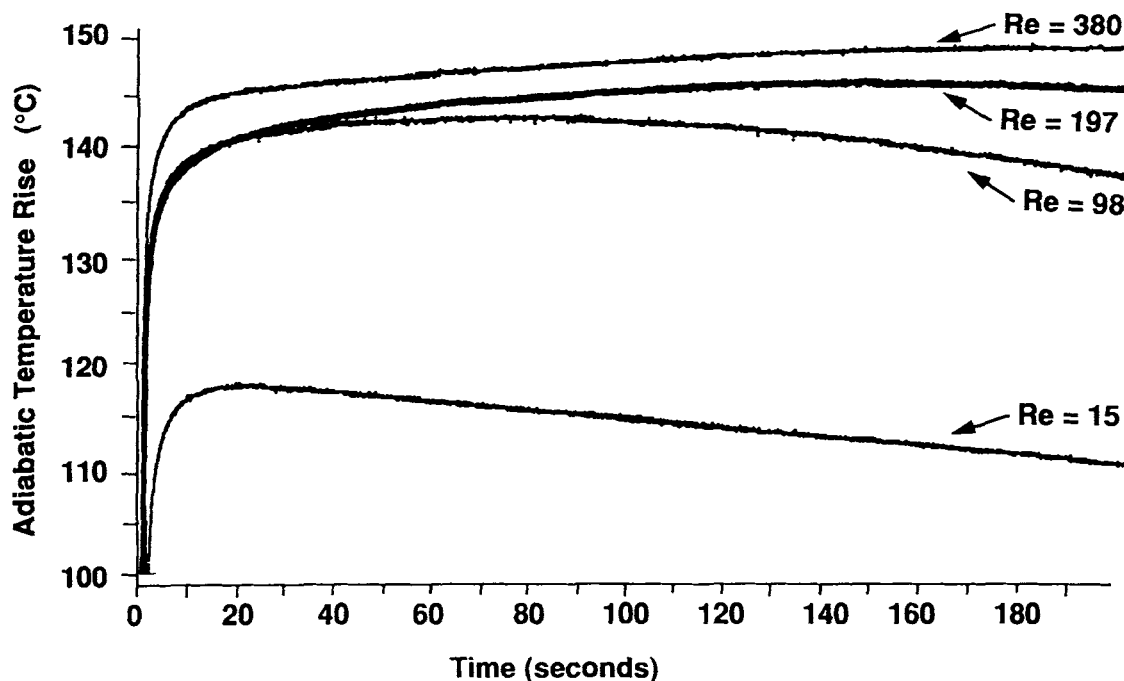


Figure 4 Effect of Reynolds number on adiabatic temperature rise.

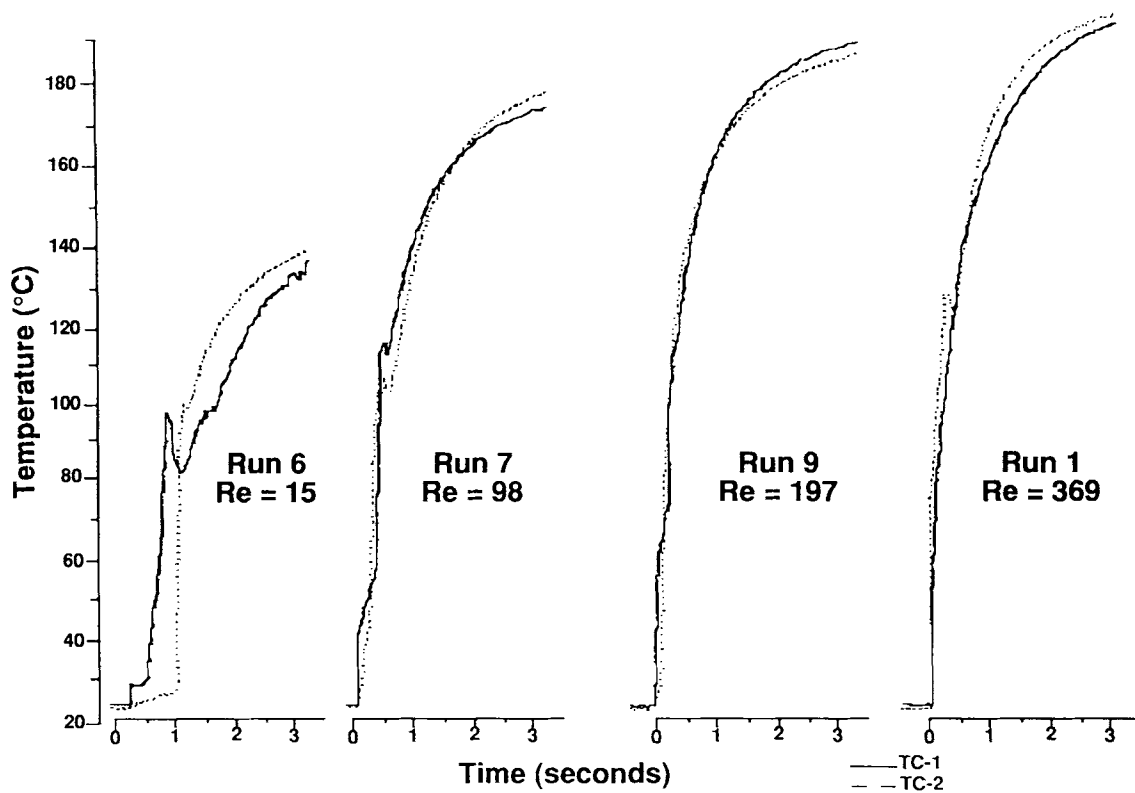


Figure 5 Initial shape of temperature rise curves.

lecular weight and, therefore, has a backbone structure and molecular weight similar to the diamines of this study, except it has no urea moieties in its

backbone. A comparison of properties between Jeffamine D-2000 and the polyether diamines containing approximately one (1-urea diamine) and four

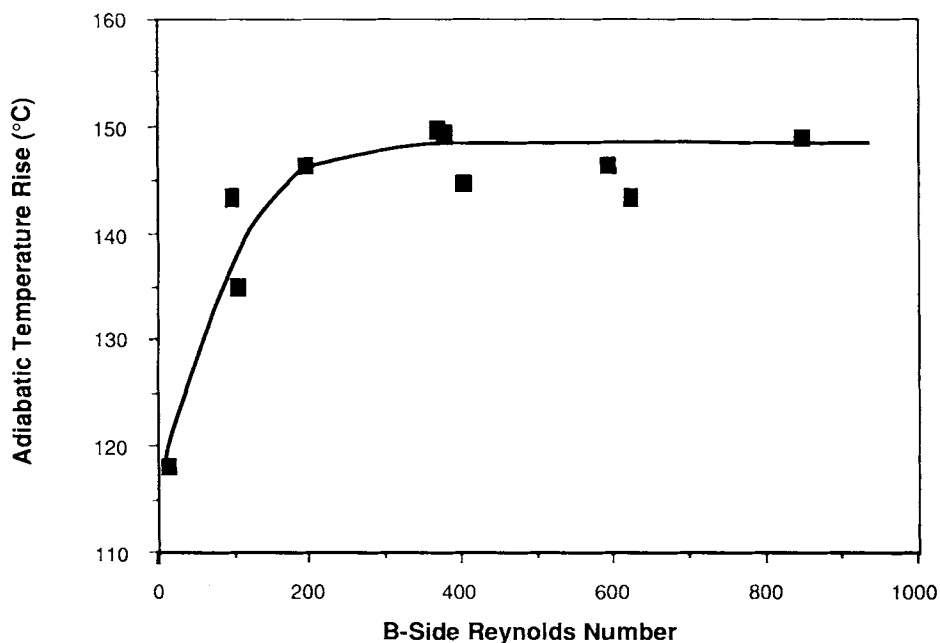


Figure 6 Effect of B-side Reynolds number on adiabatic temperature rise.

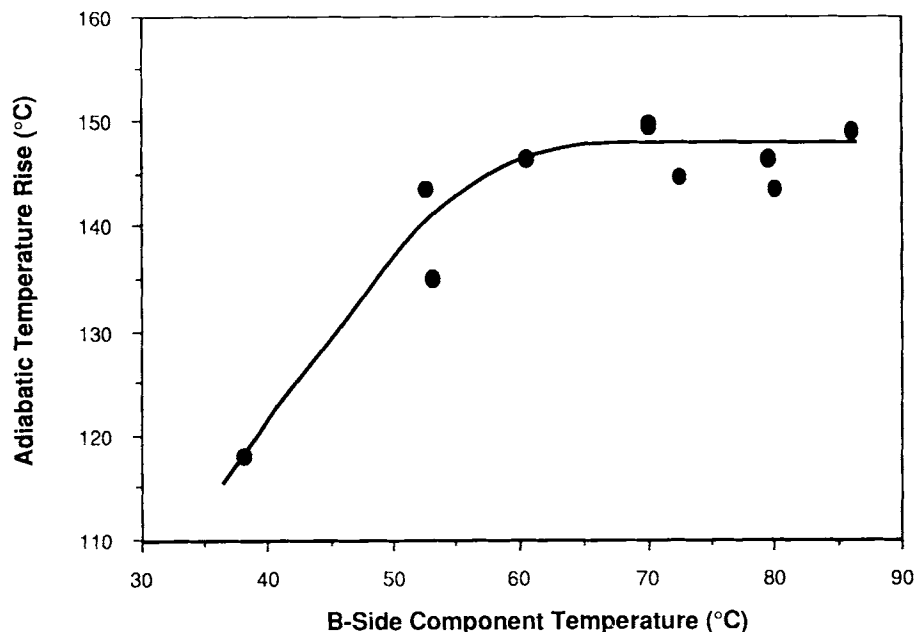


Figure 7 Adiabatic temperature rise vs. B-side component temperature.

(4-urea diamine) urea moieties per molecule should reflect differences due to the urea moieties. The polyether diamine formulations are given in Table I.

In addition to adiabatic temperature rise data, several temperature profiles of mold filling were also measured. This was accomplished by positioning a rapid response thermocouple in the center of the mold (in a Teflon jig) prior to mold filling. Figure 8 is a temperature versus time plot of a representative mold filling experiment using the formulation based on 4-urea diamine. The internal plaque temperature drops momentarily as the cool reactants enter the mold. The reaction exotherm quickly raises the plaque temperature above the mold temperature. An exotherm of nearly 30°C was experienced in about 4 s when shooting into the 165°C mold.

Properties of Plaques

Modulus

Initial tensile and flexural modulus results are given in Table V. The presence of one urea moiety in the backbone of the polyether diamine had little or no effect on modulus even after post curing. However, the presence of four urea moieties in the backbone of the polyether diamine had a dramatic effect on modulus.³ The Young's modulus was increased by about 75% when half of the Jeffamine D-2000 was replaced by the polyether diamine containing four

urea moieties per molecule. The Young's modulus was increased by about 100% when all of the Jeffamine D-2000 was replaced by the polyether diamine containing four urea moieties per molecule. Post-curing had little effect on modulus.

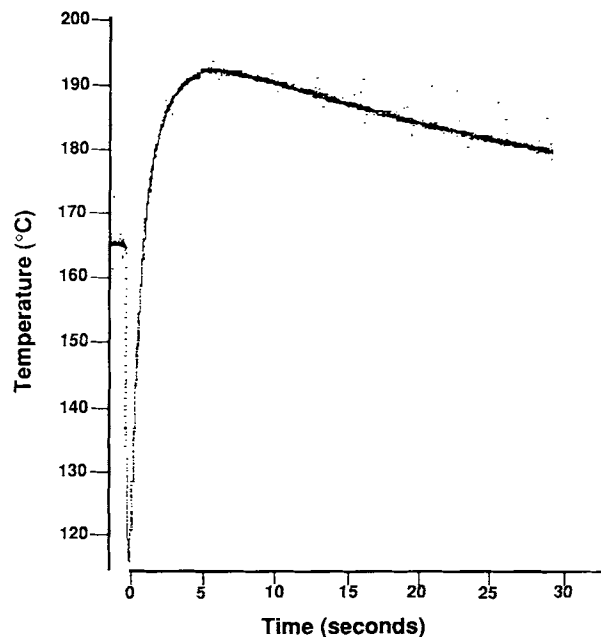


Figure 8 Mold filling experiment using a 4-urea diamine formulated at 60 vol % hard segment.

Table V Effect of Diamine Backbone Structure on Modulus at 60 Vol % Hard Segment

Plaque No.	Diamine	Diamine Molecular Weight	Urea Moieties per Diamine Molecule	Post-Cured	Youngs Modulus (psi)	Flexural Modulus (psi)
I	D-2000	2038	0	No	160,000	142,800
	D-2000	2038	0	Yes ^a	170,000	153,750
II	1-Urea	2572	1	No	175,000	131,300
	1-Urea	2572	1	Yes ^a	185,000	140,800
III	50% D-2000/ 50% 4-Urea	2038	4	No	280,000	214,750
		1912	4	Yes ^a	285,000	227,000
IV	4-Urea	1912	4	No	320,000	284,000
	4-Urea	1912	4	Yes ^a	322,000	290,750

^a Post-cured 1 h at 175°C.

Tensile Properties

Tensile property results are given in Table VI. The presence of one urea moiety in the backbone of the polyether diamine had little or no effect even after post curing. However, the presence of four urea moieties in the backbone of the polyether diamine had an effect on tensile properties.³ The ultimate stress was increased by about 35% when half of the Jeffamine D-2000 was replaced by the polyether diamine containing four urea moieties per molecule. Post-curing had little effect. However, when all of the Jeffamine D-2000 was replaced by the polyether diamine containing four urea moieties per molecule, the ultimate stress was increased by about 60% in the post-cured samples. There is little or no change in the non-post-cured samples. Elongation decreases with increasing amounts of the polyether diamine containing four urea moieties. However, this decrease was much less pronounced in post cured samples.

Solvent Resistance

Solvent resistance properties are given in Table VII. This is a static soak test to measure the weight gain of a sample immersed in a given solvent at ambient temperature. The weight gain was measured each day until no further increase was measured (6 days). The presence of one urea moiety in the backbone of the polyether diamine had little or no effect on solvent resistance, even after post-curing. However, the presence of four urea moieties in the backbone of the polyether diamine had an effect. Resistance to water improved. Plaques made with the polyether diamine containing four urea moieties per molecule picked up only one half the amount of methanol and more than an order of magnitude less toluene and methylethylketone than the corresponding plaques made from Jeffamine D-2000. Intermediate solvent resistance was obtained when 50% of the Jeffamine D-2000 was replaced with the polyether diamine containing four urea moieties per molecule. There-

Table VI Effect of Diamine Backbone Structure on Tensile Properties at 60 Vol % Hard Segment

Plaque No.	Diamine	Post-Cured	Yield Stress (psi)	Yield Strain (%)	Ultimate Stress (psi)	Ultimate Strain (%)	Work (in. lb/in. ³)
I	D-2000	No	6,240	11.1	6,020	18.2	930
	D-2000	Yes ^a	6,680	11.3	6,510	16.8	890
II	1-Urea	No	5,970	12.6	5,790	13.0	630
	1-Urea	Yes ^a	6,500	13.5	6,500	13.8	740
III	50% D-2000/ 50% 4-Urea	No	8,540	10.2	8,280	8.3	540
		Yes ^a	8,540	10.5	8,400	10.8	725
IV	4-Urea	No	—	—	6,350	2.4	85
	4-Urea	Yes ^a	6,750	2.8	10,400	9.9	715

^a Post-cured 1 h at 175°C.

Table VII Effect of Diamine Backbone Structure on Solvent Resistance at 60 Vol % Hard Segment

Plaque No.	Diamine	Post-Cured	Solvent Resistance [% Weight Gain versus Time (h)]							
			Water		Methanol		Toluene		MEK	
			24	144	24	144	24	144	24	144
I	D-2000	No	0.7	1.4	8.5	22.8	3.9	10.2	7.6	24.3
	D-2000	Yes ^a	0.6	1.2	8.7	21.2	4.4	11.9	11.2	31.4
II	1-Urea	No	0.7	1.5	10.5	26.2	4.2	11.7	12.7	41.0
	1-Urea	Yes ^a	0.7	1.6	10.2	25.6	3.4	9.6	11.4	33.7
III	50% D-2000/ 50% 4-Urea	No	0.5	1.2	6.8	16.2	1.2	2.9	4.4	11.1
		Yes ^a	0.6	1.2	5.1	13.5	0.6	1.8	2.8	8.3
IV	4-Urea	No	0.3	0.8	4.2	12.2	0.1	0.3	0.6	2.3
	4-Urea	Yes ^a	0.3	0.8	4.0	11.4	0.1	0.3	0.5	1.9

^a Post-cured 1 h at 175°C.

fore, there are very dramatic improvements in solvent resistance by having urea moieties in the polyether diamine backbone.³ Post-curing had little effect.

Hardness

Shore D hardness values are given in Table VIII. The presence of one urea moiety in the backbone of the polyether diamine had little or no effect on hardness even after post-curing. However, the presence of four urea moieties in the backbone of the polyether diamine increased the hardness of the plaques significantly.

Impact Properties

Ambient temperature impact properties were measured by both a notched test (Notched Izod) and an unnotched test (Dynatup). Results are given in

Table VIII. Impact properties experience a systematic decrease with increasing amount of the polyether diamine containing four urea moieties. Notched izod values dropped off by nearly an order of magnitude. The non-post-cured samples also decreased in value in the Dynatup test. However, post-curing helps. The Dynatup impact was increased by about 100% by post-curing, relative to the corresponding non-post-cured plaques. When half of the Jeffamine D-2000 was replaced by the polyether diamine containing four urea moieties per molecule, the Dynatup impact was actually increased slightly over the Jeffamine D-2000 standard in post-cured plaques.

Dynamic Mechanical Spectroscopy Properties

The dynamic mechanical spectroscopy (DMS) traces (at 1 Hz) of plaque I (made with Jeffamine

Table VIII Effect of Diamine Backbone Structure on Impact Properties and Hardness at 60 Vol % Hard Segment

Plaque No.	Diamine	Post-Cured	Hardness (Shore D)	Yield (ft-lb/in. crack)	Maximum Force (lb)	Energy to Max Force	Energy to Break (ft lb)	Type of Failure
I	D-2000	No	75	3.1	600	4.8	5.3	Brittle
	D-2000	Yes ^a	76	3.7	554	4.4	5.7	Brittle
II	1-Urea	No	73	2.0	358	2.1	4.9	Brittle
	1-Urea	Yes ^a	75	2.0	400	2.2	5.4	Brittle
III	50% D-2000/ 50% 4-Urea	No	76	2.4	361	2.0	3.2	Brittle
		Yes ^a	77	1.9	624	4.5	6.4	Brittle
IV	4-Urea	No	85	0.4	174	0.2	0.4	Brittle
	4-Urea	Yes ^a	85	0.4	298	0.6	0.9	Brittle

^a Post-cured 1 h at 175°C.

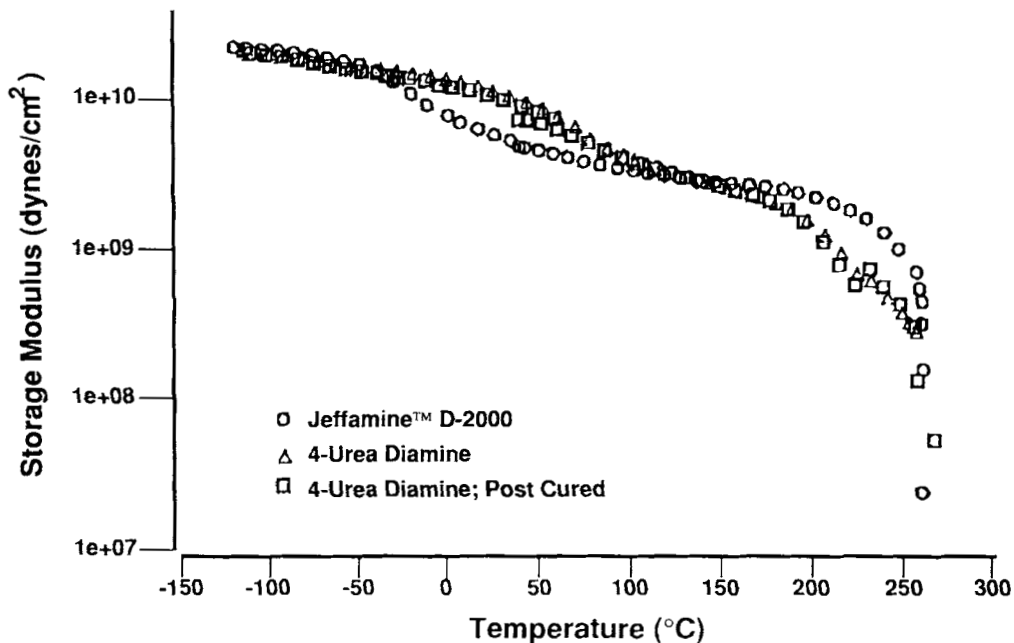


Figure 9 Effect of diamine backbone structure on storage modulus; DMS trace; frequency = 1.0 Hz.

D-2000), plaque IV (made with 4-urea diamine), and plaque IV (post-cured 1 hour at 175°C) were obtained. Storage moduli and tan δ curves are com-

pared in Figures 9 and 10, respectively. The traces are complex as would be expected due to the number of interactions possible. The trace of storage mod-

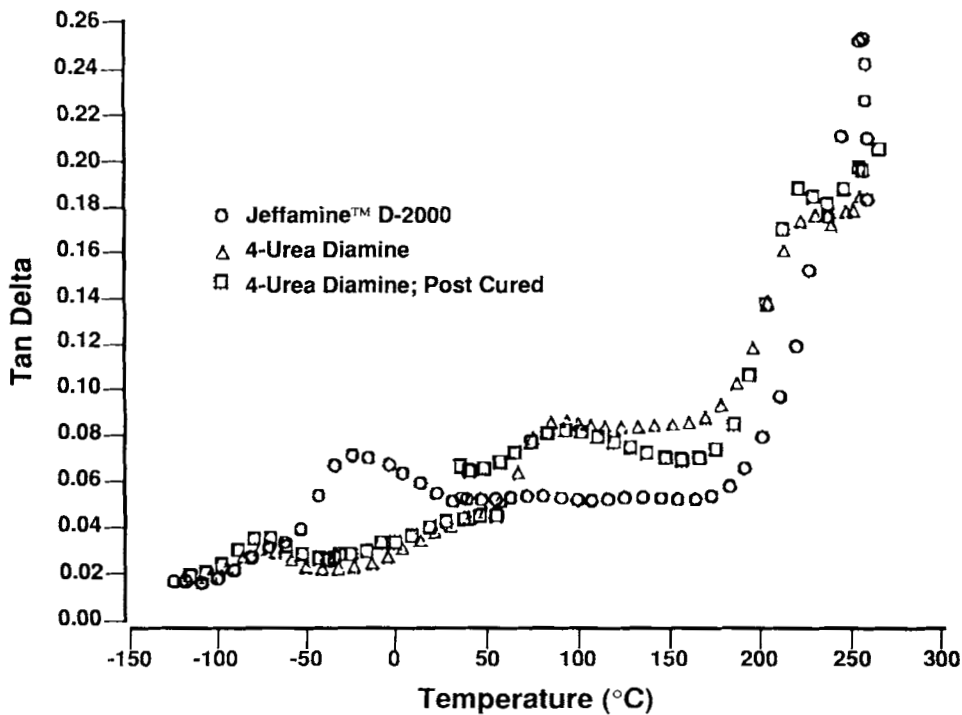


Figure 10 Effect of diamine backbone structure on tan Δ ; DMS trace; frequency = 1.0 Hz.

ulus versus temperature confirms that the room temperature modulus is much higher for the materials with urea moieties in their backbones. However, there is a crossover point around 135°C, and the modulus of the plaque based on Jeffamine D-2000 is higher at higher (>135°C) temperatures. The slope of the storage modulus curve indicates much more phase mixing for the plaques containing urea moieties in the diamines. The $\tan \delta$ traces indicate a variety of states present in the plaques containing urea moieties in the polyether diamines. The $\tan \delta$ curves for the plaques made from the polyether diamines containing four urea moieties fall below the Jeffamine D-2000 standard. This suggests better low temperatures and less hysteresis loss. More detailed morphological data will be the subject of further papers.

CONCLUSIONS

Polyether polyamines containing preformed urea moieties in their backbone, prepared by the reaction of aminated polyglycols with urea, were used to fabricate high modulus urea polymers by reaction injection molding (RIM) on micro-RIM equipment. A formulation was studied based on a 2000 g/mol molecular weight polyether diamine containing about four internal urea moieties/molecule as the soft segment and Isonate 143L and diethyltoluenediamine (DETDA) as the hard segment (60 vol %). This is the first time that polyureas containing preformed urea moieties in a polyether soft segment have been reported.

Mixing was measured by the temperature rise produced by injection of the components into an adiabatic cup as a function of the B-side Reynolds number at the mixhead. B-Side Reynolds numbers of about 300 or above were required for adequate mixing in this system. This corresponds to a B-side component temperature of about 65°C, which is easily attained in RIM equipment.

Plaques were made and compared to the corresponding polyether diamine without urea moieties. The formulation containing preformed urea moieties in the soft segment produced urea polymers with superior properties such as higher modulus, greater strength, increased hardness, superior organic solvent resistance, and improved green strength at demold. Impact properties were reduced. Considerable phase mixing occurs. Subsequent papers will detail the polymer properties and morphology of urethane/urea polymers obtained by the use of soft segments containing a wide variety of hydrogen bonding moieties.

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Received September 12, 1991

Accepted February 6, 1992