

# Instrumented Impact Testing of Castor-Oil-Based Polyurethanes

T. M. LIU and V. T. BUI\*

Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, Ontario, Canada K7K 5L0

## SYNOPSIS

Instrumented impact testing has been used to study castor-oil-based polyurethanes. The energy-absorbed capacity of these materials in impact is dependent on several factors, such as the type of isocyanate, NCO/OH ratio, and testing temperature. An approximate but simple method for the low-temperature impact testing was proposed. A change from ductile response to brittle fracture was observed as the temperature of the specimen was reduced. This characteristic ductile-brittle transition temperature is to be found highly sensitive to crosslinking degree. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

As the application for toughened polymeric materials becomes more common and more severe, there is an increasing demand for tests that accurately simulate end-use conditions. It is especially important to know how these materials are affected by impact. The impact resistance of polymeric materials often determines their usefulness in many applications. Accurate evaluation of a polymer's impact resistance is, therefore, essential if optimum part performance is to be determined. The most common impact tests used in industry have been uninstrumented Izod, Charpy, and drop-weight tests. These tests provide simple impact ranking for different materials under limited test conditions but do not provide insights regarding the nature of failure needed by the materials and product designer. Consequently, these tests have recently been instrumented to generate force versus deformation data at various conditions allowing detailed analysis of specimen failure. For this reason, instrumented impact testing has become a more common test technique.<sup>1-3</sup>

Castor oil is a naturally occurring triglyceride of ricinoleic acid. Because it contains hydroxyl groups

as well as carbon-carbon double bonds, it is especially well suited to a wide range of chemical modifications. The use of castor oil as a polyol in the preparation of polyurethane has been reported. Sperling et al.<sup>4</sup> employed tolylene diisocyanate (TDI) and hexamethylene diisocyanate (HDI) to prepare castor-oil-based polyurethane. Petrovic et al.<sup>5</sup> synthesized castor-oil-based polyurethane using diphenylmethane diisocyanate (MDI). Some of the properties of these polyurethanes such as thermo-mechanical, dynamic mechanical, and tensile mechanical properties have been measured.<sup>4,5</sup> However, there is no literature on impact properties of castor-oil-based polyurethanes. In this work, a different type of isocyanate, Desmodur N-100, together with HDI is employed to produce castor-oil-based polyurethanes. The impact properties of these materials are investigated and the ductile-brittle transition temperature (DBTT) is determined.

## EXPERIMENTAL

### Materials

Castor oil was supplied from Aldrich Chemical Company, Inc. Its equivalent weight per hydroxyl group is equal to 405 g. Two kinds of isocyanate, Desmodur N-100 and HDI, were employed in this work. Desmodur N-100 is a clear, slightly yellow,

\* To whom correspondence should be addressed.

viscous, and solvent-free liquid. It is composed of an aliphatic polyisocyanate resin based on HDI, and its equivalent weight per NCO group is 191 g. It was supplied by Mobay Company through Bayer Canada. HDI has an NCO equivalent weight of 84 g and was supplied from Aldrich. *N,N*-Dimethyl formamide (DMF), from Fisher Scientific Company, was employed as a solvent to swell the polyurethane samples. The densities, molecular weights, and boiling point temperatures of the above materials are given in Table I. BP<sub>760</sub> and BP<sub>9</sub> represent the boiling points at pressures of 760 and 9 mm of mercury (mmHg), respectively.

### Synthesis

The castor-oil-based polyurethanes were prepared as follows. Castor oil and the calculated amount of isocyanate were mixed in a beaker at room temperature. The mixture was stirred vigorously with a Teflon-coated magnetic stir bar for at least 1 h. After mixing, the mixture was poured into different molds to make tensile test specimens and impact test specimens, respectively. In order to produce bubble-free specimens, the mixture in the mold was heated to 60°C and degassed under reduced pressure, 76 mmHg, for at least 30 min, until all bubbling ceased. It was then heated for 2 h at 130°C to complete the curing reaction. After curing, the mold was allowed to cool and the specimen was separated. Samples with different NCO/OH ratios and different isocyanate compositions were prepared. Their designation is given in Table II.

On the basis of BP<sub>760</sub> and BP<sub>9</sub> in Table I, the boiling point of HDI at a pressure 76 mmHg can be estimated by means of the Clausius-Clapeyron equation.<sup>6</sup> It is 176°C, which is effectively much higher than 60°C, the temperature of the reduced pressure oven. Concerning castor oil and N-100, we cannot find their boiling point data, but considering that these compounds have higher molecular weights and probably stronger intramolecular interactions,

**Table I** Properties of Castor Oil, N-100, HDI, and DMF

Material	Density (kg/m <sup>3</sup> )	Molecular Weight	BP <sub>760</sub> (°C)	BP <sub>9</sub> (°C)
Castor oil	961	933	313	—
N-100	1140	500	—	—
HDI	1040	168	255	121
DMF	947	73	153	—

**Table II** Designation of Castor-Oil-Based Polyurethanes

HDI/N-100 wt %/wt %	NCO/OH Ratio		
	1.0	1.25	1.5
100/0	A1	A2	A3
75/25	B1	B2	B3
50/50	C1	C2	C3
25/75	D1	D2	D3
0/100	E1	E2	E3

it is reasonable to assume that their boiling points are even higher than that of HDI at the same reduced pressure of 76 mmHg. Consequently, it can be assumed that there is little loss of the reactants during the degassing operation; furthermore, this process was only started about an hour after the beginning of mixing the reactants, at that moment most reactants might already have reacted to form polymer of short chains, which have nearly no volatility.

### Measurements

#### Impact Tests

Impact testing was performed using a Rheometrics Drop Weight Tester (RDT-5000). A high-speed dart weighing 3.73 kg was employed. All the tests were performed using a probe with a hemispherical end 12.7 mm in diameter. A force-sensing load cell in the dart had a full range of 1134 kg. The impact test specimens were cast in a disk shape 37.0 mm in diameter and 3.0–3.1 mm in thickness. The disk specimens were held in place on an annular stainless steel ring with an internal diameter of 25.4 mm (1 inch). The set impact speed was 7.6 m s<sup>-1</sup>. The impact force displacement trace was recorded in order to characterize the impact properties of the samples.

The lower temperature limit of the environmental chamber of the RDT-5000 system is -40°C. Initial experiments show that most of DBTTs of the castor-oil-based polyurethanes are lower than -40°C. An approximate but simple method was proposed for low-temperature impact testing. The specimen was immersed into liquid nitrogen and left to reach a uniform temperature. It was then removed from the liquid nitrogen medium to ambient air and installed in the impact specimen holder. The time which elapsed after the specimen was removed from the liquid nitrogen was measured. The temperature in the center of the disk specimen,  $T_c$ , was recorded using a digital thermocouple (model 8528-20, Cole-

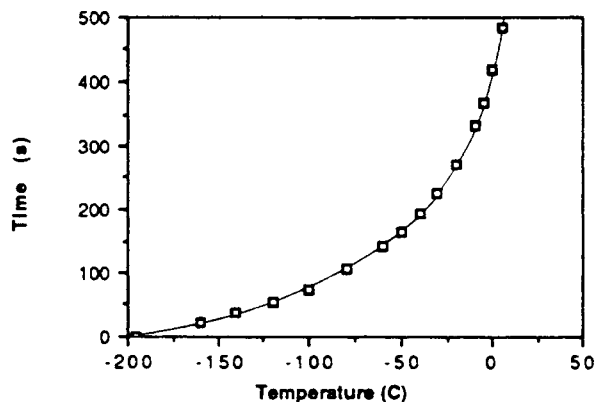
perner Instrument Co.). A curve of time versus the temperature in the center of the disk specimen is shown in Figure 1. The test temperature was varied by correspondingly changing the starting time of the impact test.

It is very important to mention that while the temperature in the center of the disk specimen is reported and used in the impact tests, the surface temperature of the specimen,  $T_s$  (usually much warmer), which actually controls the test results, is not readily determined by experimentation. Nevertheless, calculations based on a transient heat conduction method<sup>7</sup> had given rise to the conclusions that the differences between  $T_s$  and  $T_c$  are not as large as expected even though polyurethanes are known as poor thermal conducting materials. This may mainly be attributed to the small thickness of the disk specimen used. Table III summarizes the relationships between  $T_s$  and  $T_c$  for various values of  $T_c$  varying from  $-100$  to  $0^\circ\text{C}$ . Because of the small differences between  $T_s$  and  $T_c$ , the experimental data of the latter as a function of time reported in Figure 1 were used and referred in this work without committing any considerable uncertainty on the impact properties of the studied materials as a function of temperature.

#### Density Measurement

Densities of the samples were measured using the ASTM standard test method D792-A. A specimen of the solid polyurethane was weighed in air. It was then immersed in water. Its loss in weight upon immersion was determined, and its density calculated by:

$$\text{Density} = 0.9975 \frac{W_0}{W_0 - W_1} \quad (1)$$



**Figure 1** Elapsed time vs. the temperature in the center of the disk specimen of castor-oil-based polyurethane.

**Table III** Relationships between  $T_c$  and  $T_s$  of an Impact Test Disk Specimen

$T_c$ ( $^\circ\text{C}$ )	-100	-80	-60	-40	-20	0
$T_s$ ( $^\circ\text{C}$ )	-96	-77	-57	-37	-18	2

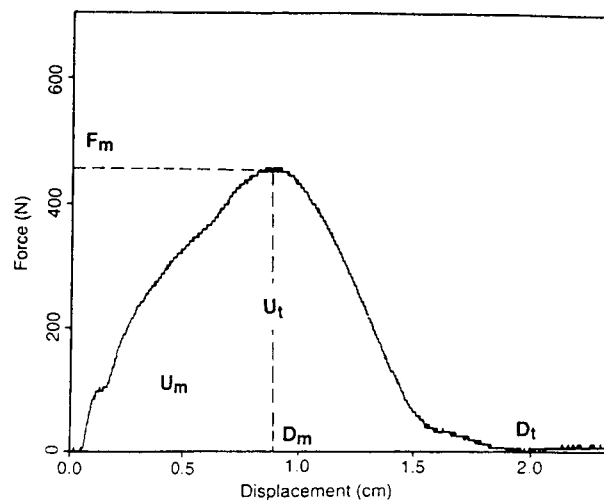
where  $W_0$  is the apparent weight of specimen in air and  $W_1$  is the apparent weight of specimen completely immersed in water. The measurement was carried out at  $23^\circ\text{C}$ . A preexperimental immersion in water indicated that sample A1 had a specific gravity less than unity. A small lead ball was therefore used as a sinker for sample A1. A Mettler lab balance was used for weighing and the accuracy in the reading is  $\pm 0.0002$  g. Since the balance had a taring function, the weights of partially immersed wire and totally immersed sinker were tared out.

#### Swelling Test

A specimen of known weight was cut from the cured sample and swollen in the DMF solvent. The degree of swelling was measured by the increase in specimen weight after immersion for 15 days at room temperature ( $23^\circ\text{C}$ ).

#### Tensile Test

Tensile tests were performed on an Instron tensile tester, model 4206, at room temperature. The samples for the tensile measurements were cast in a dumbbell shape 10 mm in width, 2.8–3.2 mm in thickness, and 25 mm in gauge length. The ASTM D638 procedure was followed employing a crosshead speed of  $10 \text{ cm min}^{-1}$ . The stress-strain curve,



**Figure 2** Typical impact force-displacement curve (sample C1).

**Table IV** Impact Properties of Castor-Oil-Based Polyurethanes

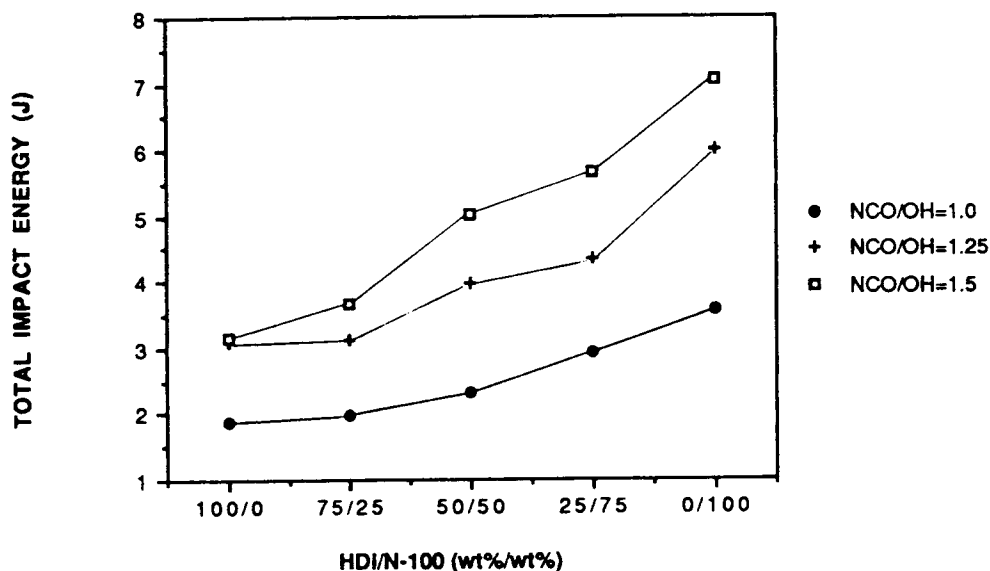
HDI/N-100 wt %/wt %	$F_m$ (N)	$D_m$ (cm)	$D_t$ (cm)	$U_m$ (J)	$U_t$ (J)	DBTT (°C)	$T_g$ (°C)
<u>NCO/OH = 1.0</u>							
100/0	137	2.0	3.43	0.86	1.88	-88	-43
75/25	141	1.75	3.12	1.09	1.98	-82	-41
50/50	163	1.75	2.90	1.39	2.32	-76	-38
25/75	209	1.07	2.41	1.83	2.90	-71	-35
0/100	378	1.02	2.29	2.43	3.57	-66	-32
<u>NCO/OH = 1.25</u>							
100/0	313	2.08	2.72	1.73	3.10	-81	-41
75/25	358	1.91	2.18	1.88	3.13	-74	-33
50/50	516	1.55	2.03	2.59	3.99	-69	-29
25/75	560	1.63	1.88	2.91	4.35	-65	-24
0/100	738	1.52	1.83	4.45	6.01	-55	-17
<u>NCO/OH = 1.5</u>							
100/0	333	1.85	2.39	2.06	3.16	-75	-35
75/25	396	1.63	2.26	2.54	3.68	-68	-28
50/50	560	1.30	2.16	3.67	5.03	-66	-26
25/75	658	1.24	1.80	4.52	5.65	-62	-23
0/100	885	1.17	1.75	6.06	7.04	-51	-15

Young's modulus, and ultimate tensile strength were measured.

#### Thermomechanical Analysis (TMA)

TMA was performed using a Mettler TA-4000 with a TMA 40 measuring cell. The approximate sample

dimensions were 3 mm thick in the direction of measurement and 6 mm in diameter. Measurements were carried out in the range of  $-100$  to  $250^\circ\text{C}$ . A low-temperature accessory was used with liquid nitrogen as refrigerant. The heating rate was  $10^\circ\text{C}/\text{min}$  and the constant probe force applied to the sample was  $0.02\text{ N}$ .



**Figure 3** Total impact energy of castor-oil-based polyurethane.

RESULTS AND DISCUSSION

A typical impact–deformation trace obtained at room temperature for the sample C1 is shown in Figure 2. Some critical values of the impact event can be measured from this trace. Parameters which can be calculated are:  $F_m$  the maximum force,  $D_m$  the displacement at maximum force,  $D_t$  the final displacement where no resistance to impact remains,  $U_m$  the absorbed energy up to the maximum force, and  $U_t$  the total absorbed energy. The impact properties of the castor-oil-based polyurethanes are tabulated in Table IV.

The impact strength of the sample is normally characterized by the total impact energy  $U_t$ , which is measured by the area under the force–displacement curve. The N-100 content and the NCO/OH ratio have a significant effect on the total impact energy, Figure 3.  $U_t$  increases with N-100 content and NCO/OH ratio. As an illustration, the force–displacement curves of the samples with NCO/OH ratio of 1.25 are shown in Figure 4. In first approximation, the shape of the impact curve looks like a triangle, and the area under the curve can be estimated by:

$$U_t = S = \frac{1}{2}F_m D_t \quad (2)$$

where  $S$  is the area under the force–displacement curve. The data in Table IV shows that when the content of N-100 for the samples of NCO/OH = 1.25 increases from 0 to 100%,  $D_t$  decreases only about

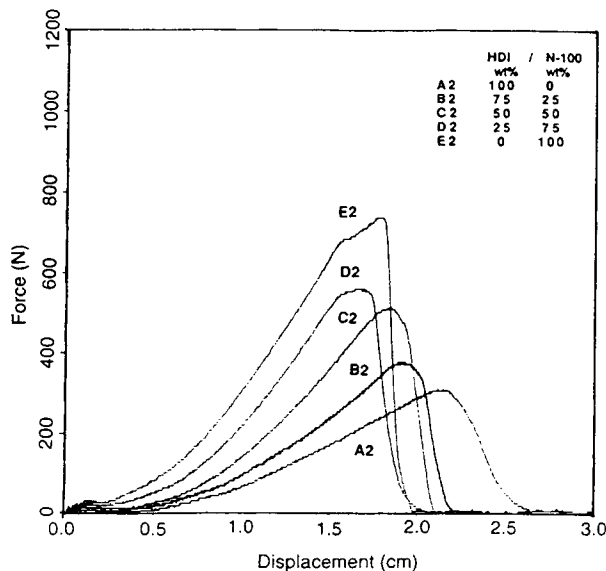


Figure 4 Impact force–displacement curves of castor-oil-based polyurethane (NCO/OH = 1.25).

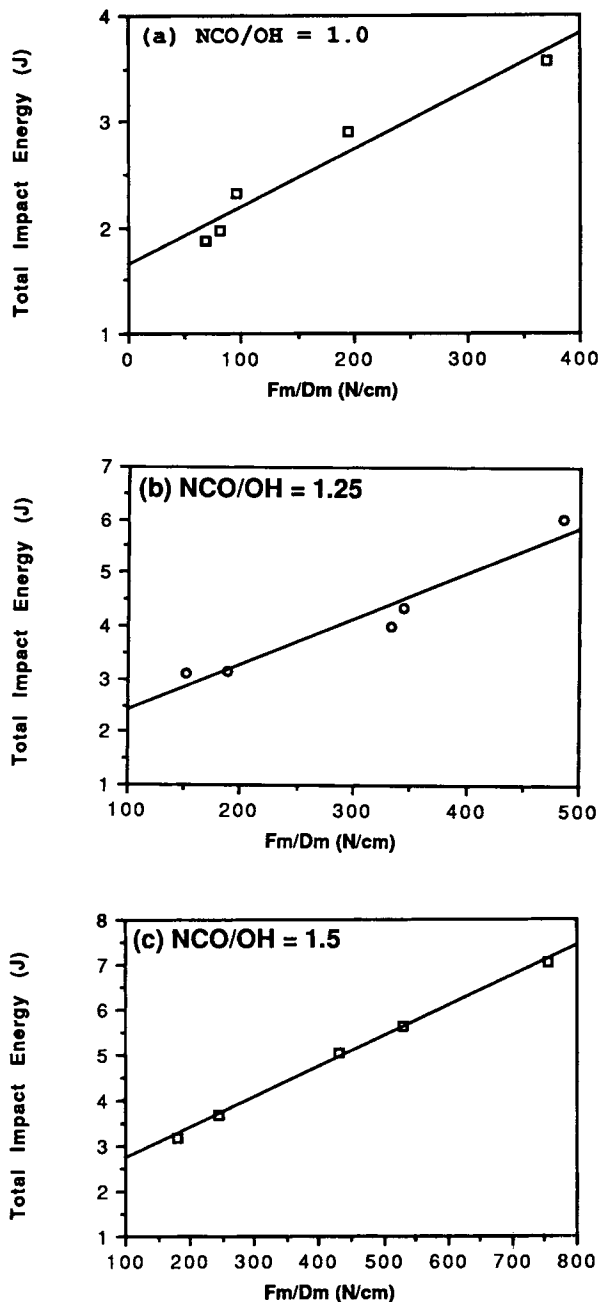


Figure 5 Total impact energy as a function of secant modulus. (a) NCO/OH = 1.0, (b) NCO/OH = 1.25, and (c) NCO/OH = 1.5.

30%, but  $F_m$  increases about 135%. A secant modulus was used to assess the stiffness of the materials in impact testing<sup>8</sup> and defined as:

$$\text{Secant modulus} = \frac{F_m}{D_m} \quad (3)$$

It should be noted that increased stiffness is accom-

**Table V** Young's Modulus and Tensile Strength of Castor Oil-Based Polyurethanes

HDI/N-100 wt %/wt %	Young's Modulus (MPa)	Tensile Strength (MPa)
NCO/OH = 1.0		
100/0	0.562	0.480
75/25	0.844	0.492
50/50	1.070	0.676
25/75	2.434	0.770
0/100	3.918	1.760
NCO/OH = 1.25		
100/0	1.398	0.876
75/25	1.655	0.979
50/50	1.931	1.014
25/75	2.709	1.459
0/100	4.510	2.012
NCO/OH = 1.5		
100/0	1.627	0.987
75/25	2.062	1.073
50/50	2.637	1.220
25/75	3.182	1.770
0/100	5.292	2.130

panied by an increase in toughness for the castor-oil-based polyurethanes, Figure 5.

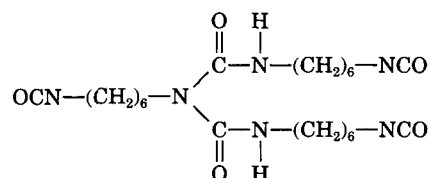
The stiffness of the disk specimen in an impact test is proportional to the Young's modulus  $E$  by<sup>8</sup>:

$$\frac{F_m}{D_m} = 1.72 \frac{t^3}{R^2(1-\nu^2)} E \quad (4)$$

where  $t$  is the thickness of the disk,  $R$  is the radius of the disk support, and  $\nu$  is Poisson's ratio. Young's

modulus and tensile strength of castor-oil-based polyurethanes were measured and are summarized in Table V. The impact secant modulus increases with Young's modulus.

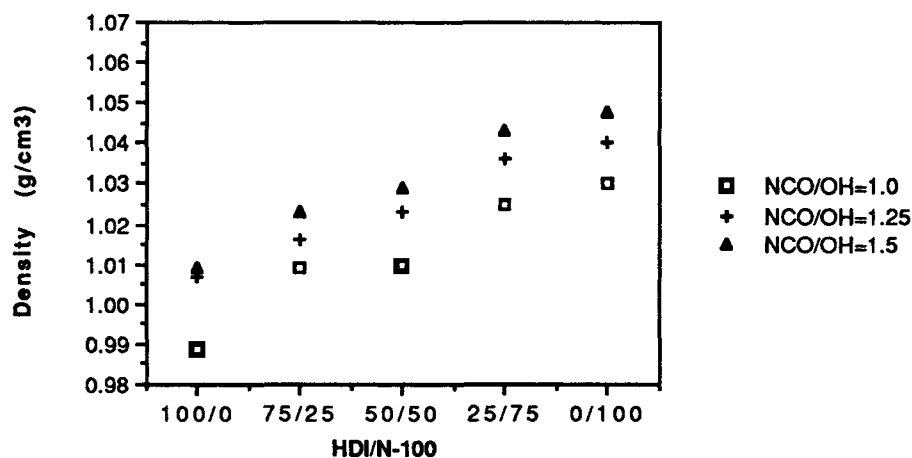
The considerable improvement in Young's modulus is believed to depend on increased chemical crosslinking of the castor-oil-based polyurethanes. Desmodur N-100 is a polymeric isocyanate based on HDI and has mainly the following structure:



This structure contains three NCO groups, and two biuret groups, and therefore N-100 itself is capable of introducing crosslinking centers.

The change in density could be used as a qualitative assessment of crosslinking density. The effect of N-100 content and NCO/OH ratio on density of castor-oil-based polyurethanes is shown in Figure 6. Density increases with both N-100 content and NCO/OH ratio. Petrovic et al.<sup>5</sup> stated that swelling experiments were more direct measures of crosslinking density. Figure 7 shows the change of degree of swelling with N-100 content and the NCO/OH ratio. By increasing the N-100 content, the degree of swelling increases. For the samples with the same N-100 content, their degree of swelling increases with a higher NCO/OH ratio.

The total impact energy can be divided into two parts: the elastic deformation energy ( $U_m$ ) and the plastic deformation energy ( $U_p = U_t - U_m$ ). Figure 8 shows the effect of N-100 content on  $U_t$ ,  $U_m$ , and



**Figure 6** Density as a function of N-100 content and NCO/OH ratio.

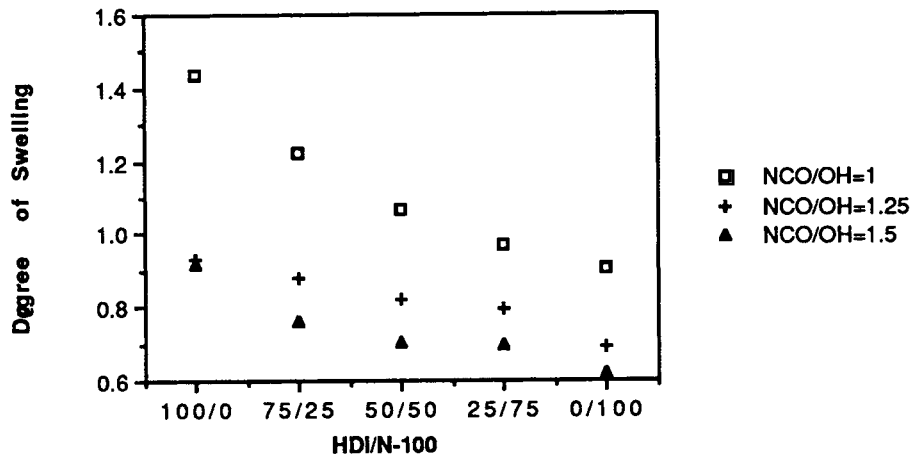


Figure 7 Degree of swelling as a function of N-100 content and NCO/OH ratio.

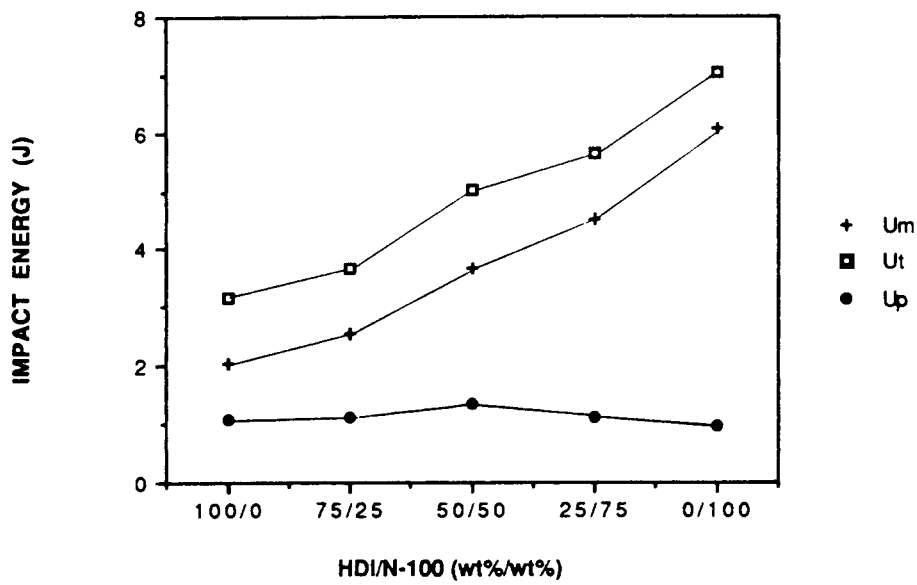


Figure 8 Total impact energy, elastic energy, and plastic energy of castor-oil-based polyurethane (NCO/OH = 1.5).

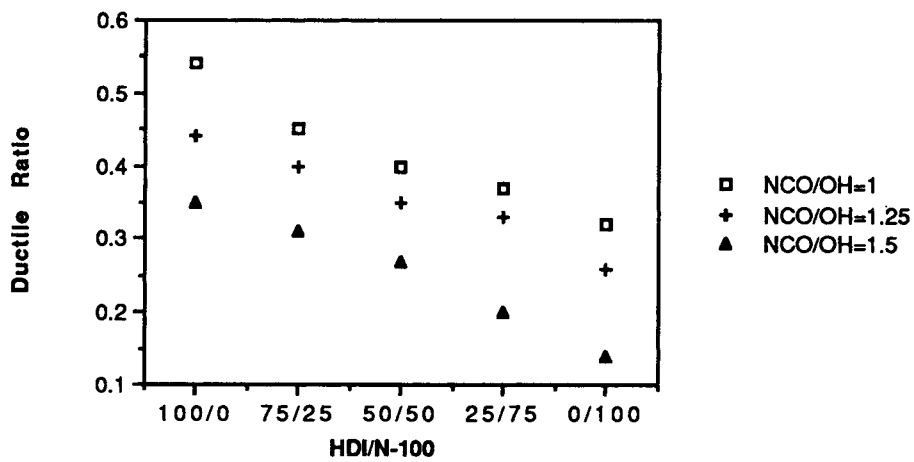


Figure 9 Ductile ratio as a function of N-100 content and NCO/OH ratio.

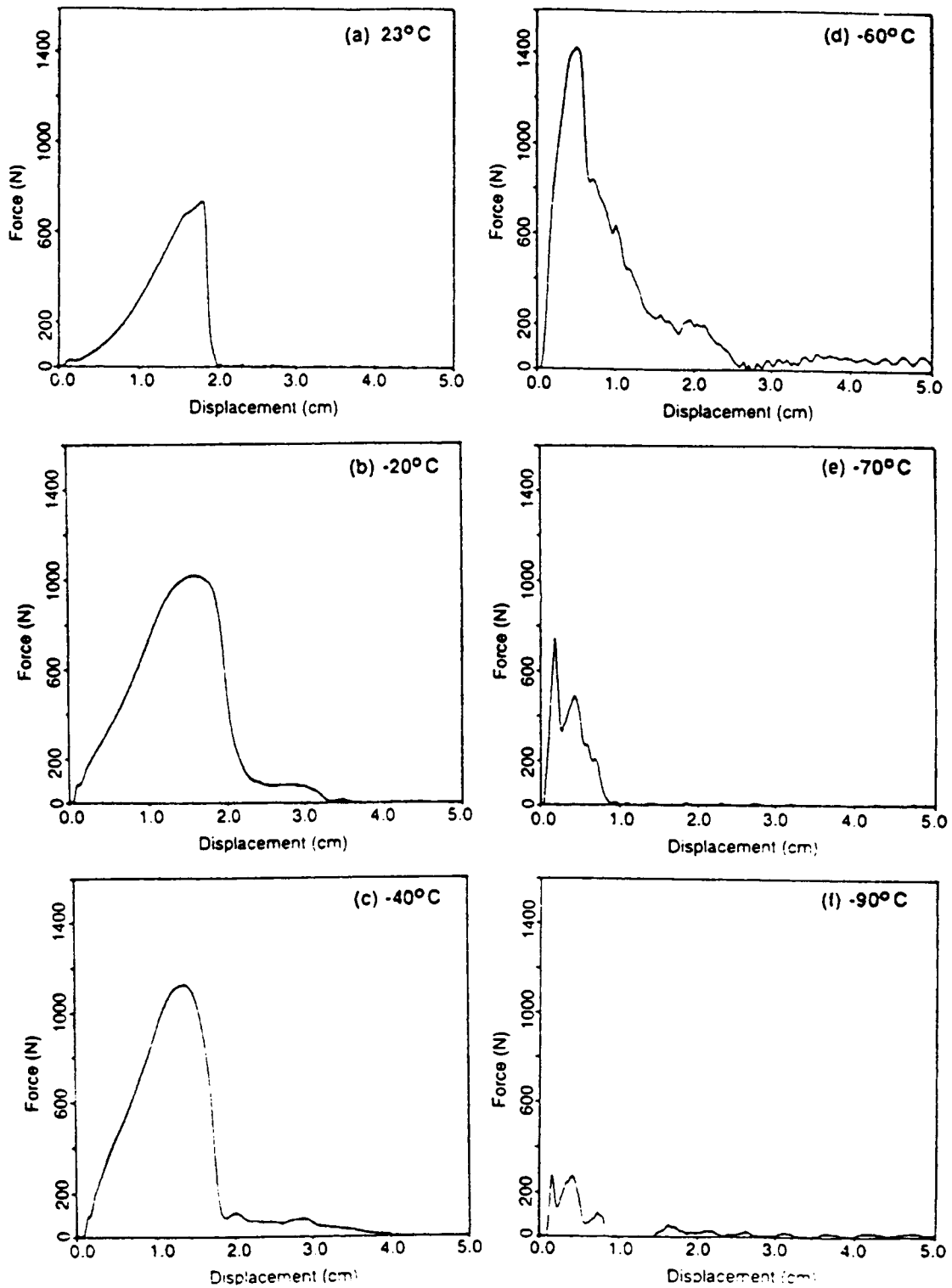


Figure 10 Effect of temperature on impact curves.



$U_p$  of samples with  $NCO/OH = 1.5$ .  $U_p$  remains almost constant and the increase in  $U_t$  results from an increase in  $U_m$ .

The ductility of a polymer can be characterized from  $U_t$  and  $U_m$ . The ductile ratio of a material is defined as:

$$\text{Ductile ratio} = \frac{U_t - U_m}{U_t} \quad (5)$$

For an ideal brittle material which does not exhibit any plasticity,  $U_t$  is equal to  $U_m$ , and its ductile ratio is equal to zero. For an ideal ductile material which exhibits little elasticity,  $U_t \gg U_m$ , the ductile ratio approaches unity. A real polymer normally shows a ductile ratio between zero and one. The effect of N-100 content and NCO/OH ratio on the ductile ratio of castor-oil-based polyurethanes is shown in Figure 9. As N-100 content and NCO/OH ratio increase, the ductile ratio decreases. Sample A1 has the highest ductile ratio of 0.54 and sample E3 has the lowest ductile ratio of 0.14.

Bucknall<sup>9</sup> has been investigating impact testing of polymers for years. He pointed out that the impact behavior of a polymer was affected to a greater extent by changes in the experimental temperature. For example, a change in fracture mode (ductile to brittle) can occur by decreasing temperature.<sup>10</sup>

Various types of failure arise in castor-oil-based polyurethane samples in the temperature range from 23 to  $-120^\circ\text{C}$ . This is illustrated in Figure 10(a)–10(f) for sample E2 that was tested at 23,  $-20$ ,  $-40$ ,

$-60$ ,  $-70$ , and  $-90^\circ\text{C}$ . The failures at 23,  $-20$ , and  $-40^\circ\text{C}$  were ductile, with the specimen absorbing a large amount of energy, and damage to the specimen was localized. At  $-60^\circ\text{C}$  the specimen which underwent impact still absorbed a large amount of energy, but sharp cracks were observed. After the maximum force, the force–deformation curve becomes irregular. The failures at  $-70$  and  $-90^\circ\text{C}$  can be classed as brittle since the energy to failure is low, and the impacted sample produces catastrophic free-running cracks. The effect of testing temperature on the total impact energy of sample E2 is given in Figure 11. A ductile–brittle transition was observed at about  $-65^\circ\text{C}$ . The DBTTs of castor-oil-based polyurethanes are given in Table IV. As is indicated by the data, the ductile–brittle transition temperature increases with increasing N-100 content and NCO/OH ratio.

The glass transition temperature ( $T_g$ ) of the castor-oil-based polyurethane was measured by TMA and is listed in Table IV. Generally, the DBTT of this polyurethane was lower than the  $T_g$  of the same sample by approximately  $40^\circ\text{C}$ . This difference may be due to two possible reasons. First, the nature of DBTT is different from that of  $T_g$ . DBTT indicates a change in fracture mode from ductile to brittle. The basis for the glass transition is the onset of coordinated molecular motion in the polymer chain.<sup>11</sup> Second, there is a significant difference in testing time scale. During impact testing, the dart moves at a speed of 8 m/s, which corresponds to milliseconds. This is much less than the time scale of seconds and minutes used in TMA measurement.

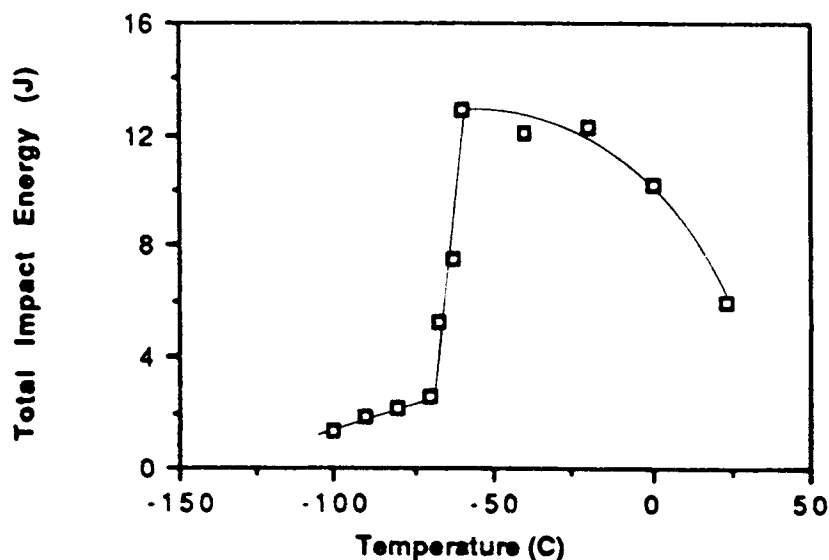


Figure 11 Effect of temperature on total impact energy.

## CONCLUSIONS

Polyurethane samples based on castor oil, Desmodur N-100, and HDI were synthesized by varying the composition of the isocyanate mixture and the NCO/OH ratio. It was demonstrated that the N-100 content and NCO/OH ratio have significant effects on their mechanical properties. The instrumented impact test is a convenient and useful method for characterizing the impact behavior of castor-oil-based polyurethanes. The improvement in the impact properties can be attributed to an increase in crosslinking density. An impact transition temperature, which represents a change from ductile to brittle behavior, can be determined. The ductile-brittle transition temperature of castor-oil-based polyurethane is highly sensitive to the composition of the isocyanate mixture and NCO/OH ratio.

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