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MTL TR 91-26

AD-A239 397

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STRUCTURE PROPERTY RELATIONSHIP OF ALIPHATIC POLYURETHANE ELASTOMERS PREPARED FROM CHDI

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July 1991

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91-07393

US ARMY
LABORATORY COMMAND
MATERIALS TECHNOLOGY LABORATORY

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UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER MTL TR 91-26	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (*and Subtitle*) STRUCTURE PROPERTY RELATIONSHIP OF ALIPHATIC POLYURETHANE ELASTOMERS PREPARED FROM CHDI		5. TYPE OF REPORT & PERIOD COVERED Final Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(*s*) Catherine A. Byrne, Joey L. Mead, and C. Richard Desper		8. CONTRACT OR GRANT NUMBER(*s*)
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Materials Technology Laboratory Watertown, Massachusetts 02172-0001 SLCMT-EMP		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Laboratory Command 2800 Powder Mill Road Adelphi, Maryland 20783-1145		12. REPORT DATE July 1991 13. NUMBER OF PAGES 37
14. MONITORING AGENCY NAME & ADDRESS (*if different from Controlling Office*)		15. SECURITY CLASS. (*of this report*) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (*of this Report*)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (*of the abstract entered in Block 20, if different from Report*)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (*Continue on reverse side if necessary and identify by block number*)

Polyurethanes	Crystllinity	Thermal analysis
Elastomers	Hysteresis	Solvent resistance
Microphase	Mechanical analysis	

20. ABSTRACT (*Continue on reverse side if necess ary and identify by block number*)

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ABSTRACT

Aliphatic polyurethane elastomers have been prepared from trans-1,4-diisocyanatocyclohexane, poly(tetramethylene oxide), 1,4-butanediol and optionally trimethylolpropane. CHDI is a compact symmetrical diisocyanate which is responsible for remarkable properties in these polymers. They are nearly transparent elastomers with low glass tranisiton temperatures of approximately -80°C, and high final softening temperatures up to 270°C, for polymers with low hard phase contents of 20% to 30%. They are well phase separated and exhibit either paracrystallinity or crystallinity with small crystallite size after preparation. Considerable crystallinity develops after scanning up in temperature to 275°C or holding at 150°C to 160°C for six hours. The polymers are insoluble even when heated in polymer solvents and this is attributed to ordering even in the as-synthesized polymers. They have excellent mechanical properties compared to other polyurethane elastomers and retain their modulus up to high temperatures. Because of their excellent phase separation and low hard segment content, with the resultant discrete domains, they exhibit very low hysteresis in compression and tension.

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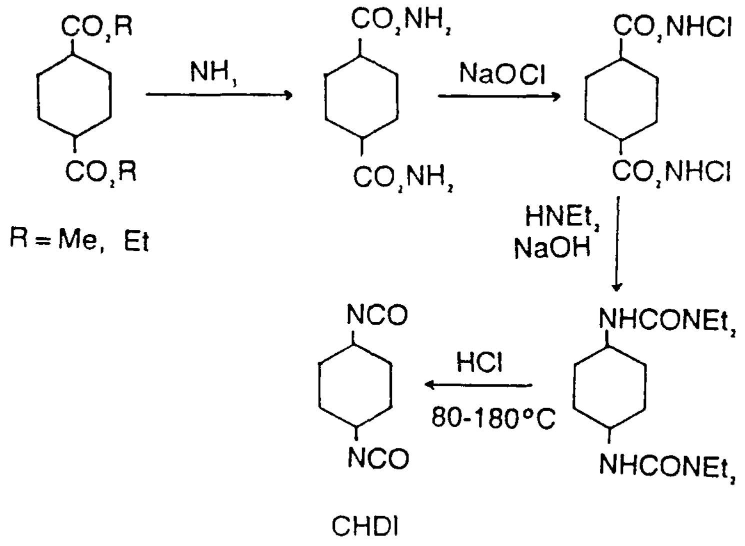
EXPERIMENTAL

INTRODUCTION

The research reported here is part of a long-term research program in which the goal is to investigate new starting materials for polyurethane elastomers and to incrementally improve the properties and expand the temperature range of use and the list of applications for these polymers. The new aliphatic diisocyanate which this study is based upon is trans-1,4-diisocyanatocyclohexane (CHDI, Elate 166, AKZO Chemie America). This material is made by a process which does not use phosgene (as shown in Scheme 1), therefore, the product is the pure trans isomer.[1] In this study, polyurethane elastomers have been prepared using poly(tetramethylene oxide) polyols (PTMO) and 1,4-butanediol (BD) as chain extender. In a limited number of sample, trimethylolpropane (TMP) was used as the crosslinker. It should be noted that the molecular weight and size of CHDI are very small compared to many diisocyanates and that it has high symmetry. It can be used in very small quantities in a polyurethane to achieve remarkable properties. This report is a summary of research on CHDI-based polyurethane elastomer block copolymers including synthesis, thermal properties, X-ray studies, and mechanical properties including mechanical hysteresis. The available literature on CHDI-based polymers is reviewed, as well as studies of microphase separation in polyurethanes and hysteresis behavior in polyurethanes, both in compression and tension.



Scheme 1

The study described here was related to a larger program in which new elastomers for tank track pads and solid tires were being investigated. Polyurethanes prepared from CHDI offered two advantages: there was some evidence that they were more likely to exhibit reduced hysteresis compared to most polyurethane elastomers; also, they offered a simple system on which to investigate some basic questions about hysteresis behavior in polyurethane elastomers. Since CHDI is a relatively new commercially available diisocyanate, it fit nicely into the long-term objectives of our research (to investigate the preparation and properties of new and improved polyurethane elastomers). Probably the cost of this diisocyanate would prohibit its use in high volume applications such as tires or track pads.

Review of the Literature on CHDI

Several reports of the properties of polyurethanes prepared from CHDI have appeared. Wong and Frisch[2] reported on model compound studies of the relative reactivities of important diisocyanates and found that CHDI is intermediate in reactivity between methylene bis(4-phenylisocyanate) (MDI) and methylene bis(4-cyclohexylisocyanate) ($H_{12}MDI$) in the reaction to form the urethane group with an aliphatic alcohol and a tin catalyst. In the same report the thermal stabilities of polyether-based polyurethanes were compared using mechanical tests. Polyurethanes prepared from CHDI retained more than 50% of their tensile modulus at 150°C compared to about 10% for similar samples prepared from MDI, a very important diisocyanate used in hand cast polyurethanes, as well as in reaction injection molding. The greater thermal stability of aliphatic urethane linkages has been reported,[3] as well as the greater hydrolytic stability of polymers prepared from CHDI compared to tolylene diisocyanate- (TDI) based samples.[4] A report summarizing the thermal and mechanical properties of these aliphatic polyurethanes has also appeared.[5] The high melting transitions observed in these materials have led to other studies in which the CHDI has been blended with $H_{12}MDI$ or TDI. Use of the CHDI in these samples potentially improves the temperature range of the plateau modulus in dynamic mechanical analysis experiments.[6] The processing characteristics and properties of injection molded materials have also been reported.[7]

Review of Microphase Separation

The elastic properties of urethane elastomers are derived from the phenomenon of microphase separation. In microphase separation the two constituent species of the segmented urethane chain (the hard segment and the soft segment) are driven by thermodynamic factors to separate into two phases for which, owing to the limited length of either segment, domains are constrained to sizes in the range of tens to hundreds of Angstroms. The microphase separation model for polyurethanes, developed over several decades through use of X-ray diffraction, Differential Scanning Calorimetry (DSC), and spectroscopic methods has recently been confirmed by Li and Cooper[8] by direct observation using high-voltage electron microscopy. The mechanical and thermal properties of the elastomer are dependent upon details of the microphase separation morphology. Such a polymer is elastic, for instance, only in the temperature range in which the soft segment microphase is rubbery and the hard segment microphase is glassy or crystalline. The upper limit of rubbery properties is, thus, either the glass transition temperature of the hard segment microphase, or the crystalline softening temperature of that microphase, as may be appropriate. In the extensively studied class of urethane elastomers based upon hard segments containing MDI and BD, microphase separation can occur either with[9-13] or without[14-16] three-dimensional crystallization of the hard segment microphase, depending upon sample composition and thermomechanical history. In either event, extensive urethane proton to carbonyl oxygen hydrogen bonding takes place, as shown by Bonart et al.[15] This provides, in thermodynamic terms, much of the driving force for the microphase separation in the form of an attractive interaction between like species. Bonart proposes a paracrystalline model for those cases in which the hard segment lacks three-dimensional order but, nonetheless, shows evidence of parallel ordering of hard segment chains. Further studies using hard segment species formed from piperazine and 1,4-butanediol bischloroformate[17,18] have demonstrated that hydrogen bonding between hard segment species is not a prerequisite for urethane elastomeric properties; this was done by the use of urethane linkages in which there was no protonated urethane.

The only reported X-ray diffraction results in the class of urethane elastomers having a hard segment prepared from CHDI and BD are those of Siegmann et al.[19] which show rudimentary evidence of hard segment crystallization as small peaks superimposed on a strong amorphous halo. It should be noted that this class of elastomers suffers an unusually severe signal-to-noise problem in that the useful range of hard segment content is quite low (20% to 30%), so that the preponderance of X-ray scattering in the wide angle region is from the soft segment micro-phases. This presents difficulties in terms of detecting hard segment crystallinity by X-ray diffraction.

Review of Compression Experiments on Polyurethanes

The polymer science literature contains very few studies of mechanical hysteresis during compression experiments. There are several recent reports of such studies and the results are reported for samples on which very little chemical information is reported. Inferences can be made about what broad classes of polyurethanes might perform best during compressive fatigue.

Screening experiments were run by Grasso[20] on 14 different compositions of polyurethanes and polyurethaneureas, using four different diisocyanates, polyether or polyester polyols, and diol or diamine chain extenders. The compositions in terms of stoichiometry are not mentioned in the report. The effect of the test specimen geometry on the compression fatigue behavior of the samples was investigated and a shape factor (defined as the ratio of the loaded area to the total force free area) of 1.0 was determined to produce the least heat buildup in compression fatigue on all the polyurethane-type polymers tested. Grasso's study was related to finding potential replacement materials for Styrene-Butadiene rubber (SBR) in tank track pads. Of all the samples tested, a sample prepared from TDI, polyether, and a proprietary diamine chain extender performed best. Another sample which passed all the tests is reported to contain TDI, a polyether, and methylene bis (o-chloroaniline) (MOCA). From the limited information in the report, it is possible to speculate that polyether-based materials perform better during hysteresis experiments and that polyurethaneureas might be better than diol cured materials.

The report of polyether-based systems performing better has also been reported by Alesi, Houghton, Roylance, and Simoneau[21] and perhaps is due to better phase segregation in polyether-based materials. Alesi et al. report that polymers based upon TDI, poly (tetramethylene oxide) 1000, and trimethylene glycol bis (p-aminobenzoate) perform better in compressive fatigue than samples prepared with higher molecular weight polyol with nominal weight 2000. These are rather hard materials, exhibiting Shore A hardness values of approximately 90 to 94 and Shore D values of 50. In the PTMO 1000-based materials, internal temperatures in the sample blocks during compression fatigue decreased as the ratio of isocyanate to amine groups increased. Similar materials were also studied by Mead, Singh, and Roylance.[22] The effect of fatigue on the elastic modulus of the materials was studied. A reduction in modulus after 5,000 cycles was attributed to the stress-softening analogous to the "Mullins Effect". Preliminary reports of compression fatigue experiments on CHDI-based polyurethanes have appeared.[23]

Review of Tension Experiments on Polyurethanes

Schollenberger and Dinbergs[24] reported a decrease in hysteresis for a series of polyurethane elastomers as the molecular weight increased. The molecular weight of the polymer was controlled by adjusting the ratio of NCO/OH from 0.96 to 1.0 in these MDI-based polyester polyurethanes extended with 1,4-butanediol. The molecular weights were analyzed by GPC and showed a range of 47,900 to 366,800. The soft segment T_g increased with increasing molecular weight of the polymer. The decrease in hysteresis in these experiments run to constant strain (the area inside the hysteresis loop) is attributed to a reduction of polymer-free volume due to a decrease in the number of free chain ends. In stress-strain curves up to 300% elongation there was no systematic relationship between molecular weight and tensile modulus. Hardness values did not vary in a systematic way.

Sung, Smith, Hu, and Sung[25] discuss hysteresis behavior in completely amorphous polyurethaneureas containing soft segments of two different lengths prepared from PTMO 1000 and PTMO 2000, and also different hard segment lengths prepared from 2,4-TDI and ethylene diamine. The samples prepared with the shorter soft segment are considerably more phase mixed and show a greater amount of hysteresis. The percent hysteresis values for two samples prepared from PTMO 1000 are very nearly the same (about 75% to 80%). It should be noted that these experiments are tensile hysteresis experiments, made by loading and unloading the strip specimens at constant crosshead speed to an increasing strain level at each cycle, from 25% to 450% for the PTMO 1000 samples and from 25% to 1050% for the sample prepared from PTMO 2000. In the samples prepared from PTMO 1000, the weight percent hard segments are 29% and 54%, and yet the percent hysteresis values are nearly the same. This suggests that the degree of interconnectivity in the domains is very similar in the two samples. The percent hysteresis in the one sample examined that was prepared with PTMO 2000 is much lower, and it also has a soft segment T_g of -73°C. The conclusion is drawn that the sample is phase separated and, therefore, is likely to have domains that are less connected than the PTMO 1000 polymer.

Abouzahr, Wilkes, and Ophir[26] studied four polyurethane samples varying in hard segment content from 15% to 45% which were prepared by the one-shot technique. PTMO 2000 was the soft segment. Tensile hysteresis experiments were made by stretching and unloading the dogbone specimens to an increasing strain level for each cycle. Elongation rate was 50%/min and strain levels were from 25% to 600%. Percent hysteresis was calculated as the area bounded by the loading/unloading curve to the total area under the corresponding stretching curve. The lowest mechanical hysteresis was exhibited by the sample with 25 weight percent hard segment. Samples with 35% and 45% hard segment show very high hysteresis, and the sample with 15% shows values between 25 and the other two. The results are explained on the basis of morphological models derived from small angle X-ray scattering (SAXS) and other experiments. The sample with the lowest hard segment content contains solubilized hard segments and, thus the polymer readily flows on deformation. The samples containing 35 weight percent and 45 weight percent hard segment suffer irreversible deformation under stress resulting in both higher hysteresis and permanent set. The best sample containing 24 weight percent hard segment has isolated discrete hard segment domains. Orientational effects are minimal and deformation at low elongation is principally that of the soft segment. Different processes are suggested to account for changes in the shape of the curves for percent hysteresis versus elongation in the polymers with different amounts of hard segment.

Wang and Cooper[27] refer to hard segment interconnectivity in polyurethaneureas with weight percent hard segments of 36% and 46%; the former was prepared with PTMO 2000 and the latter with both PTMO 1000 and PTMO 2000. The percent hysteresis at low strains for these samples is much higher than for similar samples with 25% hard segment prepared with both PTMO 2000 and PTMO 1000, and also one with 36% hard segment based upon PTMO 1000 where the hard segments form discrete domains.

From these references it is clear that low hysteresis results when a polyurethane has well separated phases and well formed discrete hard domains. This occurs when the amount of hard phase is relatively low so that the domains are not continuous and the molecular weight of the soft phase is generally greater than 1000.

EXPERIMENTAL

Materials

CHDI (Elate 166, AKZO Chemie America, 99% trans isomer) was distilled in vacuo (100°C to 102°C, 2.5 mm Hg). PTMO 2000 was obtained from Quaker Oats. The actual molecular wight calculated from the hydroxyl number was 2033. PTMO 2695 and 2900 were obtained from DuPont. The chain extenders 1,4-butanediol and trimethylolpropane were obtained from Aldrich and used as received.

Synthesis

The polymers were prepared using the prepolymer technique. Poly(tetramethylene oxide) was degassed with stirring under vacuum for one hour at 100°C. The CHDI was melted and added all at once and the reaction mixture was stirred under nitrogen at 100°C for one and one-half hours, or until the theoretical amount of isocyanate group remained (within 0.3%), as determined by titration. The titration procedure involved dissolving approximately seven grams of the prepolymer in 50 ml dry toluene and reacting with an excess of 2N di-n-butylamine for 15 minutes. Brom cresol green indicator solution and 200 ml isopropanol were added and the solution was titrated with 1N HCl.

The prepolymer was chain extended with BD and also trimethylolpropane (TMP) in a few samples. The chain extender was preheated to 100°C and mixed with the prepolymer rapidly for about one minute. The mixture was degassed to collapse for one to two minutes and poured into the mold. Several different types of mold were used. In some cases, two sheets of polypropylene were used with a metal picture frame of the desired thickness, approximately 1.3 mm (50 mils). Stainless steel molds with cavities 152.4 x 152.4 x 1.3 mm were also used. These samples were generally heated to 100°C at 100 psi in a press for about one hour and then cured in the oven for an additional 15 hours. Thicker samples (63.5 x 63.5 x 15.9 mm) were prepared in Teflon molds, covered loosely, and cured in the oven at 100°C for 16 hours.

Hardness and Abrasion

Shore A and Shore D hardness values were measured using D2240-75. Abrasion tests were run using the National Bureau of Standards (NBS) abrader described in the ASTM standard D 1630.

Thermal Analysis

Dynamic DSC was performed on a Perkin-Elmer DSC-2 or the P-E 7 Series Thermal Analysis System. In the low temperature range, 150°K to 300°K, the system was purged with Helium and the temperature was maintained with liquid nitrogen. In the high temperature range, 300°K to 550°K, the temperature was maintained with an Intercooler II two-stage cooling unit and the purge gas was nitrogen. Samples weighing 10mg to 40mg were encapsulated in stainless steel pans sealed with Viton O-rings. Earlier study was performed on larger samples but smaller ones were used later giving better results in the high temperature range. Heating rates were 10°C/min or 20°C/min and the cooling rate was 40°C/min. The resulting curves were analyzed using the Thermal Analysis Data Station or the Perkin-Elmer 7700 Professional Computer. Thermomechanical analysis (TMA) was performed on a Perkin-Elmer Thermomechanical Analyzer TMS-1 with a Perkin-Elmer Model UU-1 temperature program controller. Results were recorded on a Soltec Chart Recorder, Model 1242. The samples were 1.3 mm to 1.5 mm thick; the weight used on the TMA probe was 20 g and the heating rate was 20°C/min. Samples were heated in a helium atmosphere from -100°C to the softening point of the sample or 270°C.

X-ray Diffraction

X-ray diffraction patterns were obtained in both the small angle and wide angle ranges using the facilities of the National Synchrotron Light Source at the Brookhaven National Laboratory in Upton, New York. The instrumentation consisted of a primary beam collimation system, a sample heating cell, and a Braun position-sensitive proportional counter interfaced to a Microvac II computer. Wide and small angle diffraction patterns were obtained by placing the detector at different working distances from the sample. The complete results of these studies shall form a separate publication but certain data shall be used here for illustrative purposes. In addition, supplemental data were obtained at the U.S. Army Materials Technology Laboratory (MTL) utilizing a different position-sensitive proportional detector in conjunction with a conventional X-ray generator and four-circle diffractometer. This instrumentation is described in a recent publication by Hsie' et al.[28]

Mechanical Testing

The heat buildup properties of these materials were studied using load controlled cyclic compression tests. A load controlled test, rather than a displacement controlled test, more accurately simulates the operating environment of a tank track pad. An Instron Model 1350 servohydraulic test machine was used for all compression testing. Polyurethane blocks (6.35 cm x 6.35 cm x 1.59 cm) were compressed to a maximum load of 20,016 N and cycled between 2,002 and 20,016 N (450 lbs and 4500 lbs) for 200,000 cycles at 18.5 Hz. The internal temperature of each block was measured using a J-type thermocouple inserted into a drilled hole in the center of the block. Throughout the test, load and displacement data were acquired using a Nicolet Model 4094 digital oscilloscope and stored on a floppy disk. The data were reduced by displaying and plotting load versus displacement at various times during each fatigue test. Hysteresis was calculated from the area between the loading and unloading curves using a program supplied by Nicolet.

Cyclic tensile tests were performed on rectangular strips to study the hysteresis behavior in a simpler testing mode and without the effects of heat buildup. Strip specimens, 2.54 cm wide with a 5.08 cm gage length, were tested on a Instron Model 1331 equipped with MTS Systems Corp. constant pressure hydraulic grips with the following test procedure: one cycle at 25% extension, increase the extension to 50%, then 10 cycles at 100% extension. Immediately following the tenth cycle at 100%, two cycles to a stress value of 4.96×10^6 Pa (720 psi) were run; the displacement rate was 2.54 cm/min. After each cycle the specimen was extended to take up the slack produced from permanent set and the specimen was extended from this point using the initial gage length to calculate the distance to elongate. The data from these tests was reduced to obtain hysteresis and percent hysteresis.

Dynamic mechanical analysis (DMA) was performed on small specimens cut from tested and untested samples. These extension tests were performed on strip specimens with a 3.81 cm gage length using a floor model universal testing machine (Instron); the displacement rate was 2.54 cm/min. The following two sets of tests were performed: one cycle at 25% extension and gradually increased the extension to 350% through 4 cycles (50, 100, 150, 250), then 10 cycles at 350% extension; and 10 cycles at 25% extension. After one week the tests were repeated on the same specimen, remarking a 3.81 cm gage length. The DMA system used for this analysis was an Autovibron, which uses the basic Rheovibron DDV-II (Toyo Baldwin Company), but also includes an automation package (Imass, Incorporated). The automation package controls sample tensioning, temperature, phase angle measurements, data collection, and data reduction. The Autovibron is capable of analyzing three frequencies (110, 11, and 1.1 Hz) alternately as the temperature range is scanned. Tested specimens for Rheovibron analysis were cut from samples that had been tested twice using the 350% procedure and rested for one week. A few specimens were cut from samples stretched to 25% to study the effect of different strain levels. The specimens were cut from tested pieces in two directions, parallel and perpendicular, to the stretch direction. Because the width of stretched specimens was rather small, specimens cut perpendicular to the stretch direction were short. To avoid any length effects all specimens tested were 1.45 cm long.

RESULTS AND DISCUSSION

The CHDI is a white solid which was melted (m.p. 58°C to 62°C) before addition to the polyol. When the liquid was heated to 100°C, a small amount of white solid always remained, therefore, the CHDI was always distilled and then frozen until needed. One could speculate that the remaining white solid was a higher melting dimer or other oligomer of the diisocyanate. It was never isolated in this study. If the CHDI had not contained this impurity, it might have been added as the white flake form in which it was received. It has been reported by the supplier that while this is somewhat unconventional, the polymers prepared are not adversely affected.

The polyurethanes reported here were prepared without a catalyst. In earlier studies, 0.002% by weight of dibutyl tin dilaurate was used to prepare some samples. The reaction rate was difficult to control when more catalyst was used and samples could not be molded into sheets. The samples prepared without catalyst still set up rapidly and produced very good properties, therefore, no catalyst was used. This was done with the knowledge that a study of the relative reactivities of commercially important diisocyanates had been reported and had shown that CHDI was more than twice as reactive with 1-butanol in the presence of a catalyst as $H_{12}MDI$, and about one-third as reactive as MDI.[2]

Several samples were prepared by a one step technique in which the polyol and chain extender were heated and premixed and the heated diisocyanate was added. Rapid mixing for one or two minutes was followed by degassing for similar time periods and pouring. After the 16 hour cure and appropriate aging, the properties of the polymers were, in general, much poorer than those prepared by the prepolymer technique.

A representative list of polyurethanes prepared appears in Table 1A. The CHDI-based polyurethanes are very hard materials considering the low weight percent hard segments compared to other polyurethane elastomers. The CHDI is a relatively low molecular weight diisocyanate with a compact structure, but it should offer some flexibility because of the presence of the aliphatic ring. The aromatic analog p-phenylene diisocyanate (PPDI) has also been studied.[29] Polyurethane elastomers based on CHDI are nearly transparent in thin samples, and this is consistent with the low level of hard phase crystallinity in the polymers at room temperature to be discussed later. The polyurethanes prepared by the two step technique with NCO/OH greater than 0.85 were not soluble even on heating in any solvent tried, including tetrahydrofuran (THF), acetone, methyl ethyl ketone, chloroform, methanol, dimethylformamide (DMF), dimethylsulfoxide (DMSO), and N-methylpyrrollidinone (NMP). They were swelled by 10% to 15% by weight in THF, DMF, DMSO, and NMP. Entry 15 in Table 1B with NCO/OH = 0.85 was soluble on gentle heating in N,N-dimethylformamide. The crystallinity of the polymers and the relationship between hard segment crystallinity and solubility will be discussed later.

Table 1A. COMPOSITION OF CHDI POLYURETHANES REPRESENTATIVE SAMPLES

Entry	Formulation moles-1mole-moles-moles CHDI-PTMO-BD-TMP	Wt % Hard Segment	NCO/OH Ratio	Shore A (D)* Hardness
1	1.7-2000-1.0-0	16	0.85	89
2	2.0-2000-1.0-0	18	1.0	90 (34)
3	2.5-2000-1.5-0	22	1.0	95 (40)
4	3.0-2000-2.0-0	25	1.0	95 (37)
5	3.5-2000-2.5-0	29	1.0	99
6	4.0-2000-3.0-0	32	1.0	97 (48)
7	1.7-2000-0.8-0.13	16	0.85	88 (27)
8	2.0-2000-0.8-0.13	18	1.0	91 (34)
9	2.5-2000-1.35-0.1	22	1.0	95
10	2.5-2000-1.2-0.2	22	1.0	94 (36)
11	2.5-2000-0.9-0.4	22	1.0	91
12	2.5-2695-1.2-0.2	17	1.0	86
13	3.0-2900-2.0-0	19	1.0	93 (38)
14	5.0-2900-4.0-0	29	1.0	95 (44)

*Shore D values in parentheses.

Table 1B. COMPOSITION OF CHDI POLYURETHANES SAMPLES WITH VARIED NCO/OH

Entry	Formulation moles-1mole-moles-moles CHDI-PTMO-BD-TMP	Wt % Hard Segment	NCO/OH Ratio	Shore A Hardness
15	2.125-2000-1.5	19.35	0.85	90
16	2.250-2000-1.5	20.00	0.90	92
17	2.375-2000-1.5	20.66	0.95	93
18	2.500-2000-1.5	21.29	1.0	95
19	2.625-2000-1.5	21.92	1.05	91
20	2.750-2000-1.5	22.54	1.1	99*
21	2.875-2000-1.5	23.15	1.15	99*
22	3.000-2000-1.5	23.74	1.2	97*
23	2.500-2000-1.5	21.29	1.0	†
24	2.500-2000-1.4	21.02	1.04	†
25	2.500-2000-1.3	20.74	1.09	†
26	2.500-2000-1.2	20.46	1.14	†
27	2.500-2000-1.1	20.18	1.19	†

*Accuracy questionable because the Shore A scale is not reliable at these high values.
†Not measured.

It is possible that CHDI will be made commercially in the future by use of phosgene and, in that case, mixtures of cis and trans isomers will be available. Use of a mixture of isomers would probably improve the solubility of the block polymers. This would be very helpful because it would then be possible to analyze the molecular weight characteristics of all the polyurethanes prepared and more complete explanations for the behavior could be offered.

Polyurethane samples prepared for indepth hysteresis studies both in compression and tension are listed in Table 1B. These two series of polyurethane elastomers with varying NCO/OH ratios were prepared in different ways. In one series, Entries 15 through 22 in the table, the weight percent hard segment increases as the NCO/OH increases. This is because in each succeeding synthetic procedure more and more diisocyanate is added. In the other series, Entries 23 through 27, the weight percent hard segment decreases as the NCO/OH increases. This occurs because the amount of diisocyanate is constant and less and less BD is added. If properties are considered which can be effected by small changes in the weight percent hard segment such as modulus, specification of the method used can be important.

Discussion of DSC

DSC was used to determine low and high temperature transitions in the synthesized samples; the results are shown in Table 2 and Figure 1. It was also used to analyze postcured samples and samples subjected to compression fatigue. These last two samples will be discussed later. The low temperature glass transition temperature ranged from -85°C to -79°C for samples prepared from PTMO 2000 and PTMO 3000. No samples prepared with PTMO 1000 are reported here, but they would be expected to have higher T_g's based upon the tendency of polyurethanes with shorter soft segments to phase mix. The samples prepared in this study have exceptionally well phase segregated soft phases, based upon the presence of little or no elevation of the soft segment T_g above that of the pure PTMO, which has been reported to be -85°C. Another measure of soft phase purity is the presence of soft segment melting transitions for every sample prepared, ranging in temperature from -9°C to -1°C for polymers prepared by the two step technique using PTMO. A sample prepared by the one step technique (not shown in the tables) exhibited a melt at 6°C, which is still considerably lower than that reported for the pure soft phase at 45°C. Polyurethanes prepared from PTMO 2900 exhibited two endotherms due to soft phase melting for two of the samples be-tween 3°C and 15°C. The others melted at a single temperature. Regarding hard phase transitions, only a few samples showed measurable T_g's, but there were discernable bumps on the DSC curves between 50°C and 90°C for all of the samples examined. Those prepared with shorter hard segments showed T_g's closer to 50°C and those with somewhat longer hard segments showed transitions at the high end of the range. All of the polymers examined showed high temperature exotherms, presumably due to crystallization, the minimum in the transition ranging from 170°C to 199°C. It is because of the presence of this exotherm that hard segment crystallinity in the synthesized samples cannot be determined by DSC. The synthesized samples are the ones which were analyzed after preparation before they had been subjected to any thermal treatment or mechanical stress. The exotherms were followed by one, and sometimes two, melting transitions in the temperature range studied, up to 277°C for some samples. These included the samples with the lowest weight percent hard segment and also those with crosslinking in the hard phase which leads to poorer crystal formation. Samples with 2.5 moles of CHDI and above showed what appeared to be a maximum at the end of the curve or were flat up to 277°C, suggesting the presence of higher melting crystals. A cooling curve on one sample showed no transitions on the cool down and no transitions on the rescan up to the same high temperature. This sample will be discussed later in the section on X-ray studies. Thermomechanical analysis on a group of samples with 2.125 to 2.75 moles of CHDI and different NCO/OH ratios (Entries 15 to 22 in Table 1B) exhibited final softening temperatures of 240°C to 270°C. This supports the idea that hard segment crystals melt above 270°C.

Table 2. THERMAL PROPERTIES OF POLYURETHANE ELASTOMERS PREPARED FROM CHDI BY DIFFERENTIAL SCANNING CALORIMETRY (DSC) (°C)

	Soft Segment		Hard Segment		
Entry*	T_g	T_m	T_g†	T_c	T_m
1	-80	-1	57	170	225, 265
2	-79	-2	--	195	235, 277
3	-81	-5	80	195	277
4	-82	-7	--	190	††
5	-85	-9	--	184	††
7	-83	-5	55	185	221, ††
8	-80	-1	--	186	233, ††
10	-83	-7	--	192	222, ††
12	-80	11	--	199	††
13	-84	3, 11	--	177	††

*Compositions shown in Table 1.

†Virtually all samples show a hard segment T_g. Except for the reported values, the other samples exhibited a hard segment T_g too small to be analyzed. They occur in the temperature range of 50°C to 90°C.

††Either no melting is observed or the baseline is rising at 275°C, the temperature at the end of the scan. See text for further discussion.

X-ray Diffraction Results

A typical small angle X-ray scattering (SAXS) pattern of the polyurethanes, in this case 2.625-2000-1.5 (Entry 19 in Table 1B), is shown in Figure 2. The strong pattern confirms the expected microphase separation morphology, with a diffraction maximum at $Q \equiv (4\pi/\lambda) \sin \theta = 0.32 \text{ nm}^{-1}$, corresponding to a lamellar repeat period of $d \equiv 2\pi/Q = 19.6$ nm or 196 A°. Similar patterns are seen for other polyurethanes with a variety of compositions with CHDI/PTMO molar ratios in the range 2 to 5.

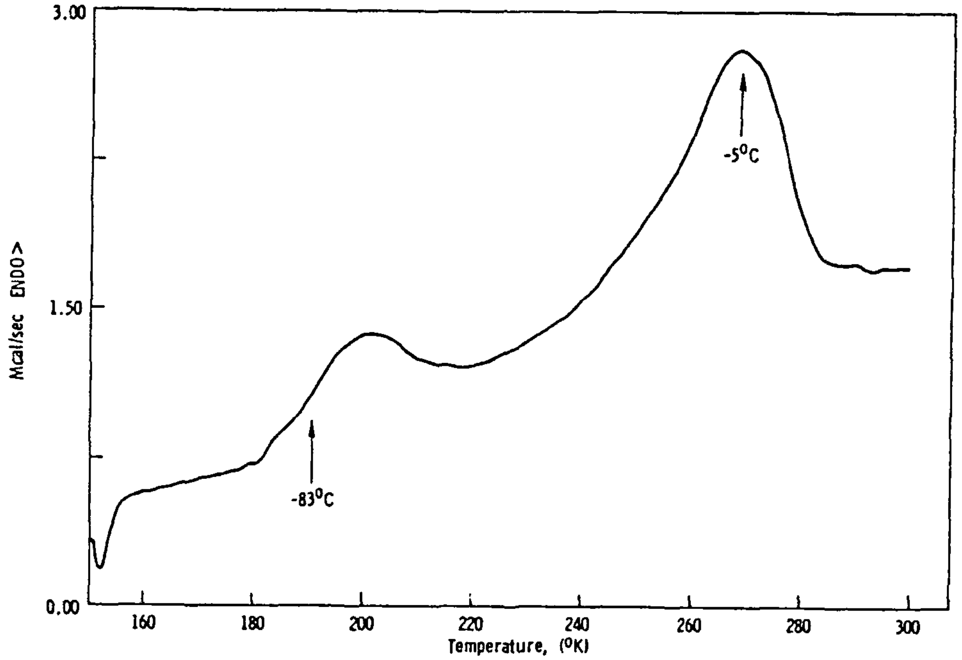


Figure 1A. DSC curves for 1.7-2000-0.8-0.13 CHDI-PTMO-BD-TMP.
Low temperature scan at 20°C/min. Sample size = 21.14 mg.

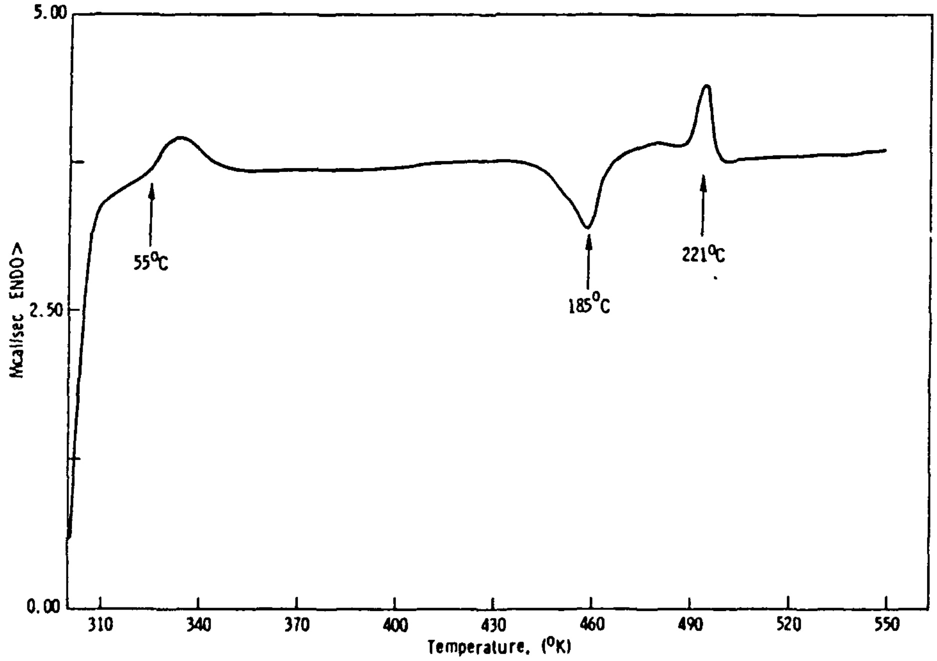


Figure 1B. DSC curves for 1.7-2000-0.8-0.13 CHDI-PTMO-BD-TMP.
High temperature scan at 10°C/min. Sample size = 38.17 mg.

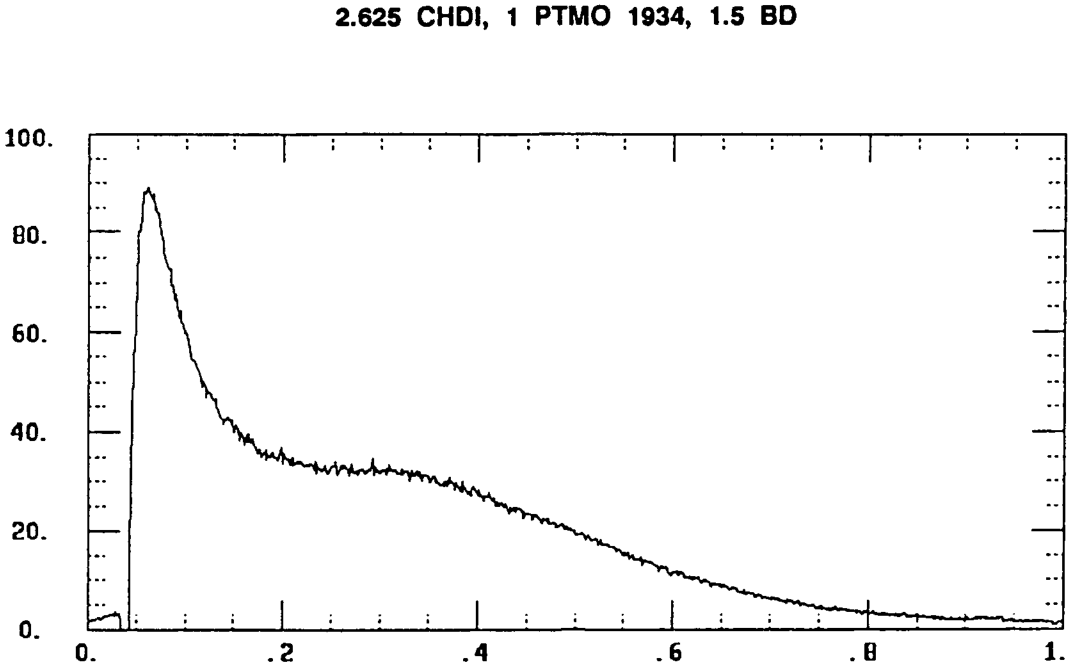


Figure 2. SAXS pattern of polyurethane of composition 2.625-2000-1.5. The abscissa Q is $(4\pi/\lambda) \sin \theta$, in nm^{-1}. Instrument collimation is such that no desmearing of this data is necessary.

Figure 3 shows the wide angle patterns of the same urethane elastomer at temperatures beginning at 30°C, up to a high value of 211°C, and returning to 30°C. The temperature range was chosen because of the DSC exotherm around 185°C, thought to be due to hard segment crystallization. The intention was to pass beyond this transition and return to room temperature, enhancing the crystallinity in the process. The beginning and ending patterns, obtained near room temperature, do not show the multiple sharp peaks characteristic of crystallinity, but neither is the single peak near $2\theta = 20°$ a typical amorphous peak. Comparing the lower temperature patterns to the pattern at 211°C, it is evident that the near-room-temperature patterns have a sharpness at the top of the peak which is quite different from the rounded maximum at 211°C, which is more typical of an amorphous scattering halo. The "sharpness" of the peak is believed to consist of a small, fairly sharp peak of either paracrystalline or crystalline (with small crystallite size) origin superimposed on a rounded amorphous peak. Examining the other patterns in Figure 3, as well as others not shown obtained at additional intermediate temperatures, it is seen that the characteristic sharpness at the peak persists up to around 100°C with ascending temperature then reappears in that same temperature range with descending temperature. The phenomenon is definitely reversible and appears in similar experiments with other urethane molar compositions. The temperature of disappearance and reappearance of this peak is well above any possible soft segment transitions; thus, the peak is believed to be associated with the hard segment microphase. Comparison with the published data of Siegmann, Cohen, and Narkis[19] a remarkably similar "sharpened" peak is seen (see their Figure 5c) for an elastomer consisting of CHDI, BD, and Hydroxy-terminated polybutadiene (HTPB) soft segment. Since a different soft segment is used there, the association of the "sharpened" peak at $2\theta = 20°$ with the CHDI/BD hard segment is reinforced.

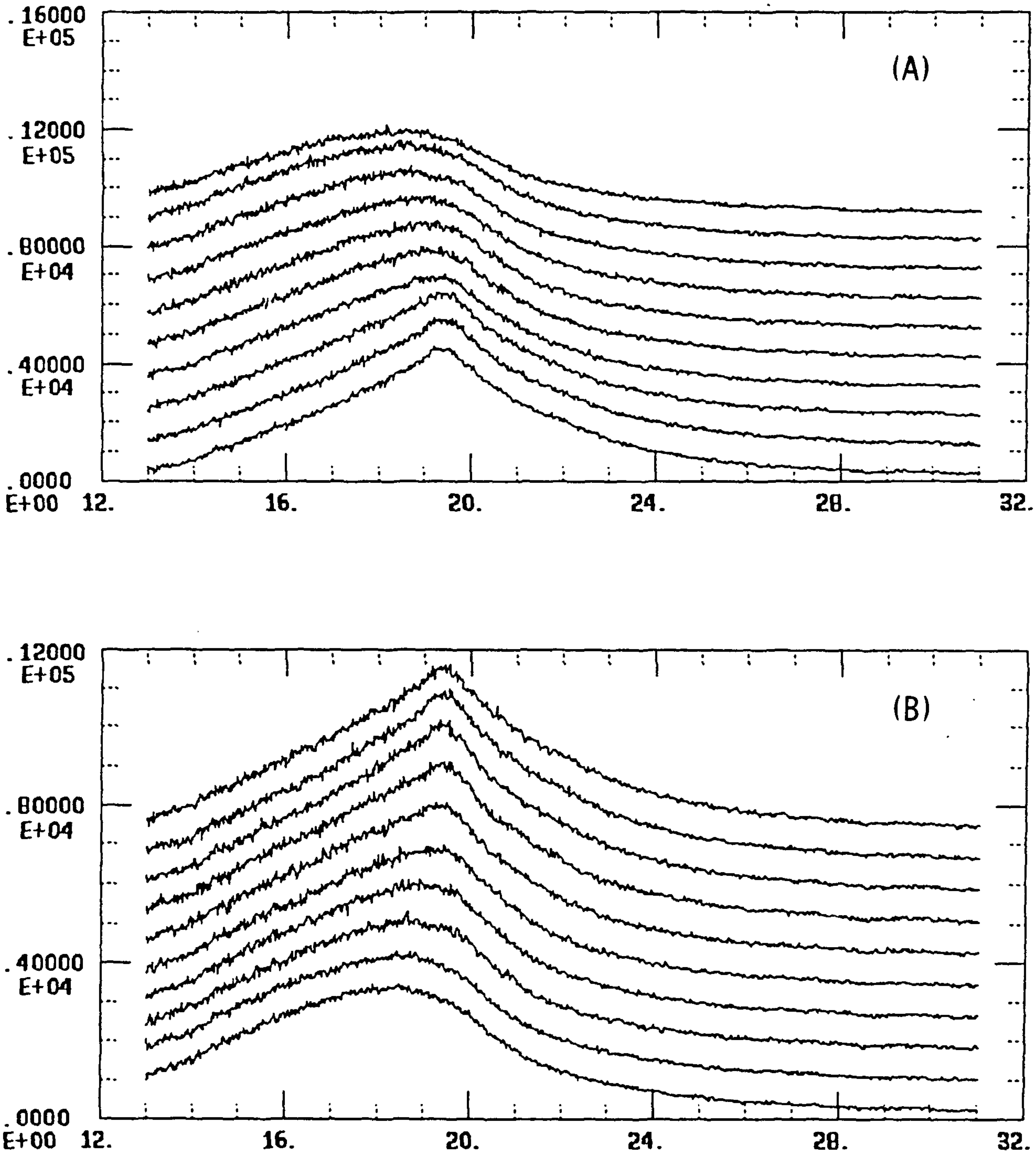


Figure 3. WAXS heating experiment of polyurethane of composition 2.625-2000-1.5. A) Scans at ascending temperatures, beginning with the lowest plot: 30°C, 45°C, 66°C, 111°C, 129°C, 146°C, 165°C, 184°C, 195°C, and 209°C. B) Scans at descending temperatures, beginning with the lowest plot: 211°C, 196°C, 167°C, 143°C, 119°C, 101°C, 80°C, 56°C, 39°C, and 30°C. Temperature was held fixed within 1°C as each pattern was obtained. The average rate of temperature change was 1.5°/min. The abscissa is 2θ in degrees; wavelength is 0.154 nm (1.54 A°).

The results of the heating experiment of Figure 3 indicate that more severe heat treatment is necessary to more fully develop the crystallinity. Two approaches were taken in efforts to develop higher crystallinity: samples were taken up to 275°C and back in the DSC at 20°/min; and samples were postcured at 150°C to 160°C for six hours. The resulting data, as shown in Figure 4, demonstrates that both methods were successful. Instead of the single peak at $2\theta = 20°$, a strong peak at d = 4.45 A° ($2\theta = 19.9°$), is now seen in all four patterns of Figure 4 along with peaks or shoulders at d = 4.3 A° ($2\theta = 20.6°$), and at d = 4.0 A° ($2\theta = 22.1°$). One of the patterns shows additional peaks at d = 3.7 A° ($2\theta = 24°$) and at d = 2.9 A° ($2\theta = 31°$); the polymer for this sample has a particularly long average hard segment length corresponding to its composition 4.0-2000-3-0.

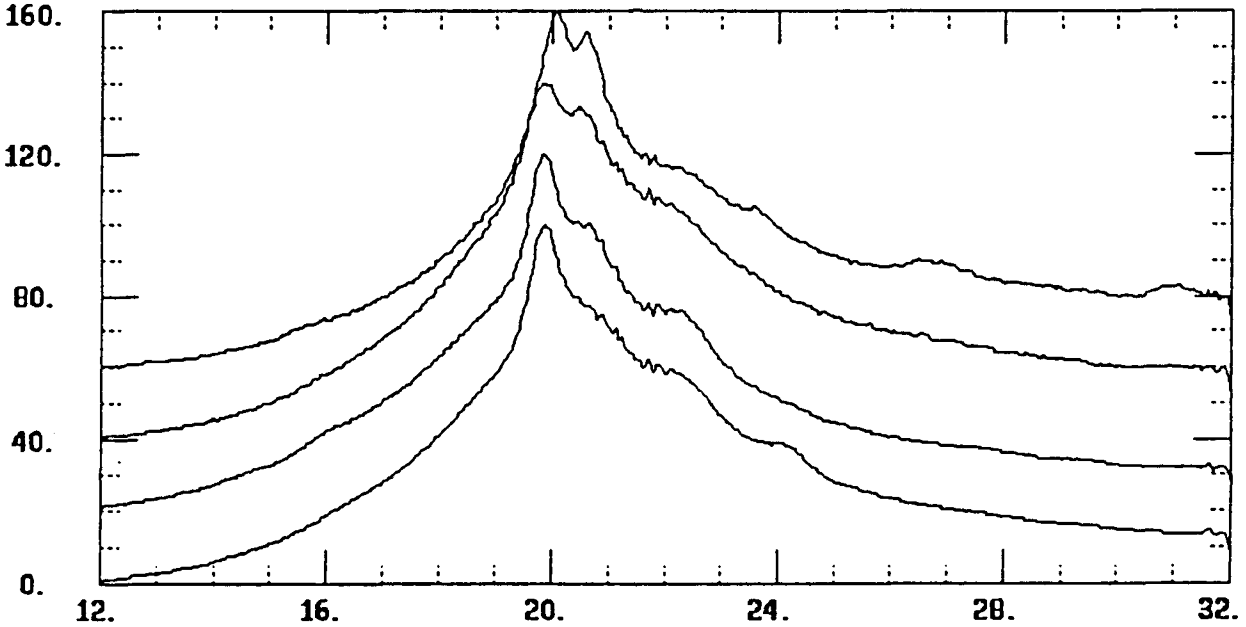


Figure 4. WAXS patterns at 25°C of four polyurethanes subjected to heating treatments. Reading from the lowest pattern upwards: a) Composition 2.5-2000-1.5, heated in DSC to 275°C and back at 20°/min; b) Composition 3.5-2000-2.5, heated in DSC to 275°C and back at 20°/min; c) Composition 2.5-2000-1.5, postcured for six hours at 150°C through 160°C; d) Composition 4.0-2000-3.0, postcured for six hours at 150°C through 160°C.

Discussion

The X-ray diffraction results indicate that small, highly imperfect crystallites are readily formed by hard segments comprised of CHDI and BD. The crystallities formed at the 100°C synthesis temperature are far from equilibrium, having been formed at a temperature at which hard segment mobility becomes greatly restricted as the cure proceeds. Further crystallization takes place when the temperature is first elevated above the synthesis temperature appearing as a thermal transition on the DSC at 185°C. However, the ordering produced by such a temperature elevation is quite limited unless the temperature is raised to quite a high temperature; namely, 275°C, or prolonged heating is used; namely, six hours at 150°C to 160°C. Thus, there is a definite thermodynamic driving force for improving the order and size of the hard segment crystallites, but there is a strong kinetic barrier opposing such recrystallization.

It is suggested that neighboring CHDI moieties have a highly energetic attraction for each other. However, this attraction can be satisfied by quite local interactions which bring hard segment residues close to each other without long range crystalline order. In brief, the monomer units will readily fit next to each other, dropping into an energy well in the process, but the fit is such that order over a number of such monomer units is NOT required. Mistakes in the repeating pattern are readily tolerated although the crystallites will undergo ordering under kinetically favorable conditions. The fact that CHDI is an aliphatic diisocyanate and is not a planar molecule contributes to the crystallization behavior of the hard phase. The propensity of the hard segment moieties to prefer like neighbors provides a strong driving force for microphase separation in the bulk polymer. For the hard segment microphase, this results in a paracrystalline state characterized by a single "sharpened" diffraction peak at 4.3-4.4 A°, which can be annealed into a more ordered crystalline state only with prolonged or quite elevated heating. The strength of these local interactions of like hard segment residues is also indicated by the fact that, unlike most other segmented urethanes, the CHDI/BD segmented urethanes do not readily dissolve in solvents. Again, the hard segment moieties prefer the energy benefit of having like neighbors to the entropy benefit of possible mixing with solvent leaving an unfavorable free energy change for solution.

Abrasion Tests

The CHDI-based polyurethanes performed well in the NBS abrasion test compared to the other unfilled polyurethanes, but all of the polyurethanes were much poorer than the carbon black filled rubber triblend; the results are shown in Table 3. The behavior of the samples in the NBS abrasion test is reflected in the performance of these materials on different road surfaces in tank track pads. The filled carbon black samples usually perform well on paved road surfaces and less well on unpaved roads. The polyurethanes seem to melt away on paved roads and lose mass very quickly but they outperform the filled rubbers on rough gravel surfaces.

Table 3. THE RESULTS OF ABRASION TESTING

Sample	Shore A Hardness	Abrasion Index
H_{12} MDI Polyurethane*	77	159
TDI Polyurethane† NCO/OH = 1.2	97	254
TDI Polyurethane† NCO/OH = 1.0	96	329
Track Pad Reference Compound (Triblend)††	78	2847
CHDI Polyurethanes**		
2.5-2695-1.20-0.20	86	476
2.0-2000-0.80-0.13	87	331
2.5-2000-0.90-0.40	91	172
2.5-2000-1.20-0.20	91	336
2.5-2000-1.50-0.00	92	521

*The sample has composition of 3 moles H_{12} MDI, 1 mole PTMO 1934, 1.6 moles 1,4-BD, and 0.27 moles TMP.

†The TDI-based samples were prepared with Polaroid XPE-20, a PTMO 1000-based prepolymer and chain extended with trimethylene glycol bis (p-aminobenzoate).

††The triblend is based upon nearly equal amounts of styrene-butadiene rubber, polybutadiene, and natural rubber containing 65 phrs carbon black per 100 phr rubber, and other ingredients and sulfur cured.[30]

**The quantities are moles CHDI-1 mole PTMO-moles BD-moles TMP.

Compression Tests

Compression tests as described in the Experimental section were run on several sets of samples. The results are shown in Figures 5, 6, and 7.

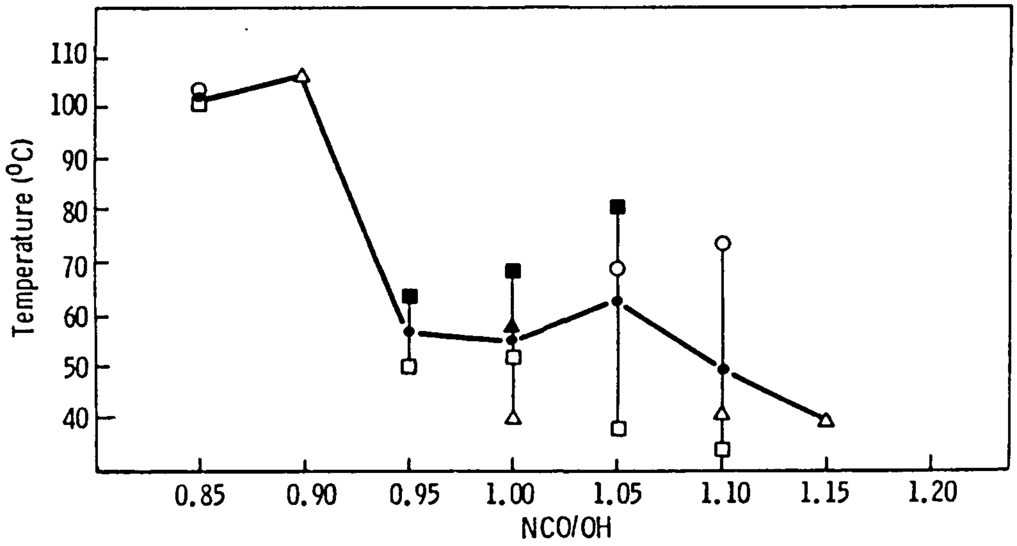


Figure 5. Internal temperatures under cyclic compression tests for Samples 15 through 22 in Table 1B.

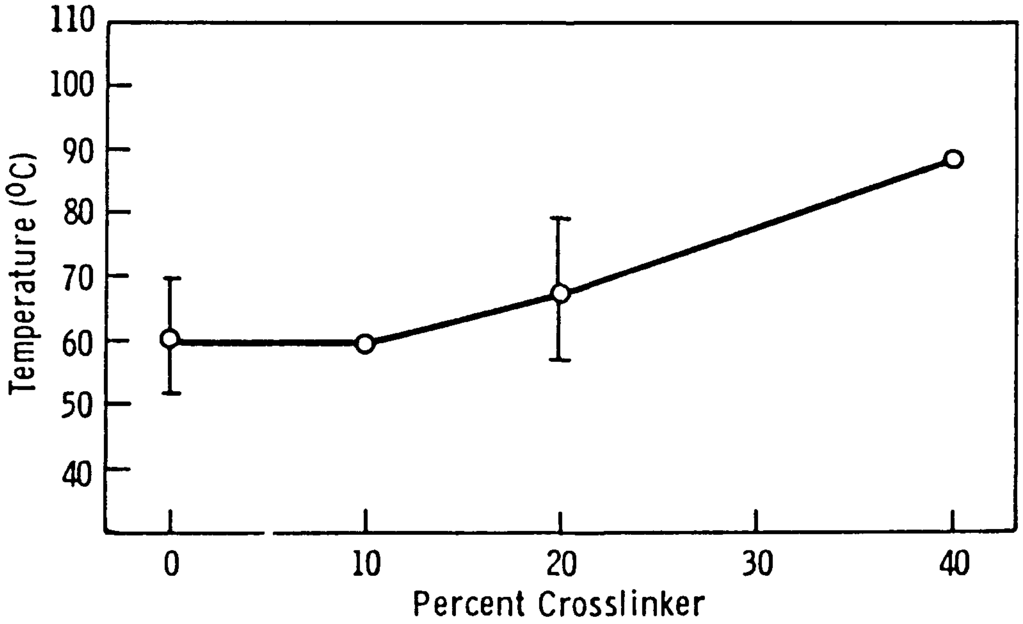


Figure 6. Internal temperatures under cyclic compression tests for Samples 3, 9, 10, and 11 in Table 1A.

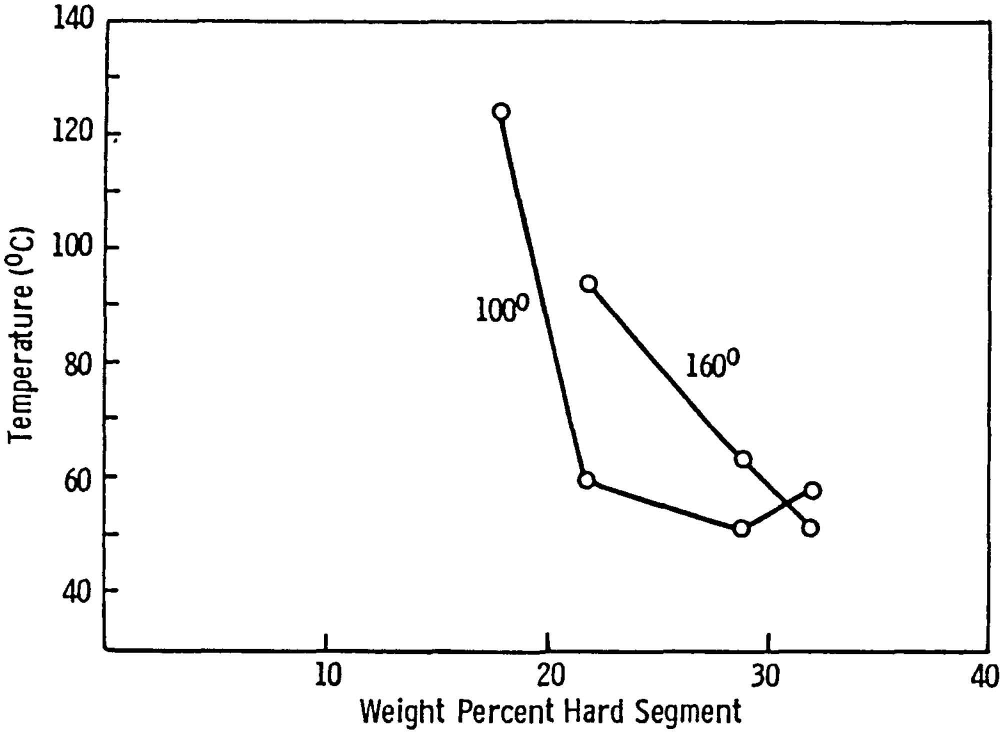


Figure 7. Internal temperature under cyclic compression tests for Samples 2, 3, 5, and 6 in Table 1A. The curve labelled 100°C resulted from testing the samples as they had been prepared at 100°C and aged for at least two weeks. The curve labelled 160°C resulted from testing samples which had been postcured for six hours at 160°C and then aged for at least two weeks.

Figure 5 shows the internal temperature under cyclic compression as a function of percent crosslinker. The internal temperature in these experiments generally plateaus in the first 25% of the test to 200,000 cycles and remains constant within a degree or two throughout. This is true for samples which survive the experiment and is not the case for samples which heat up and fracture as the test progresses. The percent crosslinker is calculated by the formula (moles BD to produce a linear polymer-moles BD in the crosslinked polymer) divided by moles BD to produce a linear polymer times 100. Early in the research with CHDI-based polyurethanes in compression experiments it was assumed that crosslinking would improve the hysteresis properties. As many compositions were tested and the internal temperatures were measured, it became apparent that the crosslinked samples performed no better than linear samples. Only linear samples were tested after that. In Figure 5, the temperature generated is shown to remain nearly constant for the linear and the 10% crosslinked and then to rise slowly with more crosslinking. This can be interpreted to mean that the organization of the hard domains in the linear and the 10% crosslinked is nearly the same and is very good. Above that amount of crosslinker the hard phase order is reduced.

Two phenomena are illustrated by Figure 6. The effect of weight percent hard segment on the internal heat generated is shown. At low hard segment content the hysteresis is high, but at values between 22 weight percent and 32 weight percent for the other three points the temperatures measured are within the experimental error of the technique. When three of the samples are postcured the internal temperature generated is considerably higher for the sample with 22% hard segment, slightly elevated for the sample with 29% and nearly the same for that with 32% hard segment. These samples were postcured for six hours at 150°C in an oven in air and showed tiny cracks and yellowing after heat treatment. They were more brittle than the as-prepared samples. In fact, thin sheets which were postcured could be cracked and broken. It is difficult to draw conclusions about this cracking behavior because the samples were postcured in air. It would be interesting to compare polyurethanes prepared with a mixture of the cis and trans isomers of CHDI as to their behavior on postcuring. The organization and crystallization of the hard phase which occurs on postcuring, and possibly leads to the brittleness, would be reduced by the use of the mixture of isomers. Based upon the literature, it might be speculated that the samples cured at 100°C, except for the one with the lowest stoichiometry, have nicely ordered isolated hard domains and sufficiently high molecular weight to generate only minimal amounts of heat. One might speculate that the postcuring somehow connects the hard domains for the sample with 22 weight percent hard segment so that more heat is generated or that the molecular weight is lowered significantly. Considering that postcuring has the smallest effect on the polymers with high hard segment content, it is unlikely that interconnection of the domains is responsible. Since other urethane bonds are known to break in the temperature range of the postcure, it is likely that a decrease in molecular weight due to urethane bond breaking is responsible for the increased heat generation for the sample with 22% hard segment.

DSC studies were performed in order to interpret the results of compression tests on postcured samples. These DSCs were run on sheets all prepared at the same time; one set of which had been postcured for six hours at 150°C. There were no differences in the low temperature behavior. The high temperature behavior was changed in that the onset of crystallization was 9°C to 15°C lower than for the nonpostcured and the magnitude of the transitions increased one and one-half to two times over that of the as-prepared. The postcuring made the hard phase easier to crystallize by ordering the hard segment chains into arrangements from which crystals could grow at lower temperatures and to a greater degree. The reader is referred back to the section on X-ray studies in which two postcured samples are described which also exhibit crystallinity in the hard phase without going through the temperature range of the exothermic transition in the DSC. The postcured samples were heated slightly above the onset of the crystallization exotherm and are crystalline, but can still be further crystallized by scanning beyond that exotherm (190°C to 195°C).

Figure 7 shows the results of compression experiments on samples in which the only variable was the NCO/OH ratio. Again, equilibrium temperature values were reached during the compression cycling and these are the temperatures shown in Figure 7. Hysteresis measured during compression testing correlated directly to the internal temperature. The samples with NCO/OH of 0.85 and 0.9 failed during the test and showed high internal temperatures. There is scatter in the data for samples where repeat experiments were run, but a trend toward reduction in internal temperature with increasing NCO/OH ratios is suggested. Entry 22 in Table 1B with NCO/OH = 1.2 exhibited an internal temperature of about 80°C which seemed unexpected. A repeat test of this sample showed an internal temperature near 40°C which is more in line with the expected trend. This is not shown in Figure 7 because of the uncertainty associated with the result. Please refer to the results of tensile experiments on these samples (see Figures 15 and 16). Schollenberger and Dinbergs[24] observed a continuing decrease in hysteresis with increasing molecular weight in a series of polyurethane elastomers in hysteresis tests to constant strain. Saunders and Frisch[31] state that above a certain molecular weight of about 15,000 for copolymers, the mechanical properties do not change which is in contradiction to those results. The CHDI-based polymers are insoluble and so molecular weight data is unavailable for the present samples. Flory[32] states that the maximum molecular weight is obtained when exactly stoichiometric amounts of reactants are used and the side reactions are minimized. Reaction with water during the polyurethane polymerization is always a possibility, therefore, usually five percent excess of diisocyanate is used to maximize molecular weight. One might speculate that the series of polymers shown in Figure 7 reaches a maximum molecular weight somewhere between NCO/OH = 1 to 1.1, a range where the internal temperature during cyclic compression to constant stress seems to be still decreasing. The compression data for Entries 15 through 22 in Table 1B was used for comparison with dynamic mechanical and stress-strain measurements to be discussed later.

DSC studies of polyurethane blocks before and after compressive fatigue were performed in order to try to interpret the behavior of these block copolymers. Permanent set in the compressed samples was very low; on the order of 1%. Low temperature DSCs were run on sheets of polymer, which were compared to the compressed blocks. Both the midpoints of the T_g's and the size and temperature of the melting transitions were the same. For the high temperature scans, two sets of blocks were prepared at the same time and scanned at the same time after one set had been compressed. Three compositions were run: the 2.125-2000-1.5, 2.5-2000-1.5, and 2.75-2000-1.5, as shown in Entries 15, 18, and 20 in Table 1B. The magnitude of the crystallization exotherm remains constant for all three at approximately 5 cal/g. The transitions are very sharp and it is possible to obtain the temperature minima accurately. The minima vary about 10° but there is no observable trend. This is true even though Sample **15** failed catastrophically and the other two survived the compression test very well.

Rheovibron Analysis

The morphology of these thermoplastic polyurethane elastomers consist of alternating blocks of soft and hard segments which are phase separated. The PTMO chains are rubbery at room temperature while the hard segments (urethanes) are glassy and act as physical crosslinks reinforcing the structure. The morphology of polyurethanes directly affects their mechanical behavior and can be studied by dynamic mechanical analysis.[33,34]

Figures 8 through 11 compare the elastic modulus (E') and tan δ values for the two series of materials at 11 Hz over a range of temperatures. The formulations for the two series are shown in Table 1B. Specimens 15 through 22 are referred to as the first series, and specimens 23 through 27 are referred to as the second series. The major relaxation observed at approximately -60°C is the glass transition temperature of the amorphous soft segment, much higher than the approximately -80°C T_g obtained by DSC. All materials exhibit nearly the same soft segment glass transition temperature. This indicates two things: first, all the materials have similar degrees of phase separation, and, second, the materials have a very high degree of phase separation as indicated by the low soft segment T_g. The glass transition temperature of the pure homopolymer is -65°C at 100 Hz.[35] In contrast to some other polyurethane systems studied[33] the T_g of the soft segment does not appear to be influenced by the hard segment content (at least over the range investigated from 16 weight percent to 32 weight percent).

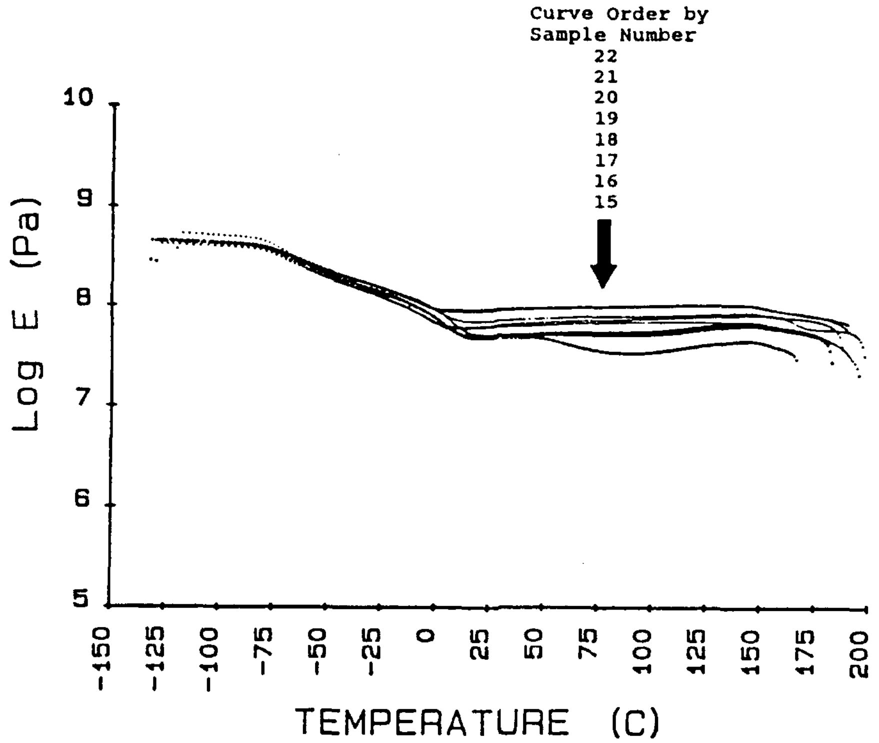


Figure 8. Elastic modulus for unstretched material, Samples 15 through 22.

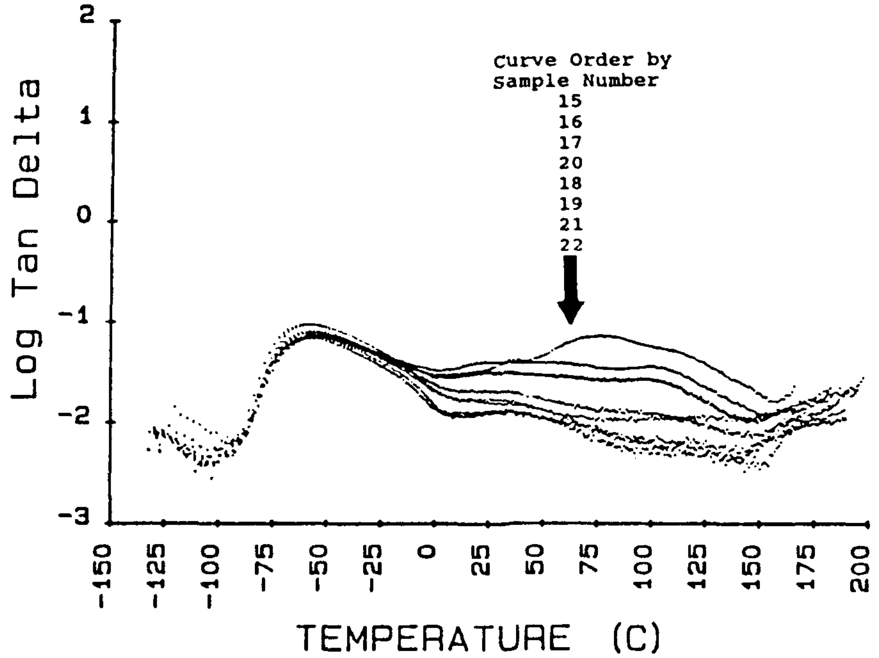


Figure 9. Tan δ for unstretched material, Samples 15 through 22.

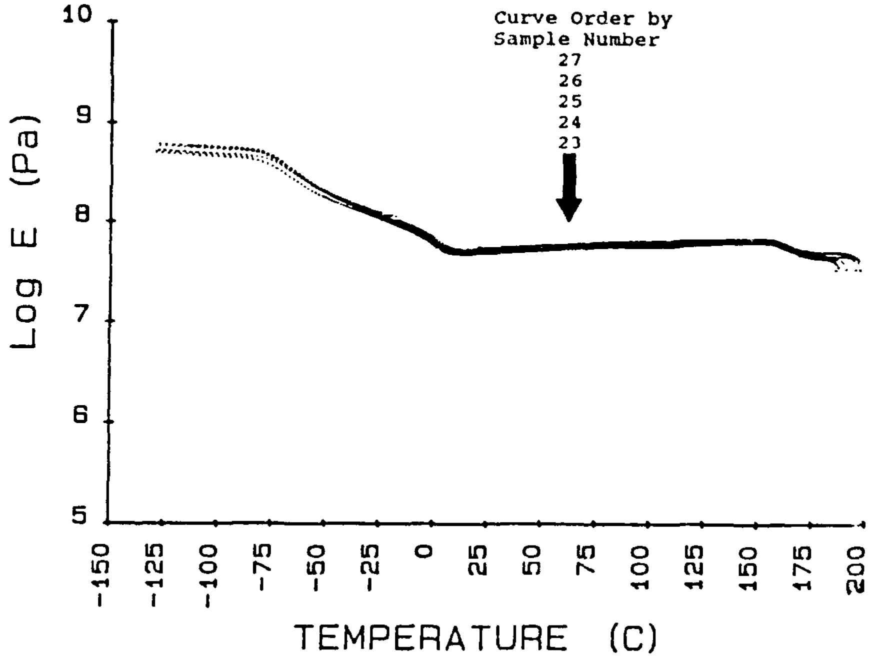


Figure 10. Elastic modulus for unstretched material, Samples 23 through 27.

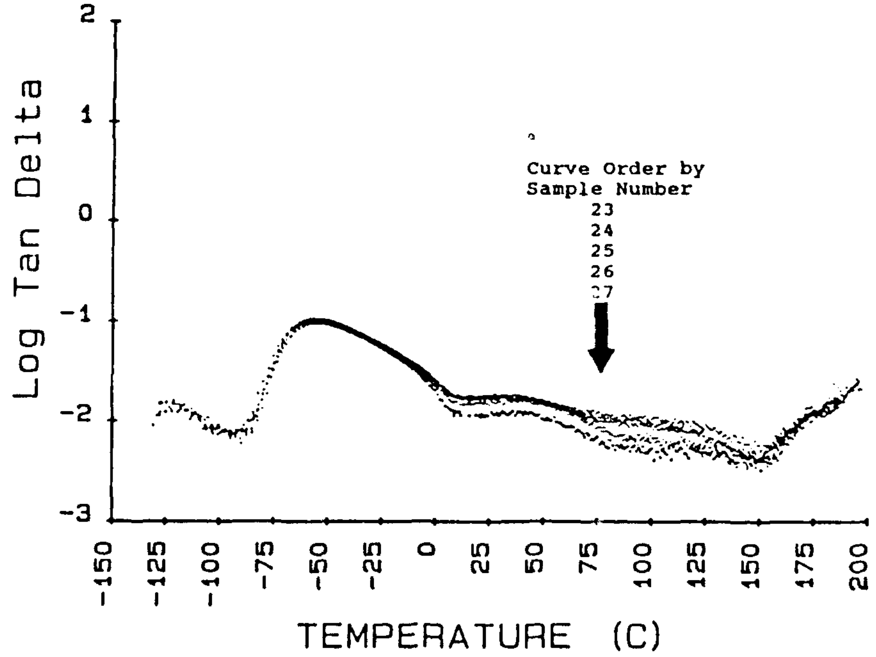


Figure 11. Tan δ for unstretched material, Samples 23 through 27.

The high temperature side of the soft segment glass transition temperature exhibits a shoulder analogous to that found in MDI systems[34] and is due to melting of small crystallites in the soft segment. This was supported by DSC results in which every sample exhibits soft segment melting in the range -9°C to -1°C for samples prepared from PTMO 2000.

Entry 15 in Table 1B and Figure 8, with composition 2.125-2000-1.5 from the first series, shows a drop in modulus above 50°C which may be attributed to the hard segment. Ng et al.[33] found a hard segment transition around 60°C for polyurethanes which they felt was the result of poorly ordered hard segments. Studies of polybutadiene/toluene diisocyanate/butane diol segmented polyurethanes showed the existence of two hard segment transitions as the result of shorter and longer hard segment length.[38] It is not unreasonable to assume that the transition found for this particular system would be from less ordered domains or shorter hard segment lengths, particularly where this system would have a large proportion of chain ends and less isocyanate compared to other samples.

In the rubbery region (above the soft segment T_g and before hard segment crystallization) the modulus values generally increase with increasing temperature as would be expected for ideal rubbery behavior. This is not always seen in polyurethanes[22,33,34] and is probably the result of the excellent phase separation and unconnected hard segment domains acting as physical crosslinks in these CHDI-based materials. In addition, for the first series there is a general trend of decreasing modulus and increasing tan δ as the ratio of NCO/OH decreases. Studies with other urethane systems have shown that increased crosslinking through high NCO/NH_2 ratios or the addition of a triol can lead to reduced modulus[31,44,45] or, in other cases, very little effect on room temperature properties.[31] The question of whether or not allophanate formation takes place in the polymers studied here remains unanswered.

For the case of the CHDI-based polyurethanes studied here it would appear that increasing the NCO/OH ratio does not act to disrupt the hard segment domains leading to a reduction in modulus. The increase in modulus with increasing NCO/OH ratio is not unexpected for the first series as the weight percent hard segment increases and would influence the modulus in the same manner as an increase in filler particles. The second series shows very little difference in modulus owing to a smaller difference in hard segment content.

Figures 12 and 13 are representative plots of the elastic modulus and tan δ before and after cyclic hysteresis tests to 350%. This information was obtained only for materials from the first series. The lower plateau modulus for stretch materials indicates that considerable irreversible (at least with time) softening after extension occurs. It was expected that the material would show differences in the directions perpendicular and parallel to the stretch direction due to orientation of the chains in the stretch direction. Although there were slight differences between the perpendicular and parallel moduli, there were no consistent differences when all the materials were examined. The stretched specimens did show a new transition near 40°C. DSC analysis suggested that this is a crystalline melt. The crystalline melting temperature of the pure soft segment occurs at about 45°C. Thus, at extensions up to 350% we have induced crystallization of the soft segment which remains after the removal of stress. This soft segment crystallization behavior has been reported for other polyurethane systems.[15]

Specimens from the first series stretched to 25% show stress-softening in tension, but based upon the Rheovibron results this softening does not give an appreciable permanent change in the modulus. At these elongations there is no evidence for any permanent stress induced crystallization of the soft segment and the similar soft segment T_g's indicate that phase mixing does not occur to any significant degree.

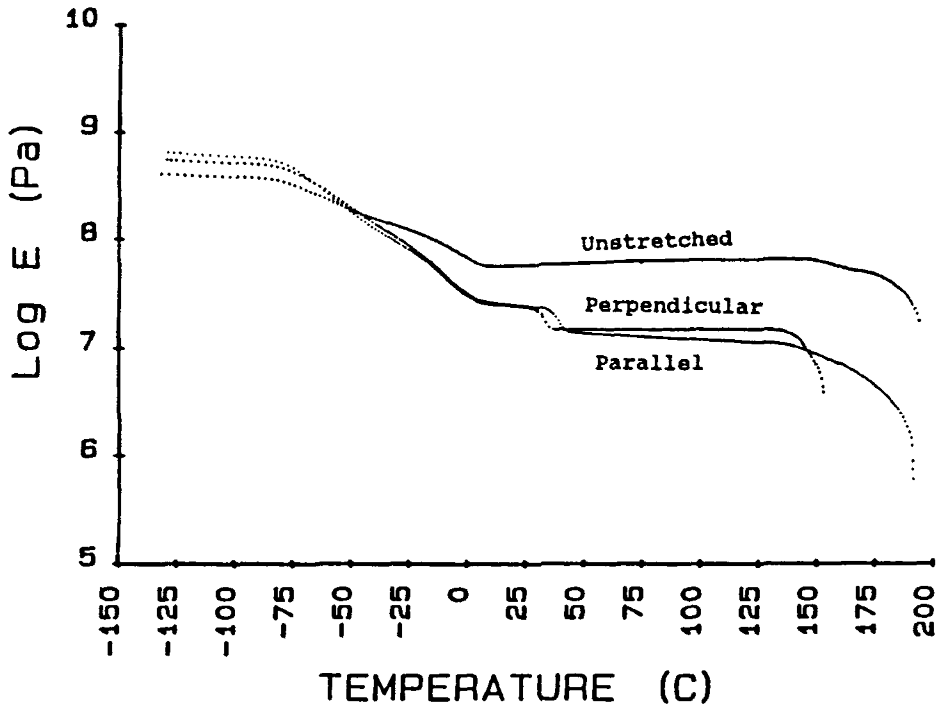


Figure 12. Elastic modulus, Sample 18, 350% elongation.

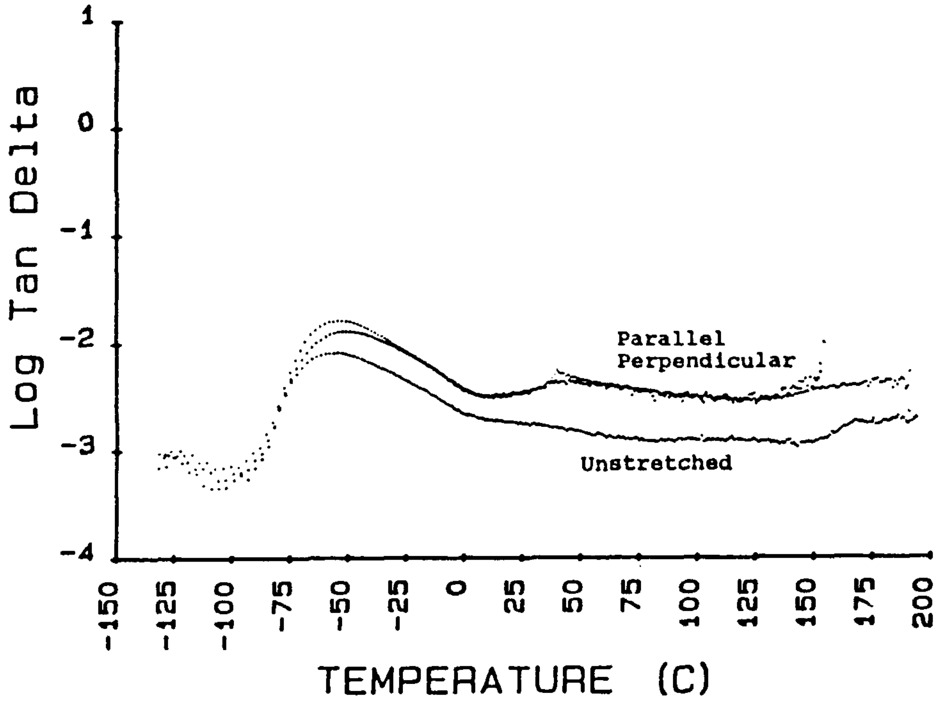


Figure 13. Tan δ, Sample 18, 350% elongation.

The tan δ curves show a slight increase in the T_g of the soft segment for specimens in the first series stretched to 350%. The increase in T_g varied from only a few degrees to as much as 10°C depending upon the sample. There did not appear to be any consistent trend for this increase. Shibayama et al. found similar behavior for a series of polyurethanes subjected to fatigue.[39] This could indicate a change in the degree of phase mixing for stretched samples. Kaneko et al.[42] also found this result for their samples which was attributed to orientation of the hard and soft segments. Interestingly, their E′ curves for fatigued samples showed an increase with temperature while the unfatigued specimens showed a decrease in modulus with temperature. Either orientation or phase mixing could explain the Rheovibron results. If this disruption were to result in phase mixing this also ought to result in an increase in the soft segment glass transition. This is the case for samples extended to 350%, but not for samples stretched to 25% that exhibit reversible stress softening in tension. The increased soft segment T_g for fatigued specimens could be explained by the presence of crystalline regions in the soft segment without a change in phase separation. The presence of crystalline regions in the soft segments would constrain the chain ends of the amorphous portions resulting in decreased mobility of the chains and an increased soft segment T_g.

Although these tests indicate that permanent stress crystallization occurs when the material is sufficiently elongated in tension, DSC results showed no difference in the amount of soft-phase crystallinity before and after compression.[23] This could be due to the elevated internal temperatures during compression fatigue or, possibly, the strains induced through bulging of the compression samples were insufficient to cause crystallization.

It is of interest to determine if the dynamic mechanical results correlate with the cyclic compression tests. The area between the loading and unloading curve of a stressed specimen is the amount of energy lost (hysteresis) or heat generated for a given strain cycle. The hysteresis per cycle under a fixed sinusoidal deformation (γ) is:[36,37]

$$H = \pi (\gamma)^2 E' \tan \delta. \tag{1}$$

Under a stress controlled cyclic test of amplitude σ, the energy loss per cycle can be approximated by

$$H = \pi (\sigma)^2 \tan \delta / E'. \tag{2}$$

If this equation is used to predict the response of the present materials under the stress controlled cyclic compression tests we should expect the internal temperatures to increase for specimens with decreasing E′ and/or increasing tan δ. The results from the Rheovibron show a trend toward increasing E′ and decreasing tan δ with increasing NCO/OH ratio, as shown in the figures and in Table 4, consistent with the results obtained from cyclic compression tests. Attempting to use E′ and tan δ values from the Rheovibron data to predict heat buildup in the compression tests should be approached with some caution since the data is obtained at very low strains. Further, for an appropriate analysis, the change in dynamic properties with temperature should be considered.

Table 4. ELASTIC MODULUS (E') AND TAN δ VALUES FOR SAMPLES WITH VARIED NCO/OH 25°C; 11 Hz

Sample Number	E' (MPa)	Tan δ
15	48	0.034
16	50	0.040
17	50	0.032
18	61	0.016
19	62	0.017
20	65	0.017
21	71	0.021
22	93	0.013
23	47	0.019
24	56	0.018
25	53	0.017
26	54	0.015
27	57	0.011

Hysteresis Tests in Tension

The CHDI polyurethanes exhibit typical stress-softening behavior in tension, where the first cycle has significantly more hysteresis than subsequent cycles. This stress-softening is reported to be the result of rearrangement of the hard segment domains.[15,40,41,43] The hard domains become oriented (often exhibiting complex behavior) under the influence of strain and this orientation remains after the removal of stress.

After several cycles the specimens reach a nearly constant hysteresis value. In the first series, material prepared with an NCO/OH ratio of 0.85 (2.125-2000-1.5, Entry 15 in Table 1B) broke before 100% elongation, but the data obtained at 25% and 50% elongation follow the same trends as the other samples. Comparison of the initial portion of the hysteresis curves for the first series of urethanes on the tenth elongation cycle showed the modulus of the materials generally increased with increasing NCO/OH ratio because of the increased amount of hard segment (19.35% for NCO/OH = 0.85 increasing to 24.0% for NCO/OH = 1.2). This cycle was chosen for comparison to compression data because the polyurethane would have been stress-softened after a few compression cycles. Figure 14 compares the different materials tested to a constant stress value (4.96 x 10^6 Pa). As a result of the increased modulus with increased NCO/OH ratio there is a decrease in the maximum deflection.

Sung et al.[25] found that the percent hysteresis was lower in well phase separated poly(urethaneureas), particularly when the hard segment domains were unconnected as in the CHDI-based polyurethanes studied here. We should expect low hysteresis for the CHDI systems studied in this report. Figures 15A and 15B show the hysteresis and percent hysteresis obtained from specimens of the first series for cycle 10 at 100% elongation, respectively.

The filled squares represent average values. Figure 15A shows that with increasing NCO/OH ratio the hysteresis value increases. In Figure 15B the percent hysteresis decreases up to 1.05 NCO/OH ratio. Above this ratio the percent hysteresis stays nearly the same (or perhaps increases slightly).

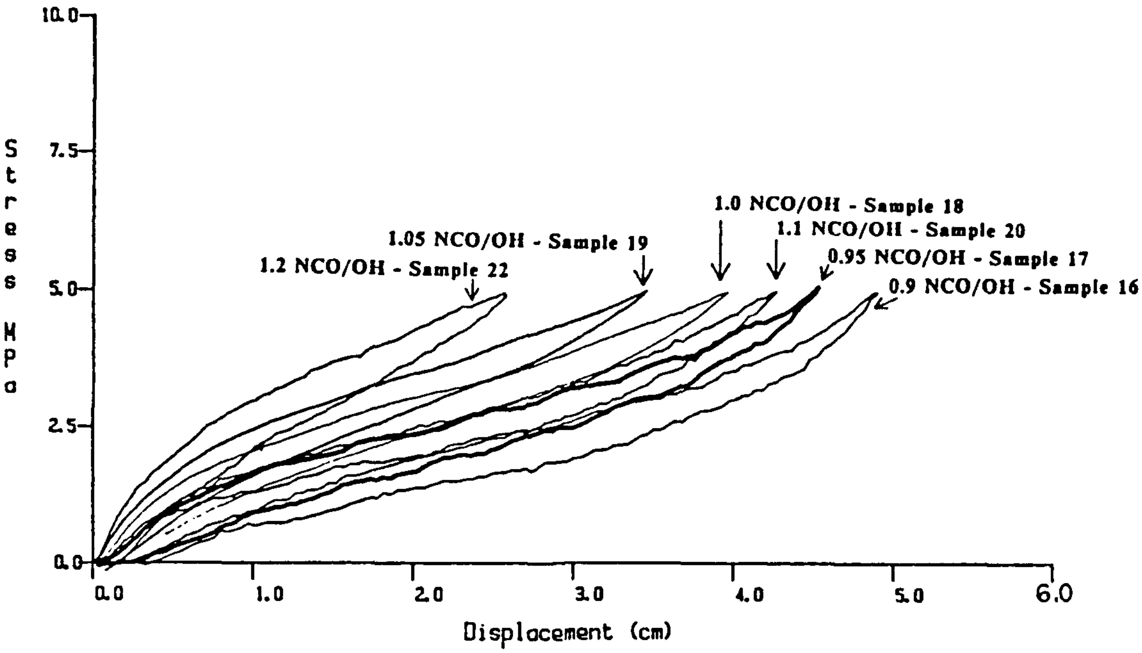


Figure 14. Hysteresis under constant stress for Samples 16 through 22.

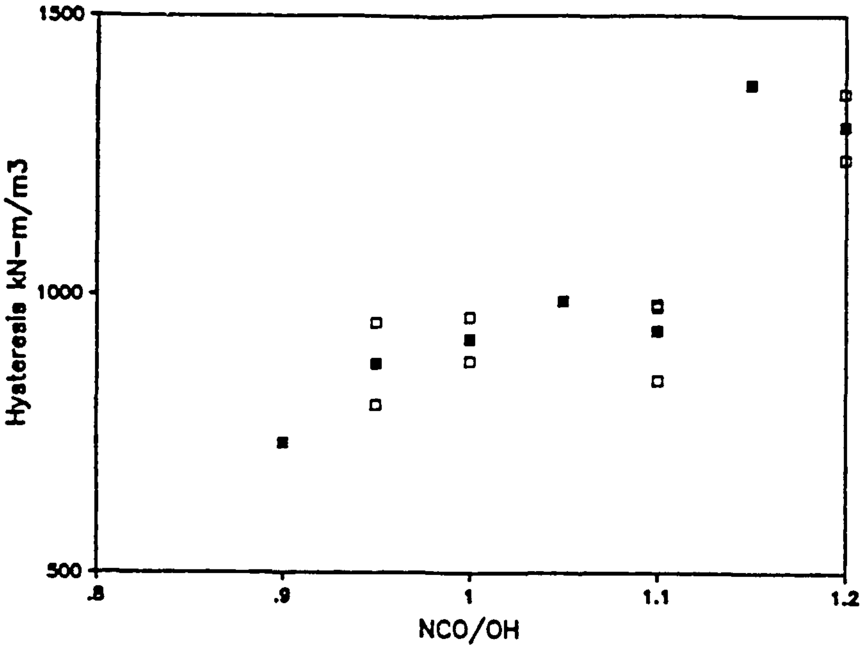


Figure 15A. Hysteresis versus NCO/OH ratio at constant elongation - tenth cycle, Samples 15 through 22.

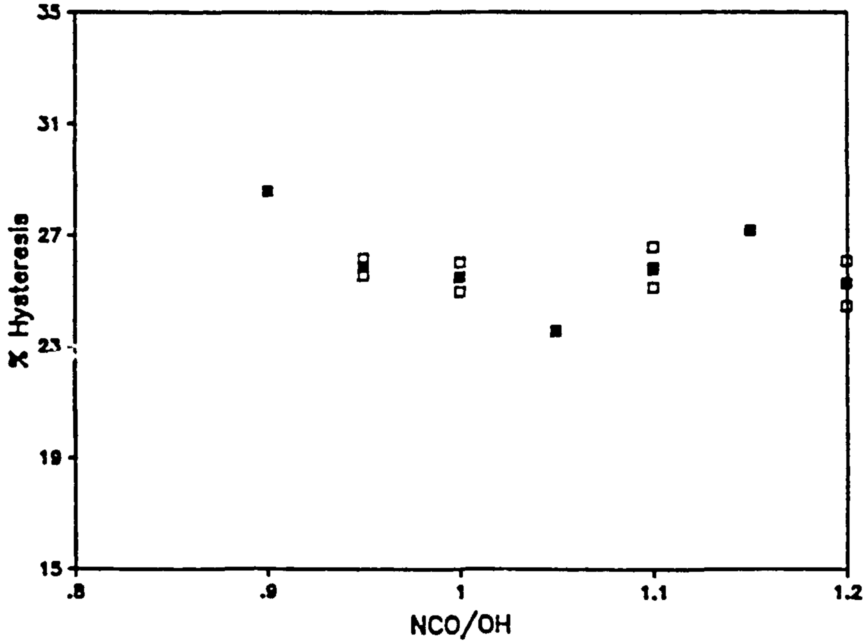


Figure 15B. Percent hysteresis versus NCO/OH ratio at constant elongation - tenth cycle, Samples 15 through 22.

Figures 16A and 16B show the hysteresis and percent hysteresis data for the same set of materials stretched to a constant stress value. Figure 16B shows that the percent hysteresis behavior is similar for materials stretched to a constant stress and stretched to a constant elongation. The percent hysteresis - NCO/OH ratio relationship is unaffected by the testing mode in this case. In the constant stress test (see Figure 16A), the hysteresis decreases with increasing NCO/OH ratio rather than increases, as was the case for materials stretched to the same elongation, showing the inverse relationship in hysteresis values that can be obtained from the two different testing modes. The elastic modulus of the material affects the resulting hysteresis behavior inversely for these two testing modes. As discussed above, in deformation to constant stress the hysteresis of a material is proportional to $\tan \delta / E'$ and for a constant amplitude test the hysteresis is proportional to $E' \tan \delta$.[36,37]

The hysteresis determined for the first series of polyurethanes from the constant stress test correlates with the heat buildup of the compression loaded blocks, emphasizing the importance of using the correct loading conditions for predicting heat buildup. In the deformation to constant stress, although the percent hysteresis appears to remain the same or slightly increase above 1.05 NCO/OH ratio, the value of the hysteresis decreases. Since the percent hysteresis for the first series of specimens shows similar trends regardless of the testing mode and the two testing modes show inverse relationships between hysteresis and NCO/OH ratio, this leads to the conclusion that the increased modulus with increasing NCO/OH ratio is the dominant influence on the hysteresis value, as hysteresis under constant stress is inversely proportional to E'. This is further supported by the Rheovibron results. For constant amplitude tests the hysteresis is proportional to $E' \tan \delta$. The value of $\tan \delta$ decreases with increasing NCO/OH ratio while E' increases. Since the hysteresis increases with increasing NCO/OH ratio this indicates that E' is the dominant influence.

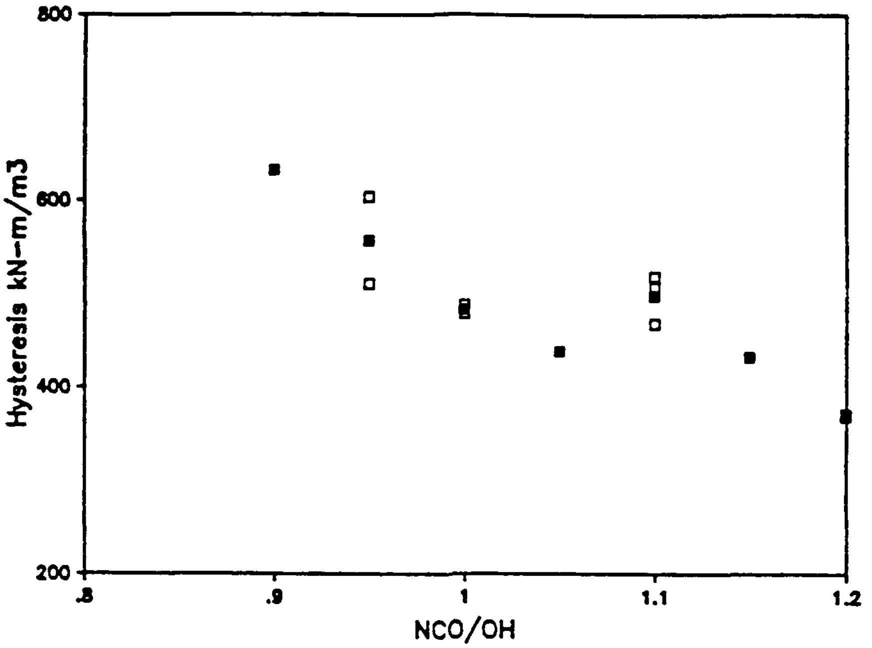


Figure 16A. Hysteresis versus NCO/OH ratio under constant stress, Samples 15 through 22.

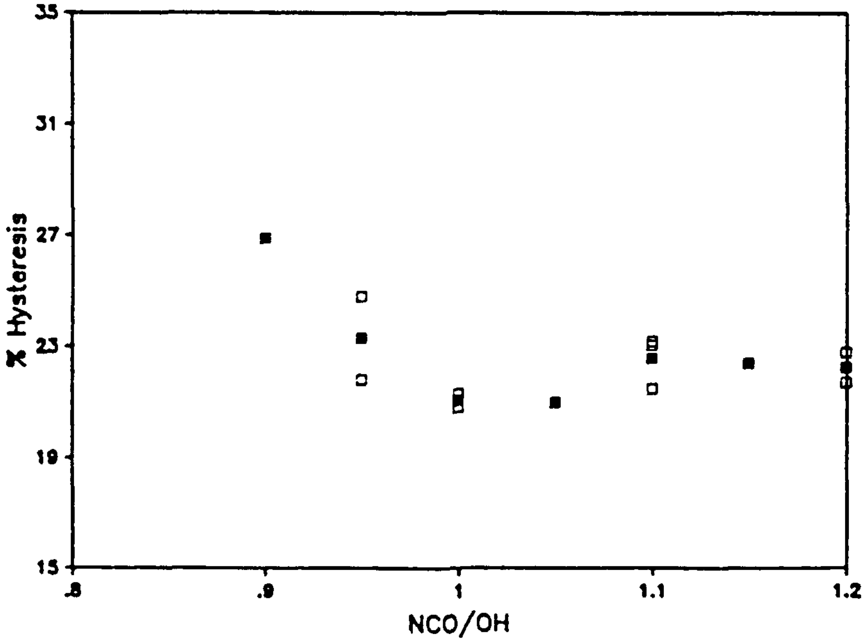


Figure 16B. Percent hysteresis versus NCO/OH ratio under constant stress, Samples 15 through 22.

To further study the effect of composition on hysteresis properties a second set of polyurethane specimens was prepared. In this case the percent hard segment decreases very slightly with increasing NCO/OH ratio. Comparison of the stress-strain behavior for this set of specimens showed a very slight trend toward increased modulus with increased NCO/OH ratio in spite of the fact that the percent hard segment decreases. Comparison of the E' values at 11 Hz and 25°C (see Table 4) showed the modulus increased less than 30% as the NCO/OH ratio increased for the second series, while the modulus increased nearly 100% with increasing NCO/OH ratio for the first series.

Figures 17a, 17b, 18a, and 18b show the percent hysteresis for the second series of polyurethanes for the first cycle and the cycle to a constant stress respectively. The filled marks represent average values. In the first cycle the percent hysteresis decreases with increasing NCO/OH ratio while the hysteresis values remain nearly the same. These trends are seen in the tenth cycle data as well (which are not shown). In this case it would appear that the influence of increased modulus with increasing NCO/OH ratio is offset by the decreased percent hysteresis with NCO/OH ratio under constant elongation conditions (where hysteresis is proportional to E' tan δ). This is in contrast to the results for the first series where the hysteresis increases with increasing NCO/OH ratio. In this series the effect of modulus is less. For the constant stress cycle, where hysteresis is proportional to tan δ/E' the percent hysteresis is nearly the same for variations in NCO/OH ratio, while the hysteresis decreases with NCO/OH ratio. This is due to the slightly increased modulus with increasing NCO/OH ratio.

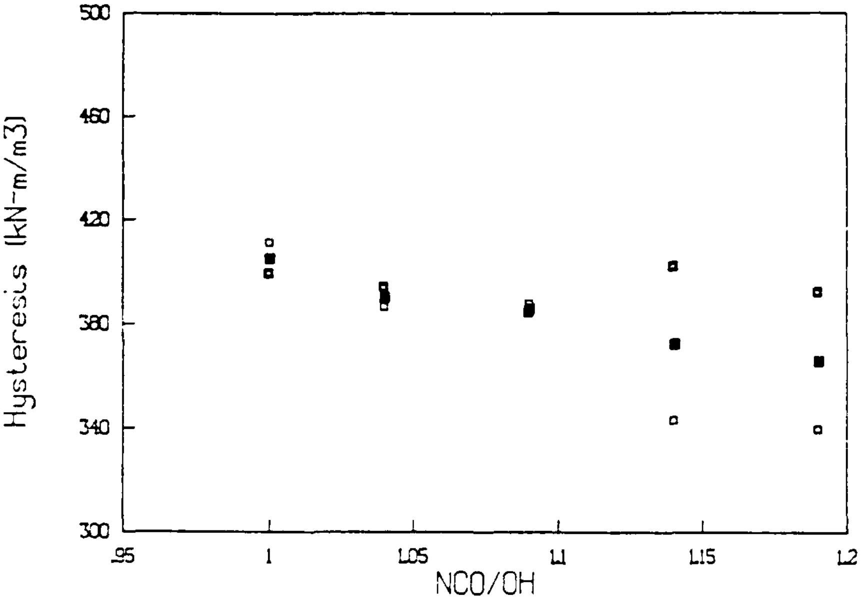


Figure 17A. Hysteresis versus NCO/OH ratio at constant elongation - first cycle, Samples 23 through 27.

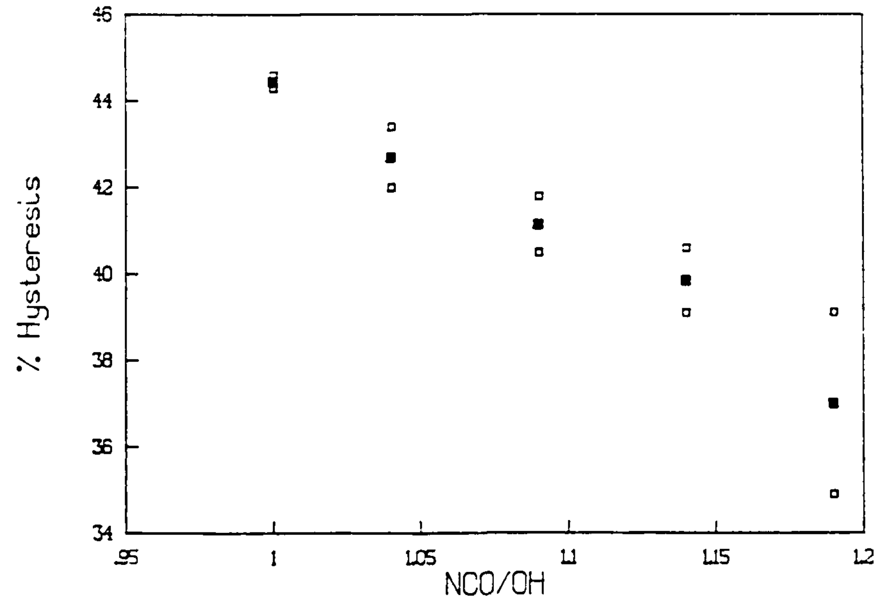


Figure 17B. Percent hysteresis versus NCO/OH ratio at constant elongation - first cycle, Samples 23 through 27.

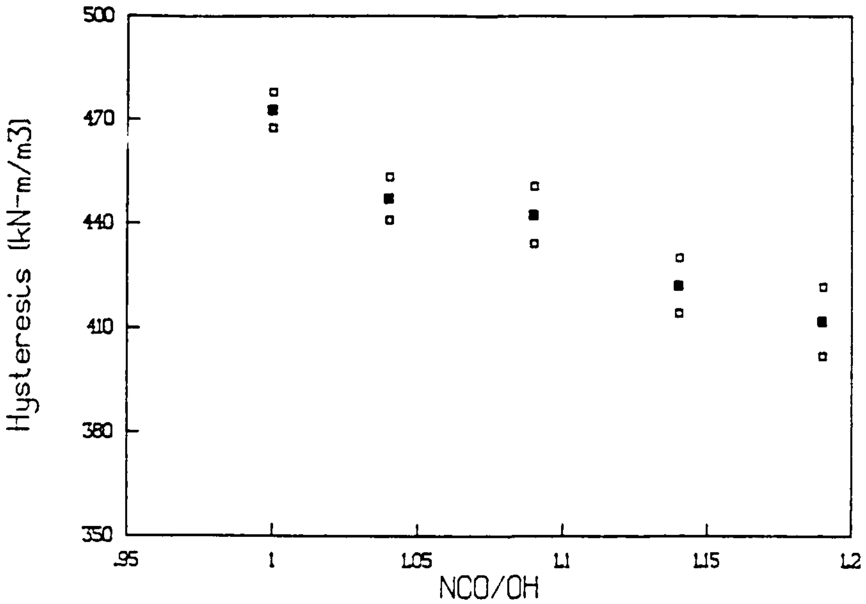


Figure 18A. Hysteresis versus NCO/OH ratio under constant stress, Samples 23 through 27.

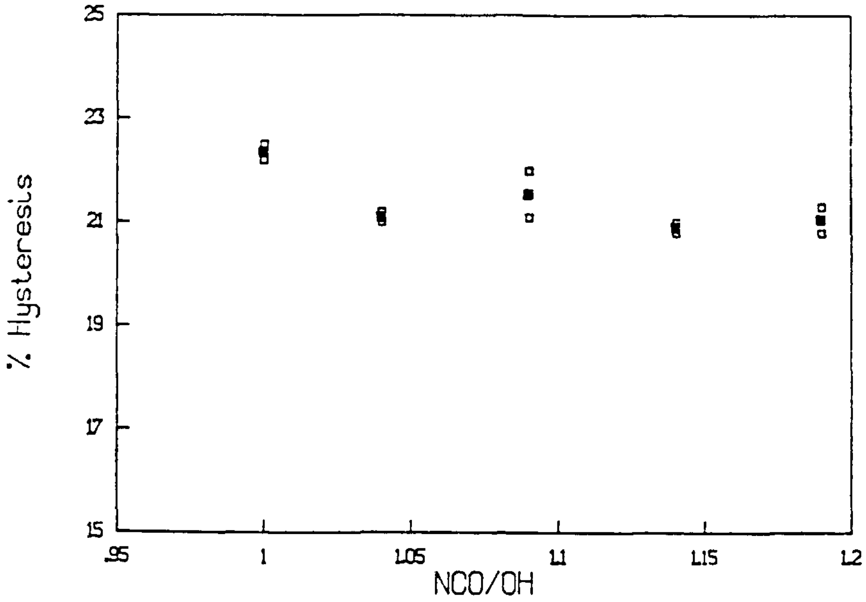


Figure 18B. Percent hysteresis versus NCO/OH ratio under constant stress, Samples 23 through 27.

As the NCO/OH ratio did not appear to affect the degree of phase separation in the CHDI-based system studied here, the decreased percent hysteresis and slight modulus increase could be the result of the formation of allophanate crosslinks in the hard segment phase, although, as mentioned above, the existence of allophanate groups has not been proved. The hysteresis behavior of polyurethane elastomers has been described as having different mechanisms at different strain levels.[26] Below 50% the hysteresis is due to orientation of the hard segments and nonaffine deformation. In the second region (50% to 500% elongation) alignment of the hard segment backbones into the stretch direction and disruption of the domains occurs. For orientation or disruption of the hard segment domains some chain slippage in the hard segments may be required. The presence of crosslinks in the hard segment domain could restrict movement within the hard segment domains. This would increase the modulus and should act to reduce the percent hysteresis assuming that orientation and disruption of the hard segments is the cause of the hysteresis. This effect of crosslinking has been suggested to describe the effect of NCO/OH ratio on the modulus of poly(urethaneureas) with good microphase separation.[46]

Another possible explanation could be poorer ordering in the hard segment domain with increased NCO/OH ratio. The energy loss for a series of CHDI elastomers was found to increase with increase in diol chain length due to increased ordering in the hard segment domains.[19] The authors felt that increased ordering would lead to increased orientation and permanence of orientation yielding greater energy loss. This does not appear to be the case for the present materials as the X-ray data indicated no significant differences in ordering for the first series of materials.

It is possible that increased NCO/OH ratios disrupt the order of the hard segment giving lower hysteresis, but, if so, one would expect decreased rather than increased percent hysteresis for the lower NCO/OH ratios, such as in the first series with an NCO/OH ratio of 0.85 where the low hard segment glass transition temperature indicates the presence of a poorly ordered phase.

CONCLUSIONS

Polyurethane elastomers often exhibit complicated structure property behavior. This makes the development of a material to fit specific requirements (such as modulus and hysteresis) quite difficult. The excellent phase separation of these CHDI-based polyurethane elastomers is reflected in the characteristics discussed in this report, the low soft phase T_g, soft segment crystallinity, order and crystallinity in the hard phase, insolubility in all common solvents, high modulus, retention of properties to high temperatures, and low hysteresis in compression and tension compared to other polyurethanes discussed in the references cited.

ACKNOWLEDGMENTS

The authors wish to thank Professor Benjamin Chu and Mr. Yingjie Li of the State University of New York at Stony Brook, and the National Synchrotron Light Source at Brookhaven National Laboratory, for assistance with the X-ray diffraction experiments. The authors also wish to thank Richard Matton, Rachel A. Michaud, and Gary E. Foley for assistance in the laboratory and for the helpful discussions.

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U.S. Army Materials Technology Laboratory
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STRUCTURE PROPERTY RELATIONSHIP OF ALIPHATIC
POLYURETHANE ELASTOMERS PREPARED FROM CHDI-
Catherine A. Byrne, Joey L. Mead, and C. Richard Desper

Technical Report MTL TR 91-26, July 1991, 37 pp-
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Key Words

Polyurethanes
Elastomers
Microphase separation

Aliphatic polyurethane elastomers have been prepared from trans-1,4-diisocyanatocyclohexane, poly(tetramethylene oxide), 1,4-butanediol and optionally trimethylolpropane. CHDI is a compact symmetrical diisocyanate which is responsible for remarkable properties in these polymers. They are nearly transparent elastomers with low glass tranisiton temperatures of approximately -80°C, and high final softening temperatures up to 270°C, for polymers with low hard phase contents of 20% to 30%. They are well phase separated and exhibit either paracrystallinity or crystallinity with small crystallite size after preparation. Considerable crystallinity develops after scanning up in temperature to 275°C or holding at 150°C to 160°C for six hours. The polymers are insoluble even when heated in polymer solvents and this is attributed to ordering even in the as-synthesized polymers. They have excellent mechanical properties compared to other polyurethane elastomers and retain their modulus up to high temperatures. Because of their excellent phase separation and low hard segment content, with the resultant discrete domains, they exhibit very low hysteresis in compression and tension.

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