

# Polyurethane Elastomers Based on 1,3 and 1,4-Bis(Isocyanatomethyl)cyclohexane

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Received 10 April 2008; accepted 28 November 2008

DOI 10.1002/app.29934

Published online 30 March 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Most polyurethane elastomers in the market place are based on aromatic isocyanates. This is partially due to the higher cost of aliphatic isocyanates compared with aromatic isocyanates which are commonly used by the industry. However, more importantly, it has been the performance deficiency of polyurethane elastomers based on commercial aliphatic isocyanates that has significantly limited their use. Though aliphatic-based polyurethane elastomers possess increased resistance to hydrolysis and thermal degradation in addition to greater light stability, these elastomers often experience a decrease in physical-mechanical properties when compared with

aromatic isocyanate-based materials. In this study, we investigated elastomers based on 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane, an experimental diisocyanate recently developed by The Dow Chemical Company. The physical properties of the elastomers are reported and discussed in comparison to similar elastomers prepared from commercially available aliphatic and aromatic isocyanates. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 839–848, 2009

**Key words:** elastomers; mechanical properties; polyurethanes; structureproperty; relations; viscoelastic properties

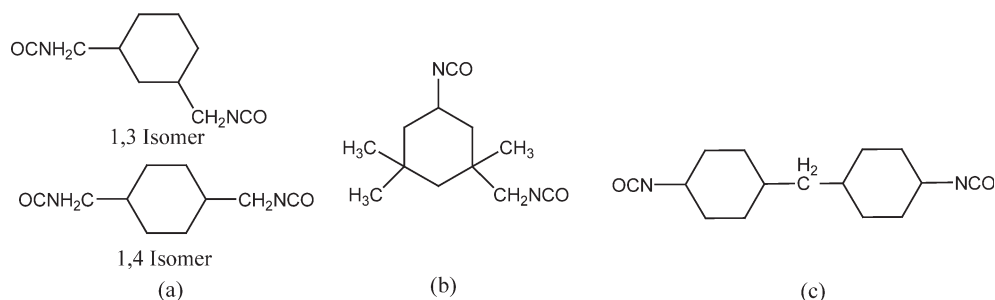
## INTRODUCTION

There are numerous compositional variations that can be employed in the preparation of polyurethane elastomers, resulting in materials with considerable differences in physical and chemical properties. Over the years, polyurethane elastomers have gained a lot of traction in the market place due to their versatility. In general, polyurethane elastomers can be prepared via a two-step or a one-shot process. Cast polyurethane elastomers are normally formed via the two-step process. First, the isocyanates are reacted with polyols to form isocyanate terminated prepolymers. The prepolymers are then chain extended by a diol or a diamine to form elastomers. As a result, the structure of polyurethane elastomers consists of alternating blocks of flexible chains of low glass-transition temperature (soft segments) and highly polar, relatively rigid blocks (hard segments). The soft segments are derived from aliphatic polyethers or polyesters and have glass-transition temperatures below room temperature. The hard segments are formed by the reaction of an isocyanate with a low-molecular-weight chain extender. Separation of these two dissimilar blocks produces

regions of hydrogen-bonded hard domains that act as cross-linking points for the soft blocks.<sup>1–3</sup>

Characteristic properties of the polyurethane elastomers depend on chemical structure and the superstructure originated from hydrogen bond and microphase-separation. The superstructure of the polyurethane elastomers strongly depends on the molecular weight of the soft segment, hard segment content, preparation conditions, and chemical structure of the raw materials. Both aliphatic and aromatic isocyanates can be used to synthesize polyurethanes. Aromatic isocyanate-based elastomers generally bear superior mechanical properties because of the strong cohesion force between the hard segment chains. In general, the presence of an aromatic isocyanate in the hard segment produces a stiffer polymer chain with higher melting point. The most commonly used isocyanates in polyurethane synthesis are aromatic isocyanates, such as toluene diisocyanate (TDI) and methylene bis(p-phenyl) isocyanate (MDI). These isocyanates can result in high-performance polyurethane elastomers by careful selection of chain extenders and polyol backbones. Other aromatic isocyanates, such as naphthalene diisocyanate (NDI) and 3,3' bitoluene diisocyanate (TODI) can also produce high performance polymers, but at a higher cost than MDI and TDI-based elastomers. Because of the aromatic diisocyanates, polyurethanes made from them are unstable toward

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**Figure 1** Chemical structures of isocyanates used in the study. (a) 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane, (b) IPDI, and (c) H<sub>12</sub>MDI.

light and become yellow with time.<sup>4–6</sup> This problem magnifies when the elastomers are required for service under direct exposure to UV or sunlight, such as in an outdoor environment. In addition to color change, crack and chalk can occur due to degradation under UV exposure, especially in the case of thin film coatings.

In contrast, polyurethane elastomers made from aliphatic isocyanates possess greater light stability. Typical aliphatic isocyanates include 1,6-hexane diisocyanate (HDI), isophorone diisocyanate (IPDI) and methylene bis(p-cyclohexyl isocyanate) (H<sub>12</sub>MDI). In addition to enhanced light stability, polyurethane elastomers based on aliphatic isocyanates possess increased resistance to hydrolysis and thermal degradation, making them ideal for high humidity applications at elevated temperatures. Moreover, aliphatic isocyanate-based polyurethane elastomers do not degrade into cyto-toxic components, as can occur with the aromatic isocyanates-based elastomers. MDI-based elastomers have been suggested to degrade into carcinogenic and mutagenic compounds.<sup>7</sup> As a result of their excellent mechanical properties, such as abrasion resistance and high flexural strength and good biocompatibility, aliphatic-based polyurethane elastomers are widely used in medical implants, medical devices and tissue engineering.<sup>8,9</sup>

Although polyurethane elastomers based on aliphatic isocyanates have been widely employed in coatings and medical applications, use of such compositions in other industrial applications is limited to small, niche applications. Despite their improved light stability, thermal and hydrolysis resistance, polyurethane elastomers based on commercial aliphatic isocyanates often experience a decrease in physical-mechanical properties when compared with aromatic isocyanate-based materials. 1,4-cyclohexane diisocyanate (CHDI)-based elastomers are exceptional according to past studies. CHDI is a diisocyanate with an unusually compact symmetrical structure. As a result, it produces highly ordered, semicrystalline polyurethane elastomers with high hardness, high softening temperature, and high tensile modulus.<sup>10–13</sup> However, these great physical

properties come with a high cost, which makes CHDI economically unfavorable for many conventional polyurethane elastomer applications. Other aliphatic isocyanates, such as HDI, H<sub>12</sub>MDI and IPDI, often produce elastomers that are weaker than their aromatic analogues. Therefore, it is highly desirable to have an aliphatic isocyanate that is both cost effective and offers the mechanical strength of commercial aromatic isocyanate-based systems.

Over the past few years, The Dow Chemical Company has been developing a new aliphatic isocyanate—1,3 and 1,4-bis(isocyanatomethyl)cyclohexane. Figure 1 compares the structure of the new aliphatic isocyanate to commercially available aliphatic isocyanates. As part of this research, we have explored the use of the isocyanate in various applications, including coatings, sealants, adhesives, and elastomers. Our interest in polyurethanes with good retention of mechanical properties at elevated temperatures for applications in heavy industrial applications has led to the examination of polyurethane elastomers prepared from 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane. In this study, we investigated mechanical and dynamic viscoelastic properties, morphology and phase transitions, and intermolecular interactions in the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based polyurethane elastomers, and studied them side-by-side with other typical aliphatic isocyanate-based elastomers. In the present paper, we focus on mechanical and dynamic viscoelastic properties of the elastomers. Morphology, phase transitions and intermolecular interactions in these elastomers will be reported in a separate article.<sup>14</sup>

## EXPERIMENTAL

Polycaprolactone polyol (Tone 2241, The Dow Chemical Company) was employed as a polyester glycol. 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane (The Dow Chemical Company), isophorone diisocyanate (IPDI: Rhodia), 4,4-dicyclohexylmethane diisocyanate (H<sub>12</sub>MDI: Bayer Corporation) were used as received. Figure 1 shows the chemical structures of

TABLE I  
General Mechanical Properties of Elastomers Based on 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane and H<sub>12</sub>MDI

Properties	Elastomer 1 <sup>a</sup>	Elastomer 2 <sup>b</sup>	Elastomer 3 <sup>a</sup>	Elastomer 4 <sup>b</sup>
Hard segment content, %	35	35	45	45
Hardness, shore A	85	78	93	87
Tensile strength, psi	6620	2285	7315	2418
Elongation, %	680	575	640	450
Tear strength				
ASTM D470, pli	139	138	155	174
ASTM D624, Die C, pli	428	375	495	451
Compression set, method B, %	33	38	30	42
Bashore rebound, %	52	42	38	35
Stoichiometry, %	98	98	98	98

<sup>a</sup> Prepolymer of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane and polycaprolactone polyol chain extended by 1,4 butanediol.

<sup>b</sup> Prepolymer of 4,4'- dicyclohexylmethane diisocyanate and polycaprolactone polyol chain extended by 1,4 butanediol.

the isocyanates used in this study. The purities of the isocyanates were confirmed to be more than 99% by an amine equivalent method. 1,4- Butanediol (BDO: International Specialty Product) and Ethacure 100 and 300 (Albermarle Corporation) were used as curing agents. To evaluate the miscibility between the hard segment and soft segment and mechanical properties, the hard segment contents of the polyurethane elastomers were varied from 20 to 45 wt %. Prepolymers were prepared from the polyol and isocyanate with the various NCO/OH ratios at 85°C for 6 h under a nitrogen atmosphere. The extent of reaction of hydroxyl group with isocyanate was pursued by an amine equivalent method. After finishing the reaction, the prepolymer was placed under vacuum at 70°C to remove bubbles. The prepolymer and curing agent were then mixed well at different stoichiometric ratios with a Falcktek DAC 400 FV Speed Mixer before being poured into a mold preheated at 115°C. The polyurethane elastomers were demolded after several hours of curing depending on the reactivity of various prepolymers, and were further postcured at 110°C for 16 h in air. After the postcure, the elastomers were aged at room temperature for at least 4 weeks before they were subjected to various tests.

The dynamic viscoelastic properties were measured with a TA Instruments ARES Rheometer between -100 and 250°C with a heating rate of 2°C/min in air. Imposed strain and frequency were 0.2% and 10 Hz, respectively. Tensile testing was performed with an Instron tensile tester at 23°C.

## RESULTS AND DISCUSSIONS

### General mechanical properties of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers

Mechanical properties of polyurethane elastomers are a direct result of their two-phase microstructure.

Typically, phase structure of polyurethane elastomers consists of crystalline "hard"-segment domains dispersed throughout a continuous rubbery "soft"-segment amorphous phase. The micro-domain structure varies with the hard segment content and can exhibit a variety of different morphologies, such as sphere, cylinder and lamellar as predicted theoretically.<sup>15</sup> In reality, segmented polyurethanes actually exhibit a very complex morphology arising from polydispersity of the hard and soft blocks and the varying degrees of phase domain purity. The size and purity of the domains control the elastomeric nature and properties of these polymers. In addition, as in other polymer systems, the molecular structure of the polyurethane elastomer affects its performance. Rosthauser et al.<sup>16</sup> found that mechanical and dynamic properties of H<sub>12</sub>MDI-based polyurethane and polyurethane urea elastomers were strongly dependent on concentration of the *trans, trans* 4,4'-dicyclohexylmethane diisocyanate. Depending on the cross-link density or linearity of the molecular structure, polyurethane elastomers can be made either thermoplastic or thermoset, which results in significant difference in the nature of the two classes of elastomers. Bearing these in mind, general mechanical properties of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers were studied side-by-side with elastomers made from IPDI and H<sub>12</sub>MDI, although varying both the hard segment content and the cross-link density of the elastomers.

General physical properties of polyurethane elastomers based on 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane and H<sub>12</sub>MDI at 35 and 45% hard segment contents are summarized in Table I. The elastomers were chain extended with 1,4 butanediol at 98% stoichiometry. With a slight excess of isocyanate groups, the elastomers are expected to be lightly cross-linked. For both 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane and H<sub>12</sub>MDI-based elastomers, increasing hard segment content increases hardness, tensile

**TABLE II**  
**General Mechanical Properties 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-Based Elastomers as a Function of Stoichiometry**

Properties	Elastomer 1 <sup>a</sup>	Elastomer 2 <sup>a</sup>	Elastomer 3 <sup>a</sup>
Hard segment content, %	45	45	45
Hardness, shore A	93	93	92
Tensile strength, psi	7000	7315	6290
Elongation, %	625	640	1285
Tear strength			
ASTM D470, pli	148	155	160
ASTM D624, Die C, pli	449	495	523
Compression set, method B, %	28	30	69
Bashore Rebound, %	40	38	38
Stoichiometry, %	95	98	102

<sup>a</sup> Prepolymer of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane and polycaprolactone polyol chain extended by 1,4 butanediol.

strength and tear strength, but reduces elongation and Bashore rebound. Similar trends were observed by Dieter and Byrne.<sup>10</sup> in study of H<sub>12</sub>MDI-based elastomers. Elongation and resilience are directly related to the rubbery “soft” segment. Increase of the hard segment reduces the soft segment content, which results in change of microdomain structure in the PU elastomers. At 35% hard segment content, it is expected that the microdomain structure represents dispersed hard domains in a continuous soft phase. At 45% hard segment content, a bi-continuous microdomain structure is expected.

Comparing physical properties of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers to those based on H<sub>12</sub>MDI at the same hard segment content, the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane elastomers demonstrate improved hardness, tensile strength, elongation, compression set and Bashore rebound. It is interesting to note that 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers are significantly harder than H<sub>12</sub>MDI-based elastomers at the same hard segment content. As a result, 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers can achieve the same level of hardness as H<sub>12</sub>MDI-based elastomers at a much lower hard segment content. Therefore, less 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane is required to reach a given hardness. As aliphatic isocyanates are the most costly component among the building blocks, lower levels of aliphatic isocyanate in the system can significantly reduce total system cost.

The improved compression set of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers indicates greater ability of these elastomers to retain elastic properties after prolonged action of compressive stresses, thus making them more suitable for prolonged stressing services than the H<sub>12</sub>MDI-based elastomers. The actual stressing services may involve the maintenance of a definite deflection, the constant

application of a known force, or the rapidly repeat deformation and recovery resulting from intermittent compressive forces. The latter dynamic stressing, like the others, produces compression set, however, its effects as a whole are simulated more closely by hysteresis tests, such as dynamic mechanical analysis discussed latter.

The ultimate tensile strength and elongation measure the polymer’s strength and extensibility, respectively. Increase of the hard segment content increases the tensile strength for both 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane and H<sub>12</sub>MDI-based elastomers, though the elongation reduces slightly. Though the H<sub>12</sub>MDI-based elastomers possess similar tear resistance, tensile strength of these elastomers is only about 30% of that demonstrated for the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane elastomers, suggesting that H<sub>12</sub>MDI-based elastomers are much weaker and thus less desirable for high demanding applications.

Table II summarizes general mechanical properties of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers containing 45% hard segment content while varying their stoichiometry. As a result of the increase in stoichiometry from 95 to 102%, molecular structure of the polyurethane elastomers is expected to change from slightly cross-linked to fully linear. Elongation, tear strength, and compression set increased with increasing stoichiometry, whereas tensile strength and resilience slightly decreased when the molecular structure became more linear. The observation is in good agreement with results on other polyurethane elastomer systems based on aromatic isocyanates.<sup>17</sup>

Besides hydroxyl groups, amines can also be used as chain extenders. Amine chain extenders react rapidly and vigorously with isocyanates to produce urea groups, and the resulting urea groups can



**TABLE III**  
**Mechanical Properties of Elastomers Chain Extended by Ethacure 100 at 20% Hard Segment Content**

Properties	Elastomer 1 <sup>a</sup>	Elastomer 2 <sup>b</sup>	Elastomer 3 <sup>c</sup>
Hard segment content, %	20	20	20
Hardness, shore A	78	75	80
Tensile strength, psi	5390	5190	5240
Elongation, %	610	610	520
Tear strength			
ASTM D470, pli	99	99	75
ASTM D624, Die C, pli	303	327	315
Compression set, method B, %	26	44	30
Bashore rebound, %	69	60	55
Stoichiometry, %	95	95	95

<sup>a</sup> Prepolymer of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane and polycaprolactone polyol chain extended by Ethacure 100 (mixture of 3,5-diethyltoluene-2,4-diamine and 3,5-diethyltoluene-2,6-diamine).

<sup>b</sup> Prepolymer of isophorone diisocyanate and polycaprolactone polyol chain extended by Ethacure 100 (mixture of 3,5-diethyltoluene-2,4-diamine and 3,5-diethyltoluene-2,6-diamine).

<sup>c</sup> Prepolymer of 4,4'-dicyclohexylmethane diisocyanate and polycaprolactone polyol chain extended by Ethacure 100 (mixture of 3,5-diethyltoluene-2,4-diamine and 3,5-diethyltoluene-2,6-diamine).

produce a polymer cross-linked with biuret links. These elastomers set so rapidly that their use is limited to a one-step reaction injection molding processes. However, aliphatic isocyanates react much more slowly than aromatic isocyanates. As a result, some of the amine chain extenders that are not suitable with aromatic-based prepolymers can be used in the aliphatic systems, especially amines with large substituent groups that sterically hinder the approach to the isocyanate group, and amines with neighboring groups that reduce the reactivity of the amine. Table III summarizes the mechanical properties of elastomers based on 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane, IPDI and H<sub>12</sub>MDI at 20% hard segment content. The elastomers were chain extended with Ethacure 100. Although the hard segment content is relatively low, use of the aromatic amine chain extender improved the hardness for all elastomers. All the elastomers demonstrated similar hardness, tensile strength, tear strength and elongation. However, the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomer clearly showed improved resilience and compression set. The data suggest that amine chain extended 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers are more suitable for dynamic and static stressing applications.

Table IV summarizes the physical properties of elastomers based on 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane, IPDI and H<sub>12</sub>MDI. The elastomers were chain extended with Ethacure 300 at 20% hard segment content. Compared with the Ethacure 100 chain extended elastomers, Ethacure 300 produced elastomers with much lower hardness. In this case,

the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomer demonstrated clear advantages in tensile strength, elongation, tear strength, compression set and resilience over the IPDI and H<sub>12</sub>MDI-based elastomers.

It is well known that the use of aliphatic isocyanates in cast elastomer applications often produces weaker polymers with lower hardness, lower softening temperature and reduced mechanical strength.<sup>18</sup> Thus, it is of great interests to compare the performance of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers with those of MDI and TDI-based elastomers. Table V compares the performance of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers to those based on TDI and MDI at similar hard segment contents. VORASTAR<sup>TM</sup> HB 6536 Iso and VORASTAR<sup>TM</sup> HB 6544 Iso are MDI prepolymers based on caprolactone polyols, and VORASTAR<sup>TM</sup> HB 6580 Iso is a TDI prepolymer based on caprolactone polyols. Vibrathane 6060, a commercial product based on TDI and caprolactone polyols from Chemtura Corporation, is also used as a reference. In the case of diol chain extended elastomer systems, it is clear that 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers match the performance of MDI-based elastomers at both 35 and 45% hard segment contents. Although demonstrating improved stress-strain properties, the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers only show minor deficiencies in compression set and resilience. As for diamine chain extended elastomers, compared with VORASTAR<sup>TM</sup> HB 6580 Iso chain extended with Ethacure 300, the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based

**TABLE IV**  
**Mechanical Properties of Elastomers Chain Extended by Ethacure 300 at 20% Hard Segment Content**

Properties	Elastomer 1 <sup>a</sup>	Elastomer 2 <sup>b</sup>	Elastomer 3 <sup>c</sup>
Hard segment content, %	20	20	20
Hardness, shore A	67	64	58
Tensile strength, psi	4015	2539	2830
Elongation, %	690	550	650
Tear strength			
ASTM D470, pli	75	38	44
ASTM D624, Die C, pli	252	152	150
Bashore rebound, %	58	40	44
Stoichiometry, %	95	95	95

<sup>a</sup> Prepolymer of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane and polycaprolactone polyol chain extended by Ethacure 300 (mixture of 3,5-dimethylthio-2,6-toluenediamine and 3,5-dimethylthio-2,4-toluenediamine).

<sup>b</sup> Prepolymer of isophorone diisocyanate and polycaprolactone polyol chain extended by Ethacure 300 (mixture of 3,5-dimethylthio-2,6-toluenediamine and 3,5-dimethylthio-2,4-toluenediamine).

<sup>c</sup> Prepolymer of 4,4'-dicyclohexylmethane diisocyanate and polycaprolactone polyol chain extended by Ethacure 300 (mixture of 3,5-dimethylthio-2,6-toluenediamine and 3,5-dimethylthio-2,4-toluenediamine).

elastomer chain extended with Ethacure 100 demonstrated improved resilience, comparable stress-strain properties and slightly inferior compression set. On the other hand, compared with Vibrathane 6060 chain extended with 4,4'-methylene-bis-(*o*-chloroaniline) (MBCA), the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomer exhibited improved stress-strain properties, tear resistance and resilience; as well as a much higher compression set than that of Vibrathane 6060. The extremely low compression set of the Vibrathane 6060 may be related to higher cross-link density in the elastomer.

As mentioned earlier, the use of aliphatic isocyanates in polyurethane elastomers is often accompanied with reduced performance, especially in the case of diol chain extended aliphatic systems. Cyclohexanediisocyanate (CHDI)-based elastomers were found to be the exception.<sup>10</sup> These elastomers demonstrated enhanced mechanical strength over other aliphatic isocyanate-based elastomers when they were chain extended with either 1,4-butanediol or 1,4-cyclohexanediol. The improvement was largely attributed to the unusually compact symmetrical structure of CHDI. The fact that 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers match or exceed performance of conventional aromatic isocyanate-based elastomers is worth noting. With the exceptional mechanical strength in addition to light stability, and resistance to hydrolysis and thermal degradation, 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers can be employed not only in services that are traditionally dominated by aromatic isocyanates but also in applications that demand superior light, heat and moisture resistance.

### Dynamic viscoelastic properties

Dynamic properties of urethane elastomers can be analyzed using a Dynamic Mechanical Analyzer. A good compound for dynamic applications is generally represented by low  $\tan \delta$  values and constant modulus values over the working temperature range in which the parts will be used. As  $\tan \delta = G''/G'$ , where  $G''$  is the loss modulus and  $G'$  is the storage modulus, a lower  $\tan \delta$  value means that energy transferred to heat is much lower than energy stored. Therefore, lower heat buildup occurs in high-speed, high-load bearing applications.

Heat generation is an aspect of the dynamic properties of a material. It is the conversion of applied mechanical energy into heat. In urethane elastomers, the viscous component, which is responsible for the heat generation, arises from molecular friction. Deformation involves dragging polymer chains, chain segments and cross-links through the polymer. If the units are forced into new locations more rapidly than vacant sites (holes) are generated by thermal motion of the surrounding molecules, the ordered mechanical motion is converted into random thermal motion of these molecules, i.e., heat. The deformation of any material can be resolved into elastic and a viscous component, often represented as a spring and a dashpot. When a cyclic sinusoidal strain is imposed on a material, the two viscoelastic components of the material respond at different speeds, which results in the actual stress of the material leading the imposed strain by a phase angle  $\delta$ . If the stress is plotted against strain, for a single deformation, a hysteresis loop is obtained. The area within this closed loop is the amount of mechanical energy

TABLE V  
Mechanical Properties of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane, MDI and TDI-Based Elastomers

Properties	HB 6536 BDO <sup>a</sup>	Elastomer 1 <sup>b</sup>	HB 6544 BDO <sup>a</sup>	Elastomer 2 <sup>b</sup>	Elastomer 3 <sup>c</sup>	HB 6580 E300 <sup>a</sup>	Elastomer 4 <sup>d</sup>	Vibrathane 6060/MOCA@
Hard segment content, %	35	35	45	45	20	21	20	23
Hardness, shore A	85	85	95	93	78	80	67	62
Tensile strength, psi	6000	6620	6285	7315	5390	5350	4015	4400
Elongation, %	620	680	490	640	610	720	690	480
Tear strength								
ASTM D470, pli	125	139	165	155	99	95	75	22
ASTM D624, Die C, pli	450	428	605	495	303	422	252	190
Compression set, method B, %	20	33	26	30	26	18	25	6
Bashore rebound, %	56	52	50	38	69	57	58	30
Stoichiometry, %	98	98	98	98	95	95	95	95

<sup>a</sup> Commercial prepolymer of MDI and polycaprolactone polyol chain extended by 1,4 butanediol.

<sup>b</sup> Prepolymer of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane and polycaprolactone polyol chain extended by 1,4 butanediol.

<sup>c</sup> Prepolymer of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane and polycaprolactone polyol chain extended by Ethacure 100 (mixture of 3,5-diethyltoluene-2,4-diamine and 3,5-diethyltoluene-2,6-diamine).

<sup>d</sup> Prepolymer of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane and polycaprolactone polyol chain extended by Ethacure 300, (mixture of 3,5-dimethylthio-2,6-toluenediamine and 3,5-dimethylthio-2,4-toluenediamine).

converted to heat ( $H$ ) during the cycle, as determined by eq. (1) where  $\sigma$  is the stress and  $\gamma$  is the strain.

$$H = \int_0^T \sigma(dy/dt)dt \quad (1)$$

Assuming the periodic deformation cycle is sinusoidal, eq. (1) can be rewritten as

$$H = \pi\sigma_0\gamma_0 \sin \delta \quad (2)$$

Because loss modulus  $G'' = \sigma_0/\gamma_0 \sin \delta$ , when the deformation is a constant strain process, eq. (2) becomes

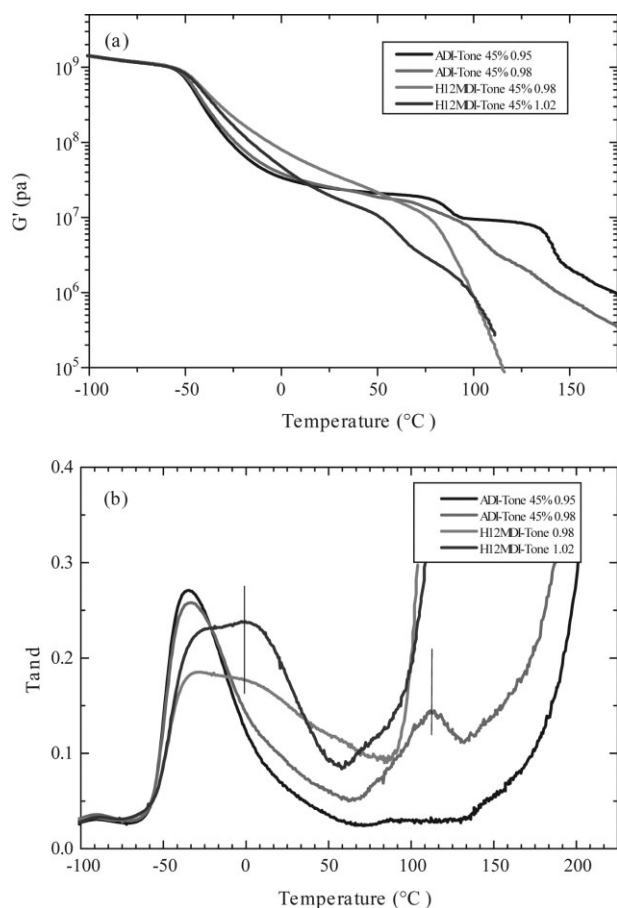
$$H = \pi\gamma_0^2 G'' \propto G' \tan \delta \quad (3)$$

whereas in the case of a constant stress process, energy loss during one periodic deformation is

$$H = \pi\sigma_0^2 G''/G^* \propto \tan \delta/G' \approx J'' \quad (4)$$

where  $J''$  is the loss compliance. Loss compliance is directly related to power loss and can be used on a quantitative basis to estimate the amount of mechanical energy converted to heat in practical applications. Loss compliance is directly proportional to the rate of heat buildup generated when an elastomer is cycled between specified peak loads or stresses like in tire, wheel and roller applications. Polyurethanes with lower loss compliance values will experience less heat buildup in service and suffer fewer field failures. Loss compliance reaches a maximum at the soft segment glass transition temperature, and again increases at the hard segment melt point or decomposition temperature.<sup>13</sup>

Figure 2 shows the elastic modulus and  $\tan \delta$  values of elastomers containing 45% hard segment content. Results of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane and H<sub>12</sub>MDI-based elastomers are shown side-by-side while varying the stoichiometry. The sharp drop in elastic modulus starting at about  $-50^\circ\text{C}$  as shown in Figure 2(a), corresponded to the glass transition temperature of the soft segment, whereas decline in modulus at the higher temperature range corresponded to melting down of the hard segment (softening temperature). The two temperatures define the working temperature range of an elastomer. A wider working temperature range is desirable as it allows the elastomer to be utilized at both lower and higher temperature applications. It is clear that the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers have a wider working temperature range than those based on H<sub>12</sub>MDI, as evident by a lower glass transition temperature and a higher softening temperature of the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers. In addition, the 1,3 and 1,4-bis(isocyanatomethyl)



**Figure 2** Temperature dependence of elastic modulus  $G'$  (a) and  $\tan \delta$  (b) of elastomers containing 45% hard segment content when chain extended with BDO at various stoichiometry ratios. ADI in the figures stands for 1,3 and 1,4 bis(isocyanatomethyl)cyclohexane, the Dow experimental aliphatic diisocyanate.

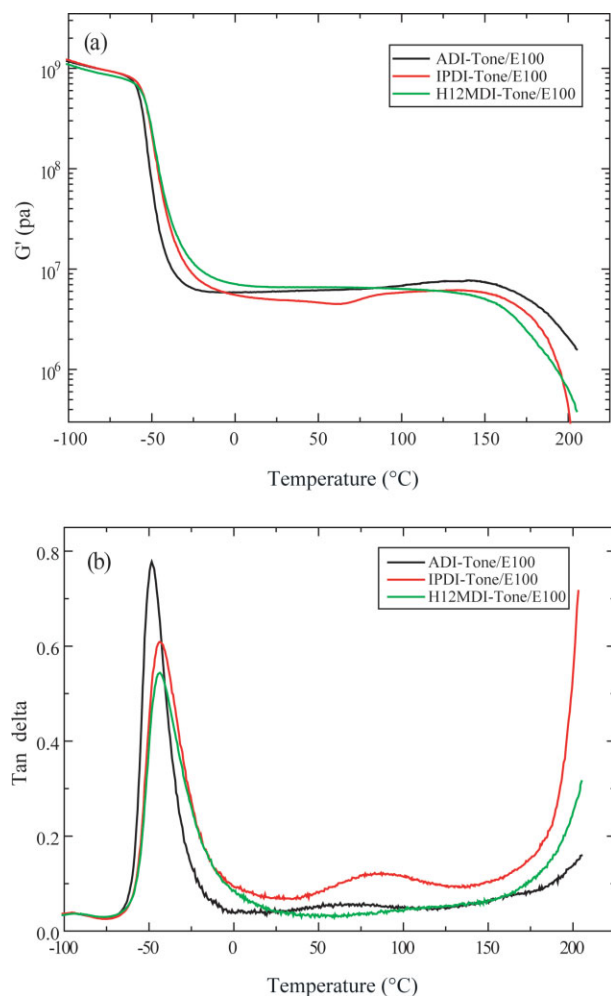
cyclohexane-based elastomers also exhibited enhanced ability in maintaining the modulus constant over the working temperature range. As elastic modulus measures a material's ability to carry load, decline in modulus over increasing temperature, as shown for the  $H_{12}$ MDI-based elastomers, is not desirable for dynamic applications. The increase of stoichiometry from 95 to 102% affected modulus retention and lowered softening temperature considerably in all elastomers. Clearly, a slightly cross-linked elastomer is more suitable for high stress dynamic applications.

The peak in the  $\tan \delta$  curves between  $-40$  and  $-20^\circ\text{C}$  shown in Figure 2(b) relates to the glass transition temperature of the soft segment in the PU elastomers. The  $T_g$  of the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers was about  $-34^\circ\text{C}$ , much lower than the  $T_g$  of  $-25^\circ\text{C}$  for the  $H_{12}$ MDI-based elastomers. In addition, the peak for the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers was much sharper and narrower

than that of the  $H_{12}$ MDI-based elastomers. Peak intensity and shape represent damping properties of the elastomers. Considering that all the elastomers were based on the same polyol backbone, the difference in  $T_g$  between the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane and  $H_{12}$ MDI-based elastomers could only be attributed to the degree of phase mixing in the elastomers. Clearly, phase separation in the  $H_{12}$ MDI-based elastomers was poorer as shown by a broad transition peak shifting to a higher temperature. Both  $H_{12}$ MDI-based elastomers at 98 and 102% stoichiometry exhibited two peaks, one at  $-25^\circ\text{C}$  and the other at  $-4^\circ\text{C}$ . Both of the peaks correspond to  $\alpha$  relaxation from soft segment phases. The lower temperature transition corresponded to relaxation of the soft segment rich phases, whereas the higher temperature transition resulted from relaxation of the soft segment mixed with hard segments. The observation of enhanced phase separation in the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers is in good agreement with results from small angle x-ray scattering and atomic force microscope study on the elastomers.<sup>14</sup>

Similarly, two peaks at around  $-34$  and  $110^\circ\text{C}$  in the  $\tan \delta$  curve of the elastomer based on 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane at 98% stoichiometry were observed. The transition at the lower temperature corresponds to  $\alpha$  relaxation from the soft segment rich phases, whereas that at the higher temperature corresponds to relaxation from the soft segments in the hard segment rich phase. Lower stoichiometry appears enhance phase separation in elastomers based on both  $H_{12}$ MDI and 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane, as evident by the less pronounced second peak in the  $\tan \delta$  curve of the  $H_{12}$ MDI-based elastomer at 98% stoichiometry, and the disappearance of the second peak at higher temperature in the  $\tan \delta$  curve of the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomer at 95% stoichiometry. Similarly, Kojio et al.<sup>19</sup> observed two peaks in  $\tan \delta$  curves of elastomers based on norborane diisocyanate, IPDI and  $H_{12}$ MDI, but not in 1,6-hexamethylene diisocyanate (HDI)-based elastomers due to stronger phase separation in the HDI-based elastomer. Wang et al.<sup>20</sup> also observed two  $\tan \delta$  peaks in highly cross-linked MDI-based elastomers due to phase mixing of the soft and hard segments. The steep increase in  $\tan \delta$  value at a higher temperature corresponded to melting of the hard segment (softening temperature). Increase of stoichiometry not only increased  $\tan \delta$  values over the working temperature range, but also significantly lowered the softening temperature. It is clear from Figure 2 that 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers are better in maintaining modulus over a much wider working temperature range, and have much lower  $\tan \delta$  values than  $H_{12}$ MDI-based





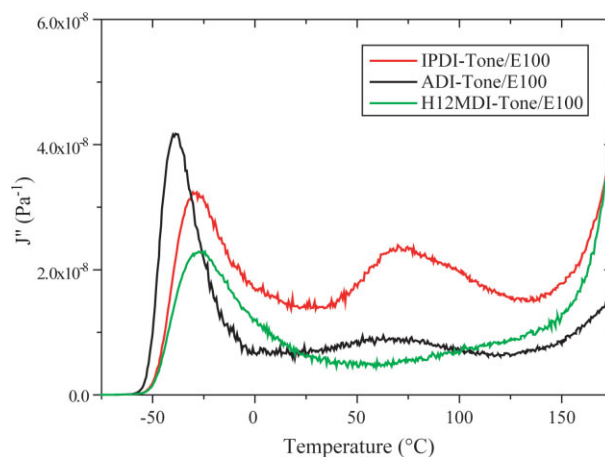
**Figure 3** Temperature dependence of elastic modulus  $G'$  (a) and  $\tan \delta$  (b) of elastomers containing 20% hard segment when chain extended with Ethacure 100. ADI in the figures stands for 1,3 and 1,4 bis(isocyanatomethyl)cyclohexane, the Dow experimental aliphatic diisocyanate. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

elastomers. As a result, 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers are more suitable for dynamic applications, especially when they are partially cross-linked at lower stoichiometry ratios.

Figure 3 shows elastic modulus  $G'$  and  $\tan \delta$  values of elastomers at 20% hard segment but chain extended with Ethacure 100, an aromatic diamine. Comparing to the diol chain extended elastomers shown in Figure 2, the amine chain extended elastomers exhibited improved ability to maintain modulus over a wider working temperature range. This was evident by a lower glass transition temperature and a higher softening temperature for all the amine chain extended elastomers, as shown in Figure 3(a). However, the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomer clearly demonstrated enhanced ability in maintaining a constant modulus over a wider working temperature range than the IPDI

and  $\text{H}_{12}\text{MDI}$ -based elastomers. In addition, the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomer also displayed overall lower  $\tan \delta$  values over the working temperature range as shown in Figure 3(b), implying lower heat build-up and hence a lower service temperature for the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomer. Moreover, the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomer had a narrower glass transition peak that occurred at a much lower temperature than IPDI and  $\text{H}_{12}\text{MDI}$ -based elastomers, implying enhanced phase separation in the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers.

As discussed earlier, loss compliance is directly related to heat buildup in polyurethane elastomers. The lower the loss compliance value and the more constant the value remains over a wide temperature range, the better an elastomer is in its ability to resist the hysteretic heat build up under dynamic load application.<sup>21,22</sup> Figure 4 shows loss compliance of the three elastomers chain extended with Ethacure 100. Loss compliance reached a peak at the glass transition temperature of the soft segment. The IPDI-based elastomer had generally higher loss compliance over the working temperature range, and had an additional peak at about 75  $^{\circ}\text{C}$  before it increased again at 130  $^{\circ}\text{C}$  due to the hard segment melting down. Loss compliance of the  $\text{H}_{12}\text{MDI}$ -based elastomer minimized at about 50  $^{\circ}\text{C}$ , and then increased gradually with rising temperature before rising steeply beyond 140  $^{\circ}\text{C}$ . Though loss compliance of the elastomer was generally low, the up trend was not favorable. The temperature at which loss compliance reaches its minimum is widely referred to as



**Figure 4** Temperature dependence of loss compliance of Ethacure 100 chain extended elastomers. ADI in the figures stands for 1,3 and 1,4 bis(isocyanatomethyl)cyclohexane, the Dow experimental aliphatic diisocyanate. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the critical point. In general, one would like to keep the material servicing at a temperature below the critical point as the tendency is for the part to heat up under dynamic loads that will shift the response toward the higher temperature region. The up trend shown by the H<sub>12</sub>MDI-based elastomer will increase heat loss at temperatures higher than 50°C, thus making it unsuitable for most dynamic applications. In contrast, the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomer had generally low loss compliance values in the working temperature range. Its loss compliance was minimized at about 125°C. The material also had much lower loss compliance than the IPDI and H<sub>12</sub>MDI-based elastomers at temperature above 100°C. With a much higher critical point temperature and much lower loss compliance values in the high temperature region, the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomer is ideal for high temperature dynamic services.

### CONCLUSIONS

Mechanical strength and dynamic viscoelastic properties of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane/polycaprolactone-based elastomers were studied and compared with other aliphatic isocyanates, such as IPDI and H<sub>12</sub>MDI-based elastomers. The 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers showed unique mechanical and dynamic properties with retention of these properties at elevated temperatures. No matter whether it was chain extended with a diol or diamine, 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers demonstrated enhanced mechanical strength over other aliphatic isocyanate-based systems. To our surprise, mechanical properties of the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers matched or even exceeded the performance of aromatic isocyanate-based elastomers, such as conventional MDI and TDI elastomers. In addition, the 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers displayed superior dynamic performance supported by constant modulus values over a wider working temperature window, lower tan  $\delta$  values, higher softening temperature, and higher critical point temperature. The good-to-excellent physical properties are in part due to the small, compact, symmetrical structure of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane. In keeping with the enhanced properties of aliphatic polyurethanes, 1,3 and 1,4-

bis(isocyanatomethyl)cyclohexane-based elastomers should be non-yellowing in the presence of ultraviolet light. As a result, 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-based elastomers can be used not only in applications of traditional aliphatic isocyanate-based systems, but also in areas that are currently dominated by aromatic isocyanate-based elastomers.

The authors thank Susan Falcone and Linda Ulmer for their assistance in conducting Dynamic Mechanical Analysis on the samples.

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