

Nanoindentation Measurements of Mechanical Properties of Polyurethane Elastomers Which Crosslinked by β -Cyclodextrin

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Abstract

A series of PUEs which use β -CD as cross-linker were synthesized. Nanoindentation measurements of mechanical properties of these PUEs were made. Load and depth sensing indentation and nano DMA mode were used to evaluate mechanical properties of PUEs in nano-scale. The difference between the results from two modes proved the microphase separation in PUEs and to investigate PUE from hard domains and soft domains was of great significance.

Keywords

Polyurethane Elastomer, Microphase Separation, Load and Depth Sensing Indentation, Nano DMA

1. Introduction

PUEs are a kind of polymers that typically synthesized by polyaddition of diisocyanate, polyol and chain-extender (CE)/cross-linker. PUEs are widely believed as segmented polymers which contain hard segments (HS) and soft segments (SS). Isocyanate and chain-extender components give rigidity to molecular chains and called HS, while polyol gives flexibility to chains and they are called SS [1] [2]. Due to the incompatibility between HS and SS, most PUEs exhibit phase separation which plays an important role in affecting PUE properties [3]. The phase separation phenomenon has been widely researched and proved by images of Atomic Force Microscope (AFM) [4] [5] that hard domains (HD) consist of agglomerate of hard segments, soft domains (SD), and

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soft segments. Mechanical properties of PUEs and the structure-properties relationship have been investigated by lots of researchers [6]–[8]. However, the mechanical properties characterized from HS/HD and SS/SD themselves attract fewer researchers' attention. It is believed that the mechanical properties of small structure are quite different from bulk materials [9] [10].

In recent years, nanoindentation measurement has become a popular method of determining mechanical properties of materials, especially thin film systems [11]. For PUEs, the nano-scaled size of indenter makes it possible to characterize mechanical properties of HD and SD directly.

In this study, normal load and depth sensing indentation and nanoscale Dynamic Mechanical Analysis were carried out. Nano-scale mechanical properties were characterized from PUEs, also from HD and SD. The results show that properties of PUEs are quite related to phase separation and the characterization from HD and SD is of great significance.

2. Experimental

2.1. Materials

Three kinds of diisocyanates (4,4'-Diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate (HDI), and isophorone diisocyanate (IPDI)) were supplied by Tosoh Industry, Tokyo, Japan and were purified by distillation under reduced pressure (267 - 400 Pa) at 100°C before use. Polytetramethylene ether glycol (molecular weight = 1000) (PTMG1000) was supplied by Invista Industry, Texas, USA. β -cyclodextrin (β -CD) was purchased from Nacalai Tesque, Inc., Kyoto, Japan (Nacalai) and was dried for 24 hours under a condition of 267 - 400 Pa/80°C before use. *N,N*-Dimethylformamide (DMF) was purchased from Nacalai and stored over 4 Å molecular sieves before use. Dibutyltin dilaurate (DBTDL) was purchased from Nacalai and initially dissolved in toluene to form 10% solution. Tetrahydrofuran (THF) was purchased from Nacalai and distilled over calcium hydride under an Ar atmosphere.

2.2. Synthesis of PUEs Crosslinked by β -Cyclodextrin

A series of PUEs were synthesized from different kinds of diisocyanates, PTMG1000, and β -CD via prepolymer method, named X-PUE_x (X = kind of diisocyanate, x = weight percent (wt%) of β -CD).

The synthesis route is as follows: β -CD was initially dissolved in DMF (10 mL) at 80°C for 20 min under an Ar atmosphere to reach a β -CD solution. Diisocyanate (0.020 mol) and PTMG1000 (10 g, 0.010 mol) were added into a 100mL four-necked separable flask equipped with a mechanical stirrer, a gas inlet tube, and a reflux condenser. The prepolymer was prepared at 80°C under an Ar atmosphere with a stirring. Temperature of reaction was controlled at 80°C for MDI- and IPDI-based prepolymer, while 100°C for HDI-based prepolymer. Then β -CD solution was added into separable flask followed by a further stirring. A small amount of bubbles in the system were removed by addition of THF (20 mL) and a high speed stirring of 5 min. Catalyst (DBTDL) was also needed when HDI and IPDI were used.

The thin PUE films (0.5 - 0.8 mm) were obtained by casting the resulting PUE solution at room temperature (23°C \pm 2°C) for 24 h, at 50°C for 24 h and at 100°C for 24 h. The DMF residues in films were removed at 80°C under vacuum for 6 h.

2.3. Nanoindentation Measurements of Mechanical Properties

The nanoindentation experiments of PUE films have been performed on a TI 950 TriboIndenter® of Hysitron Inc., MN, USA, load and depth sensing indentation mode and nanoscale Dynamic Mechanical Analysis (nano DMA) were undertaken. In nano DMA tests, surface images were also taken during the tests, the tested areas were marked in the images. A Berkovich tip is used in all nanoindentation experiments. All measurements were performed at room temperature. In Load and depth sensing indentation mode, indentation area of specimens were selected randomly. Each sample was tested for 5 to 7 times.

2.4. Theory

Some parameters in indentation with Berkovich tip are illustrated in **Figure 1**. Load-depth curves produced by instrumented indentation systems are often based on Oliver and Pharr [12]. As **Figure 2** shown, several important

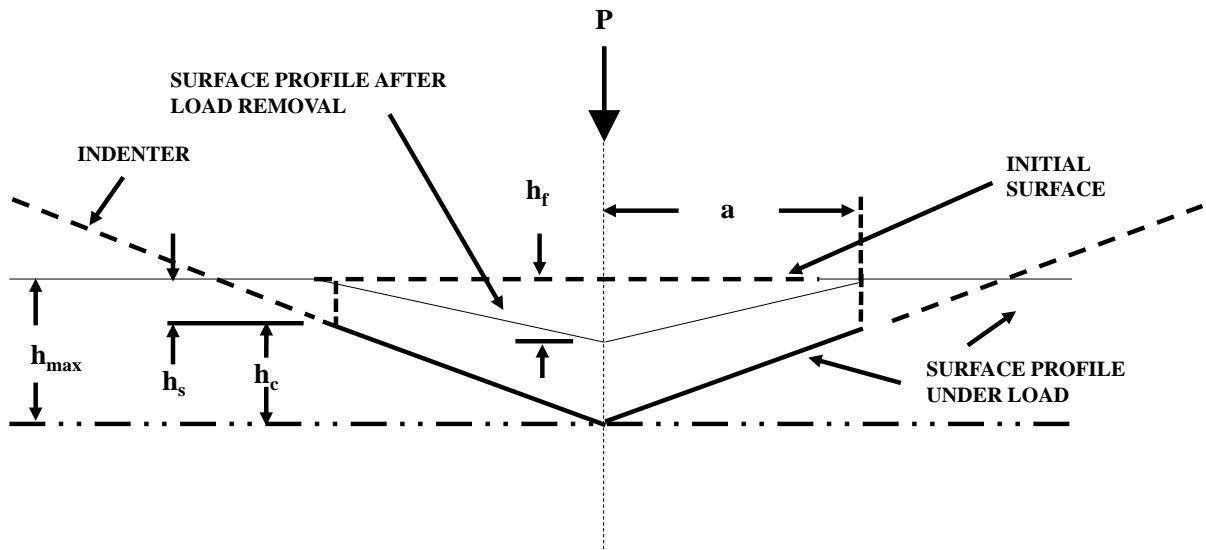


Figure 1. A schematic representation of the indentation.

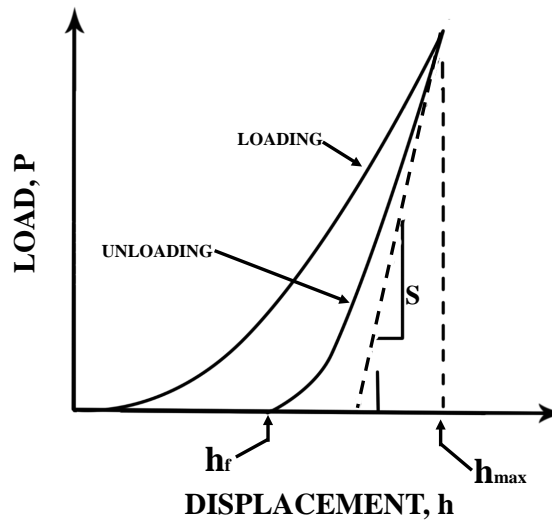


Figure 2. A schematic representation of Load-depth curve.

parameters are illustrated. The hardness H is an important parameter to evaluate mechanical property of materials. $H = P_{\max}/A$, where P_{\max} is the peak indentation load and A is projected area of the hardness impression [13] [14].

3. Results and Discussion

The load-depth curves of PUEs are shown as Figure 3. In MDI-PUEs and HDI-PUEs, h_{\max} of MDI-PUE₀ and HDI-PUE₀ are lower than the PUEs with β -CD. In contrast, IPDI-PUEs that contain β -CD have much lower h_{\max} than IPDI-PUE₀. The calculated hardness of these PUEs is shown as Table 1. It is concluded that addition of β -CD reduce the hardness of MDI-PUE₀ and HDI-PUE₀. Whereas, increase the hardness of IPDI-PUE₀. These results prove that β -CD can increase the hardness of PUEs synthesized from unsymmetrical diisocyanates and decrease the hardness of PUEs synthesized from symmetrical ones. It quite agrees with our former research.

In addition, the increase and decrease of hardness is not proportional to the additive amount of β -CD. It may relate to the tested area of indenter. Because phase separation occurs in most PUEs, the indenter may contact the HD and SD. The differences between HD and SD affect the indentation a lot.

To ensure the differences, nano DMA mode was used. As **Figures 4-6** shown, hardness of designated areas was tested. Most PUEs exhibit phase separation and brighter parts have comparatively greater hardness. Normally, brighter parts are believed to be HD while darker parts are SD. Moreover, hardness of brighter parts and darker parts reach unanimity in high depth. It may due to the unique structure of PUEs. HD are dispersed in SD matrix, thus indenter tend to contact the matrix in high depth both in SD and HD areas.

In PUEs which exhibit weak phase separation or no phase separation, such as MDI-PUE₁, MDI-PUE₃, IPDI-PUE₁ and IPDI-PUE₅, the hardness of different areas are almost the same. It is obvious that phase separation is important to PUEs and the greater the phase separation the greater difference between hardness of HD and SD.

4. Conclusion

A series of PUEs which cross-linked by β -CD were synthesized. Through nanoindentation measurements of mechanical properties of these PUEs, properties of HD and SD of PUEs can be measured directly. It is more

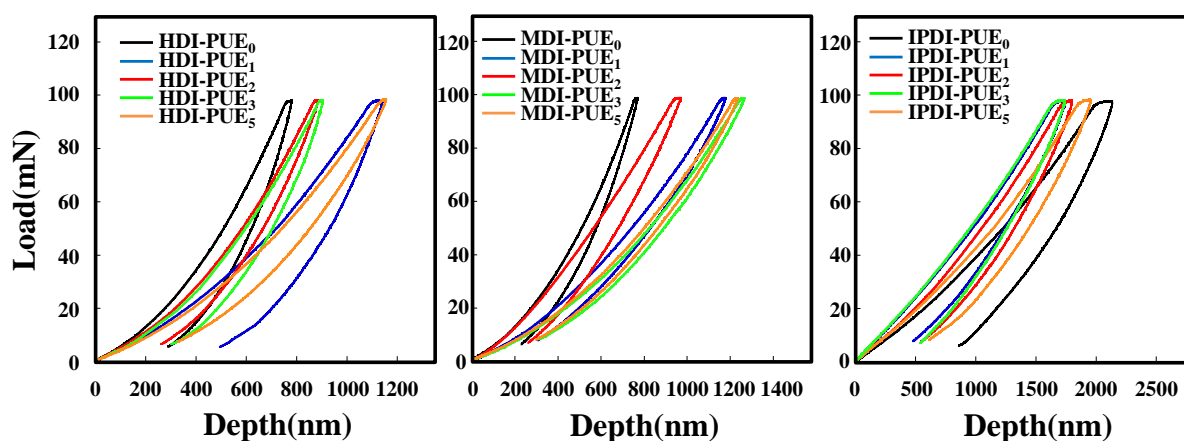


Figure 3. Load-depth curves of HDI-PUEs, MDI-PUEs and IPDI-PUEs.

Table 1. Calculated hardness of HDI-PUEs, MDI-PUEs and IPDI-PUEs.

| Sample | Calculated hardness (Gpa) |
|-----------------------|---------------------------|
| HDI-PUE ₀ | 0.0138 |
| HDI-PUE ₁ | 0.0050 |
| HDI-PUE ₂ | 0.0087 |
| HDI-PUE ₃ | 0.0072 |
| HDI-PUE ₅ | 0.0064 |
| MDI-PUE ₀ | 0.0135 |
| MDI-PUE ₁ | 0.0078 |
| MDI-PUE ₂ | 0.0113 |
| MDI-PUE ₃ | 0.0061 |
| MDI-PUE ₅ | 0.0067 |
| IPDI-PUE ₀ | 0.0016 |
| IPDI-PUE ₁ | 0.0033 |
| IPDI-PUE ₂ | 0.0028 |
| IPDI-PUE ₃ | 0.0032 |
| IPDI-PUE ₅ | 0.0024 |

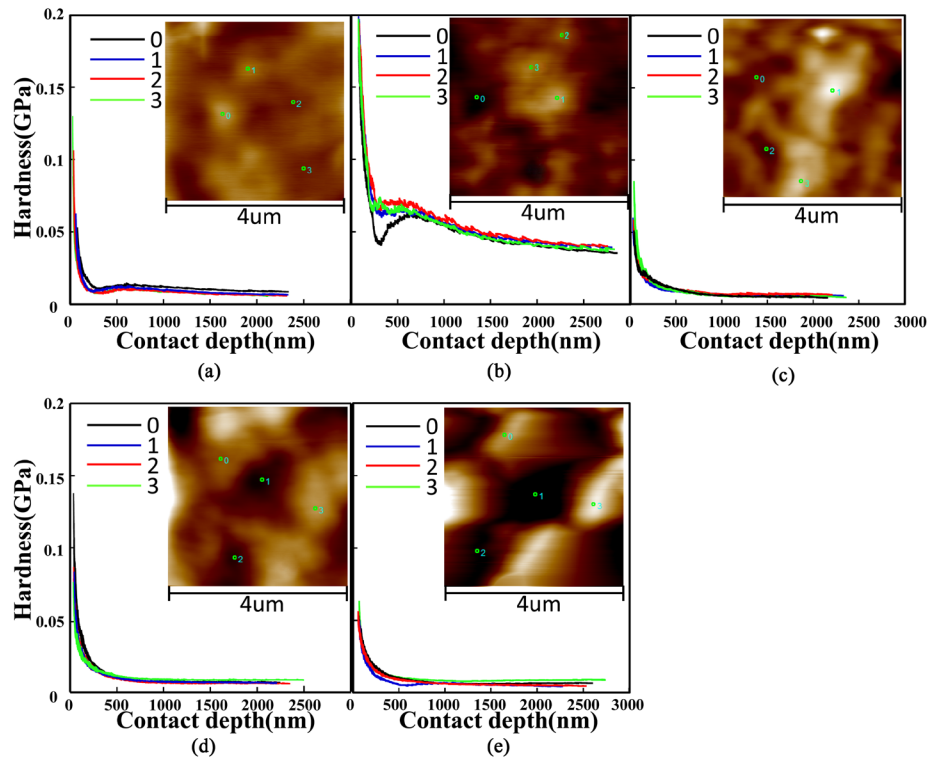


Figure 4. Hardness-depth curves of HDI-PUEs, (a) HDI-PUE₀. (b) HDI-PUE₁. (c) HDI-PUE₂. (d) HDI-PUE₃. (e) HDI-PUE₅.

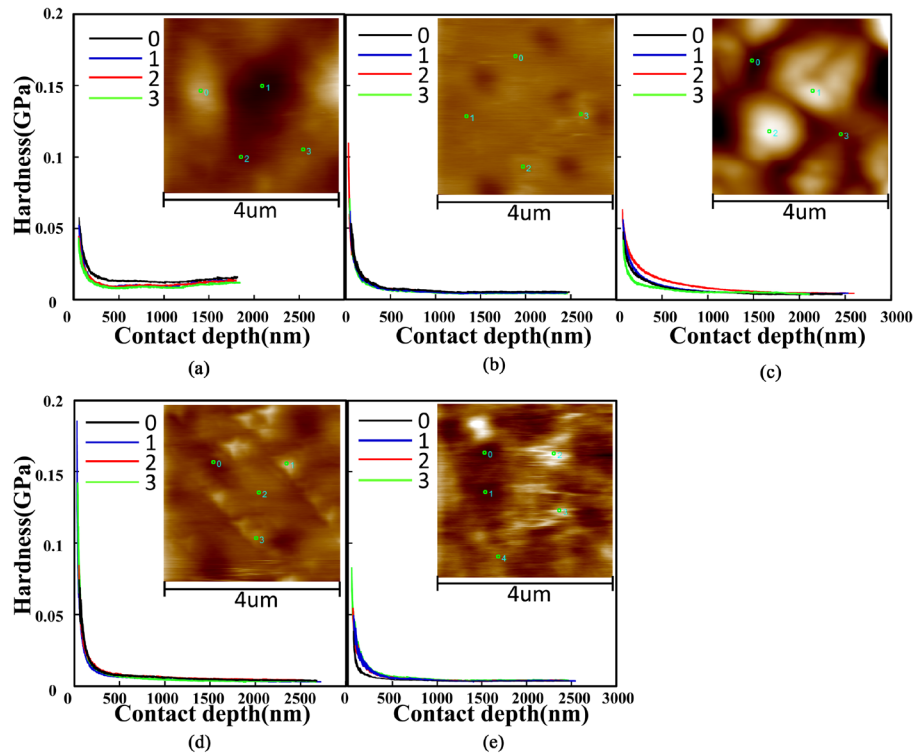


Figure 5. Hardness-depth curves of MDI-PUEs, (a) MDI-PUE₀. (b) MDI-PUE₁. (c) MDI-PUE₂. (d) MDI-PUE₃. (e) MDI-PUE₅.

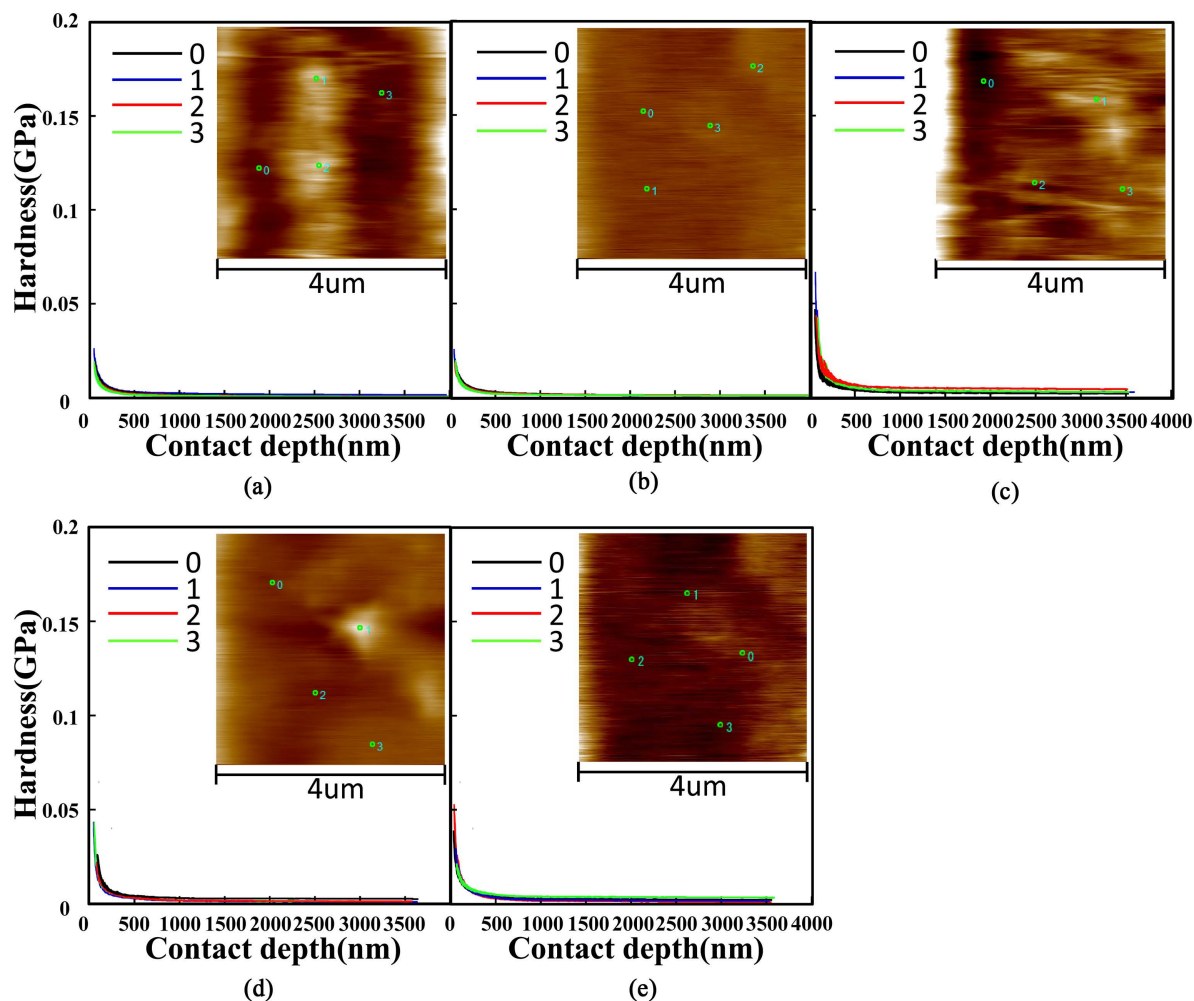


Figure 6. Hardness-depth curves of IPDI-PUEs, (a) IPDI-PUE₀. (b) IPDI-PUE₁. (c) IPDI-PUE₂. (d) IPDI-PUE₃. (e) IPDI-PUE₅.

accurately and directly to measure mechanical properties of PUEs on HD and SD of PUEs, to compare with direct characterization on PUEs.

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