Chapter 1 Introduction

1.1 Background

Elastomer is a kind of polymer materials that can be stretched many times their original dimensions and will recover to their initial shape when released. This unique feature is highly relate to the unusual structure which consists of long chain molecules that take on the conformation of a large random coil, while interconnected or crosslinked parts allow them to return to their original shape once the deforming force is removed.[1-5] Lots of polymers exhibit the elasticity due to the similar structure mentioned above, such as natural rubber (NR), polybutadiene rubber (BR), Styrene-butadiene rubber(SBR), Ethylene Propylene Rubber (EPM).etc. Polyurethane elastomer (PUE) is also a comparatively new elastomer and most applied in footwear areas because of the excellent abrasive resistance to compare with other elastomeric materials.

Nowadays, more and more resources, especially fossil fuels are used as modern industry develops. In addition, fossil fuel are non-renewable that made it a problem to solve the exhaustion of resources. One of the counter measures is to seek for renewable materials to replace the non-renewable ones. It is in good agreement with the 3R (Reduce, Reuse, Recycle) concept.

In biology and chemistry areas, lots of researches have been undertaken that use plant components to synthesize new materials.[6-10]

In polyurethane (PU) area, the most important raw materials are isocyanates and polyols. The use of vegetable oils and their derivatives in polyurethane and specialty chemicals is well known.[11-15] Plant components are expected to be replacements of polyols in synthesis of PUEs. However, we have noticed that they may also have the possibility to be used as a chain extender or cross-linker. Our groups have been aimed at synthesizing polyurethanes (PU) with plant components and relative work for years. In this study, we are trying to synthesize a kind of PUEs that use β-cyclodextrin as cross-linker.

Cyclodextrins, result from the cyclomaltodextrin glucanotransferase catalyzed degradation of starch, have three common kinds with 6, 7 or 8 α-D-glucopyranoside units (α-, β-and γ-cyclodextrin, respectively) linked by α-(1, 4) glycosidic bonds.[16-18] The multi-hydroxyl structure allows β-CD to react as a cross-linker. However, β-CD molecule is quite different from normal cross-linker especially in size and molecular weight. The success of synthesis of PUEs that use β-cyclodextrin as cross-linker is of great significance in green chemistry.

1.2 Purpose of this work

1. To clarify the structure of PUEs which crosslinked with β-CD.

2. To evaluate the crosslink effect of β-CD on PUEs.

3. To study the influence factors on crosslink effect of β-CD.

4. To investigate the phase separation-properties relationship in PUEs crosslinked with β-CD.

1.3 The thesis outline

Chapter 1 gives the background of PUE and PU with plant components in brief. The purpose of this work is also clarified.

Chapter 2 is literature review

Chapter 3 ensures the crosslink caused by β-CD in PUEs and discuss the influence of β-CD content on properties of PUEs.

In chapter 4, key word is the structure-properties relationship of PUEs which crosslinked by β-CD, as well as the relationship between symmetry of diisocyanate and crosslink effects of β-CD.

Chapter 5 gives the comparison of crosslink effects of β-CD on PUEs from different polyols.

Chapter 6 is contact mechanics of PUEs which crosslinked by β-CD, which investigate the mechanical properties of PUEs more directly.

Chapter 7 mainly provides conclusions and the future work envisaged.

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Chapter 2 Literature review

2.1 Polyurethanes

Polyurethane (PU) is a type of polymer formed by polyadditon reaction between diisocyanate and diols. Since discovered in the late 1930s by Otto Bayer, PU quickly attracted the eyeball of many countries.[1-4] However, PU chemistry didn't develop rapidly due to the limited understanding of this kind of materials. After the nomenclature adopted, the development of PU materials took a big jump. The industrial scale production of PU started in 1940 and subsequent market growth rate of these materials was seriously impacted in this decade.[2] Owing to the renewing processing methods, PU industry have achieved a great development during the past century. Now, PUs have been developed to foams, elastomers, coatings, fibers and adhesives etc. PU materials are everywhere in our daily lives, especially in automotive, furniture, construction, thermal insulation and footwear areas.[5-6]Figure 2.1 shows the polyurethane market by technology for 2000.

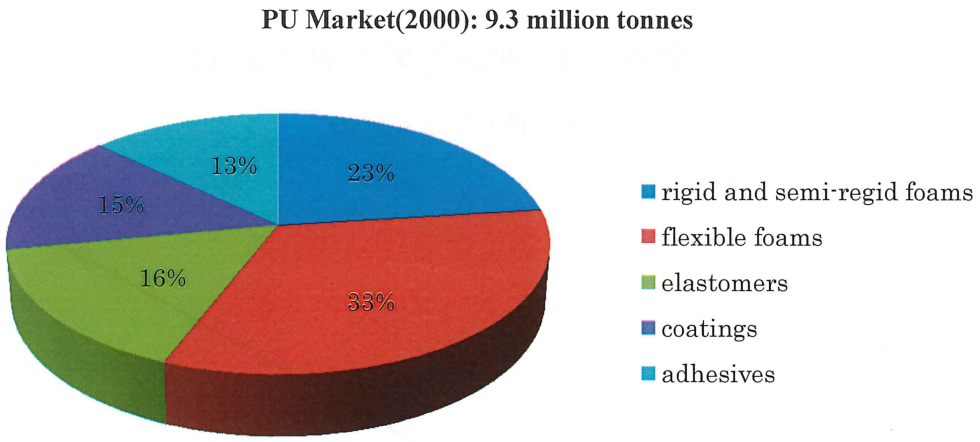


Figure 2.1 Split of polyurethane market by technology for 2000[1]

2.1.1 Types of PU

Flexible Polyurethane Foam

Flexible polyurethane foam is one of the most versatile materials ever created.[7]It is usually used as cushioning for a variety of consumer and commercial products, including bedding, furniture, automotive interiors, carpet underlay and packaging. Flexible foam can be created in almost any variety of shapes and firmness. It is light, durable, supportive and comfortable.[8]

Rigid Polyurethane Foam

Rigid polyurethane foams, most used type of PU, have better thermal properties than thermoplastic foams or other common insulation materials. Their low thermal conductivity is due to a unique combination of blowing agent properties, cell size, and closed cell morphology.[4] These foams are effective insulation materials that can be used in roof and wall insulation, insulated windows, doors and air barrier sealants.[9]

Coatings, Adhesives, Sealants and Elastomers

The uses of polyurethanes in the coatings, adhesives, sealants and elastomers market offer a broad and growing spectrum of applications and benefits. Polyurethane coatings can enhance a product's appearance and lengthen its lifespan. Polyurethane adhesives can provide strong bonding advantages, while polyurethane sealants provide tighter seals. Polyurethane elastomers are can be molded into almost any shape, are lighter than metal, offer superior stress recovery and can be resistant to many environmental factors.[10]

Thermoplastic polyurethane (TPU)

TPU is a kind of polyurethanes that only contain physical crosslinks and without chemical ones. Like all thermoplastic elastomers (TPE), TPU is elastic and melt-processable. In addition, it can be processed on extrusion, injection, blow and compression molding equipment. It can be vacuum-formed or solution-coated and is well suited for a wide variety of fabrication methodologies.

TPU can provide a considerable number of physical property combinations, making it an extremely flexible material adaptable to dozens of uses such as construction, automotive and footwear.[11-13]

Waterborne Polyurethane Dispersions (PUDs)

As the environment problems are getting greater and greater, volatile organic compounds (VOCs) became an Index that should be concerned and controlled. Waterborne polyurethane dispersions are coatings and adhesives that use water as the primary solvent. No use of organic solvent reduced hazardous air pollutants (HAPs), thus PUDs are environmental friendly and enlarge the industrial and commercial application areas.[14-16]

2.2 Polyurethane elastomers (PUEs)

Although possess only about 16% PU market share [1], polyurethane elastomer (PUE) plays an important role in PU products. Their abrasion and chemical resistance, good mechanical behavior, blood and tissue compatibility attracted peoples' attention and allow them to be replacement to rubber in some cases. Polyurethane elastomers are formed typically by reacting together three chemical constituents: a diisocyanate, a long-chain diol, and a small molecule chain-extender (CE) diol or diamine. The resulting polymer may be considered a copolymer of the polyol and diisocyanate-chain extender sequences: termed the soft segment (SS) and hard segment (HS), respectively.[3,17-20] The urethane groups link the HS and SS by means of both covalent bonds and hydrogen bonds (**Figure 2.2**). These alternating HS and SS are the key feature that distinguishes PUEs from other elastomers and is the reason that gives polyurethanes an elastic nature.

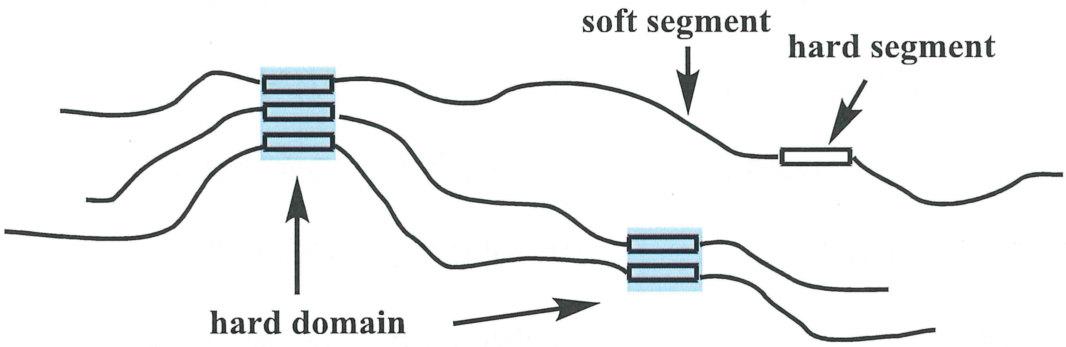


Figure 2.2 HS-SS structure of PUEs

2.2.1 Synthesis of PUEs

As mentioned in former, PUEs are achieved by the urethane linkages (-NHCOO-) which combine the HS with SS. The synthesis method can affect the PUE structure and properties greatly. The two main methods are one-shot method and prepolymer method. In one-shot method, diisocyante, polyol and chain extender are added at the same time. The process is easier, faster and more reproducible and widely used in industry. On the other hand, in prepolymer method, polyol is initially reacted with excess of diisocyanate to form a NCO terminated prepolymer.(**Figure 2.3**) Then, prepolymer is converted into polyurethane by reacting with diol or diamine. Because of the lower reactivity of isocyanate group, catalysts are also needed when aliphatic diisocyanates are used.

As the prepolymer method is more controlled, the obtained PUE structure is more regular than it

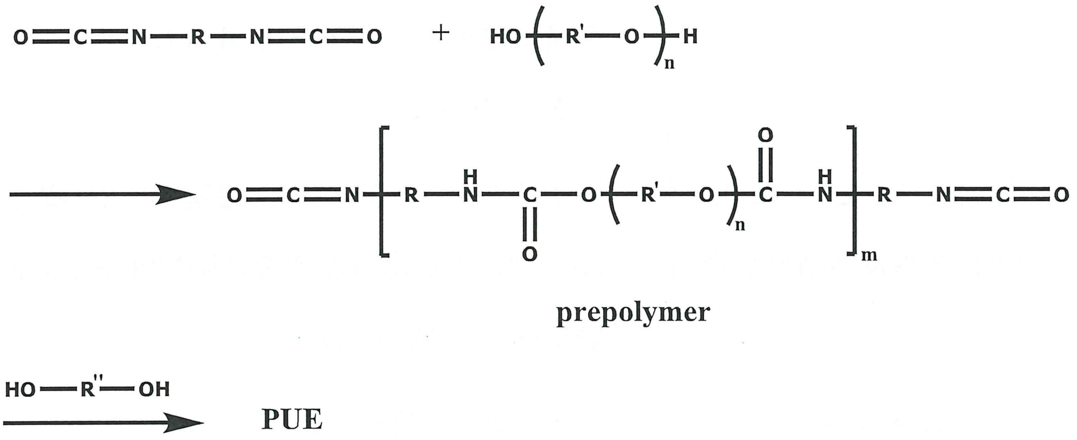


Figure 2.3 Route for prepolymer method

obtained via one-shot step.

2.2.1.1 Isocyanates

Obviously, highly reactive isocyanate group is the unique feature of polyurethane technology. Isocyanates are reactive because of the low electron density of the central carbon, as **Figure 2.4**

Figure 2.4 Resonant structures of isocyanates

Isocyanates are the raw materials for addition polymers such as polyurethanes, polyureas and polyisocyanurates. In PU fields, the most common forms and widely used of isocyanates are toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) because of the moderate cost and excellent properties of resulted PU. However, the carcinogenic reported for TDI[21] lead to the reduction of its application. Other isocyanates were also needed for special usage, such as aliphatic isocyanate HDI and IPDI. Aliphatic isocyanates are believed to avoid PUs from UV degradation.

2.2.1.2 Polyols

Typical polyols contain two to eight reactive hydroxyl groups and have average molecular weight from 400 to 5000 Daltons.[22] The nature of polyols can largely affect the properties at low temperature and lowest usable temperature of PUEs, because the polyols are the only contributor to the soft domains of PUEs. The two main kinds of polyols are polyethers and polyesters.

2.2.1.3 Chain extenders

Typical chain extenders (CE) are diols or diamines with a molecular-weight under 400, while molecules with higher functionality are considered to be cross-linkers. The function of CE is believed to increase chain length of hard segments of PU and increase the molecular weight of PU.[2,4,23-25]

Typically, both of CE and Polyol are compounds involve two active hydrogens. Actually, the differences between the nature of CE and Polyol do lead to the unique properties of PUEs.

2.2.1.4 Side reactions

During the copolymerization of diisocyanate and polyol, side reactions also exist. Reaction of isocyanate with the active hydrogen on a urethane group resulted in allophanate linkage. The allophanate cross-links are not as stable as the conventional cross-links formed from polyfunctional polyols and polyisocyanates. They are thermally labile and open quite easily at high temperature.[3,26] Isocyanates can also react to form dimer and trimer of themselves. Dimerization only occurs with aromatic isocyanates. However, trimerization occurs with both aliphatic and aromatic isocyanates. The reactions mentioned are shown as **Figure 2.5**

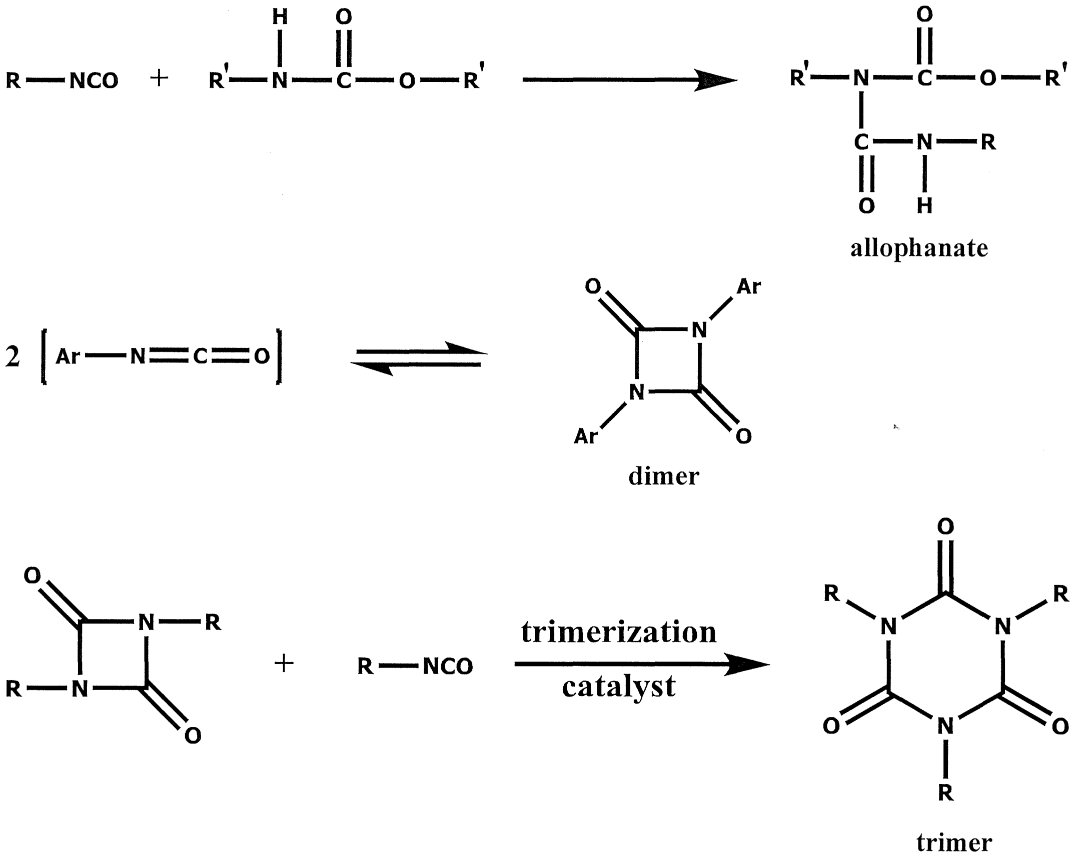


Figure 2.5 Reaction of allophanate, aromatic isocyanate dimer and isocyanurate

2.2.1.5 Applications of PUEs

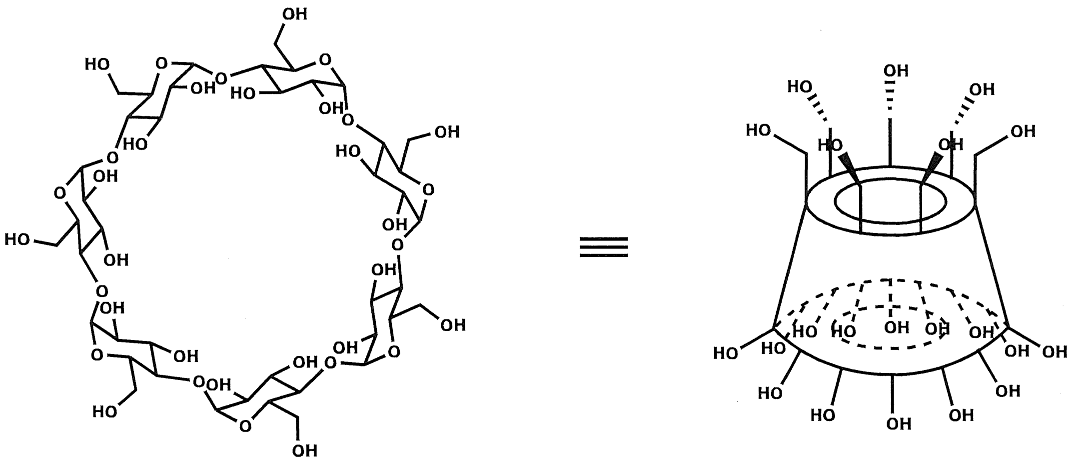
PUEs have unique properties of abrasion resistance, cut and tear resistance, higher load bearing ability, Ozone resistance, microbial resistance, oil and petroleum resistance. Thus, PUEs are expected to replace rubbers in many areas. In addition, properties of PUEs can be easily controlled only by changing the hard segment concentration (HSC). Nowadays, PUEs are widely applied in our daily lives, such as concrete mould liners, auto suspension components, membranes, PU spray coated marine fenders, medical training model, aggregate separation screens, pipeline cleaning pigs, foot wears, pipe, hose and tubes.[2]

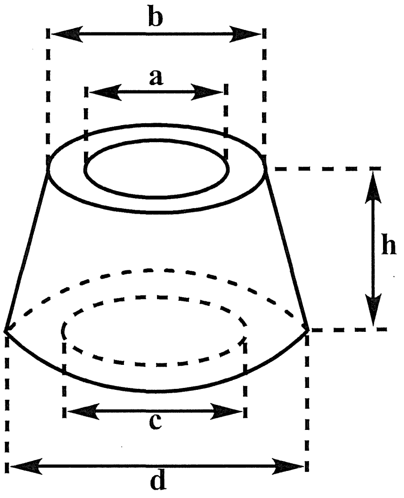
2.3 Bio-based polyurethane elastomers

Since firstly reported in 1960s[27], bio-based PUEs have caught researchers' attention mainly due to the biocompatibility and biodegradability. A wide variety of biomaterials are now commonly implanted in the human body for the treatment of various diseases. They are also used to augment tissue, bone, muscle, skin and breast either after trauma or for cosmetic reasons.[28-29] Biodegradable PUEs are friendly to environment and contribute to the concept of green chemistry. These materials are of great significance in modern society.

2.4 Cyclodextrin

Cyclodextrins (CDs), which are produced by enzymatic degradation of starch, are truncated cone shaped molecules composed of D-glucopyranoside units linked through α-(1, 4) glycosidic bonds. Typical CDs are constituted by 6, 7, 8 glucopyranoside units, named α-, β-, γ-CD.[30-31] β-CDs are most commonly used species because of the low costs. The chemical structure of β-CD is shown as **Figure 2.6**.





Dimension(nm)				
a	b	c	d	h
0.61	1.49	0.78	1.53	0.78

Figure 2.6 Chemical structure and dimensions of β-CD

Since discovered by Villiers in 1891, CDs have drawn lots of researchers' attention because of their special structure and properties.[32]The position of the hydroxyls in CD gives the exterior a hydrophilic character, while the interior is hydrophobic. Thus, a variety of molecules can fit into the hydrophobic hole to form inclusion complexes, which also called host-guest complexes. This feature allows CD to removing some organic contaminants from water.[33-34] In addition, some molecules only partially reside within the cavity, thus to form supramolecule. CDs play an important role in supramolecular chemistry.

2.5 Cyclodextrin-based polyurethanes

It can be easily conclude from structure of cyclodextrin that the direct reaction of isocyanates and cyclodextrins will result in a highly crosslinked and rigid reactant. Most reported Cyclodextrin-based polyurethanes[35-38], until now, were synthesized by direct reaction of cyclodextrins and isocyanates. In another word, the properties of polyurethanes themselves were not the most important ones to be focused. Cyclodextrin-based polyurethanes were researched mainly on scavenging properties produced by cyclodextrin ring. Actually, since firstly reported in 1981[39], PU synthesis incorporating CD molecules gained more and more attention. It was reported that β-CD-containing PU polymer had been successfully prepared coated Fe_3O_4 magnetic nanoparticle as a novel class of hybrid organic/inorganic molecular catalyst and the polymer was evaluated as solid-liquid phase-transfer catalyst and molecular host system for nucleophilic substitution reactions[40]. It was also reported that the synthesis and applications of water insoluble CD-IL polymers in the removal of model pollutants (PNP, TCP and Cr^{6+}) from water[41].

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Chapter 3 Influence of β-CD content on properties of non-chain extended polyurethane elastomers

Due to the dissimilarities in structure, β-CD may quite different from normal low-molecular weight cross-linker in crosslink effect. Influences of β-CD molecules on PUE structure and properties are most concerned about. In this chapter, to use β-CD as cross-linker, a series of PUEs with different β-CD content were synthesized.

3.1 Experimental

3.1.1 Materials

PTMG (molecular weight = 1000 Da) (PTMG1000) was supplied by Invista Industry, Texas, USA. 4,4′ -Diphenylmethane diisocyanate (MDI) was supplied by Tosoh Industry, Tokyo, Japan and was purified by distillation under reduced pressure (267-400 Pa) at 100 ° C before use. β-CD was purchased from Nacalai Tesque, Inc., Kyoto, Japan (Nacalai) and was dried for 24 h at 80 °C under a pressure of 267–400 Pa before use. Tetrahydrofuran (THF) and benzene were purchased from Nacalai and distilled over calcium hydride under an argon (Ar) atmosphere. N,N-Dimethylformamide (DMF) was purchased from Nacalai and stored over 4 Å molecular sieves before use. Hexane and acetone were procured from Nacalai and were used as received.

3.1.2 Synthesis

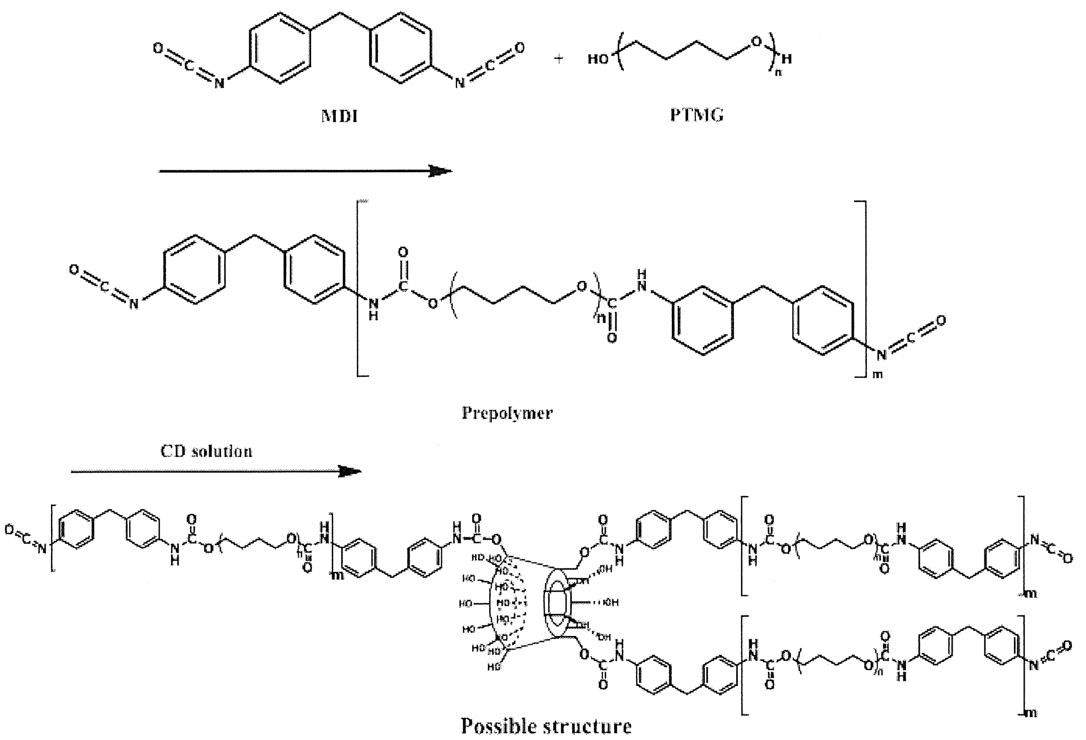
A series of β-CD-based PUEs were synthesized from MDI, PTMG1000, and β-CD via a prepolymer method (**Scheme 3.1**). It needs to be mentioned that 1 mol of β-CD molecule contains 7 mol of primary hydroxyl and 14 mol of secondary hydroxyl groups. However, not all hydroxyl groups react with the isocyanate group even in the presence of excess of isocyanate groups. In another words, the functionality of β-CD is not an exact quantity. Therefore, in this study, additive amount of β-CD was calculated by weight percent of the total weight of all the raw materials. The synthesis procedure and β-CD content for each PUE is listed in **Table 3.1**. PUEs are termed as PUEx (x = weight percent of β-CD).

The synthesis was performed as follows: a solution of β-CD in DMF (10 mL) was prepared and heated at 80 °C for 20 min under an Ar atmosphere. MDI (5.0 g, 0,020 mol) and PTMG1000 (10 g, 0.010 mol) were added to a 100-mL four-necked separable reaction flask equipped with a mechanical stirrer, gas inlet tube, and reflux condenser. The prepolymer was prepared by heating at 80 °C for 1 h under an Ar atmosphere and continuous stirring. Then β-CD solution was added to the separable flask followed by further stirring for 15 min. Small amount of bubbles in the system were removed by adding THF (20 mL) and further high-speed stirring for 5 min.

Thin PUE sheets (0.7–0.8 mm) were obtained by casting the resulting PUE solution at room temperature (23 °C ± 2 °C) for 24 h, at 50 °C for 24 h, and at 100 °C for 24 h. The DMF residue on the sheets was removed by heating at 80 °C for 6 h under vacuum.

Table 3.1 Recipe of PUE_0, PUE_1, PUE_2, PUE_3 and PUE_5

Sample	MDI		PTMG1000		β-CD		Weight percent
	(g)	(mol)	(g)	(mol)	(g)	(10^{-3}mol)	of β-CD(%)
PUE_0	5.0	0.02	10	0.01	-	-	0
PUE_1	5.0	0.02	10	0.01	0.13	0.15	1
PUE_2	5.0	0.02	10	0.01	0.27	0.31	2
PUE_3	5.0	0.02	10	0.01	0.41	0.46	3
PUE_5	5.0	0.02	10	0.01	0.70	0.79	5



Scheme 3.1: Synthesis of PUEs by using β-CD as cross-linker

3.1.3 Characterization

3.1.3.1 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were recorded on a JASCO (Tokyo, Japan) FTIR-5300 spectrometer equipped with an attenuated total reflection (ATR) system, which used an ATR500/M with an ATR prism KRS-5.

3.1.3.2 Scanning electron microscopy (SEM)

SEM was used to observe the surface morphology of PUEs by using S-4800 (Hitachi High-Technologies Corporation, Japan)

3.1.3.3 Confocal laser scanning microscopy (CLSM)

CLSM was used to capture the 2D and 3D surface images of PUEs by using LSM 700 Laser Scanning Microscope from Carl Zeiss (jena, Germany)

3.1.3.4 Swelling test

Swelling test was carried out in THF. PUE sheets were cut into 10×20 mm samples. After testing their weight, they were put into THF solution in test tube to keep 24h.Removed the THF on the surface, the weight of samples would be tested again. The degree of swelling (Rs) was calculated using the formula Rs(%) = W'-W/W × 100, where W,W' were the weight of samples before and after swelling.

3.1.3.5 Tensile test

Tensile test was measured by RTC-1225A Universal Tensile Testing Instruments (ORIENTEC Corporation, Japan) equipped with a U-4300 extensometer. Samples were cut into dumbbell strip followed JIS K 6251-3 standard. Tensile test was performed at a crosshead speed of 100mm/min at room temperature (23±2°C).

3.1.3.6 Hardness

Hardness was tested by using a Asker Durometer(KOBUNSHI KEIKI Corporation, Japan) with the A scale, which is used for rubbers in the normal hardness range. The test procedure follows JIS K 6253.

3.1.3.7 Dynamic mechanical analysis (DMA)

DMA was performed on a Seiko Instruments DMS 6100 at a heating rate of 5 °C/min over from -100 to 200 °C and at 1 Hz under an N_2 atmosphere.

3.1.3.8 Thermogravimetric analysis (TGA)

TGA was performed on a Seiko Instruments TG/DTA6200 at a heating rate of 10 °C/min from 25 to 800 °C under an Ar atmosphere.

3.2 Results and discussion

FTIR analysis

The FTIR spectra of PUEs are shown in **Fig 3.1**. Comparison of the PUEs with and without β-CD showed several differences. The peak at 1093 cm^{-1} (C–O–C stretching in polyol) observed in PUE$_0$ was absent in PUE$_1$, PUE$_2$, PUE$_3$, and PUE$_5$. However, peaks at around 1103 cm^{-1} and 1065 cm^{-1} (arising from the primary and secondary hydroxyl groups, which did not react with isocyanate groups) appeared in PUE$_1$, PUE$_2$, PUE$_3$, and PUE$_5$, which proves that β-CDs are successfully incorporated into the PUE chains. In addition, the peaks at 3301 cm^{-1}, 1716 cm^{-1}, and 1527 cm^{-1} (attributed to N–H stretching, C=O stretching, amide II C–N stretching + N–H bending, respectively) in the spectrum of PUE$_0$ indicate that nearly all the –NH and C=O moieties are hydrogen bonded. In the spectra of PUE$_1$, PUE$_2$, PUE$_3$, and PUE$_5$, a shoulder appears in the peak at 3444 cm^{-1}, whereas the peak at 1716 cm^{-1} splits into two peaks around 1726 cm^{-1} and 1708 cm^{-1}. The peak at 1527 cm^{-1} also splits into two peaks at around 1533 cm^{-1} and 1516 cm^{-1}.[22-24] It is obvious that the addition of β-CD partly destroys the hydrogen bonding. Moreover, as the mole ratio of K = [NCO]/[OH] = 2, the remaining –NCO can also react with –NHCOO–, resulting in a small number of cross-links in PUE$_0$ (allophanate), which explains the C=O (urea) stretching peak at 1647 cm^{-1}.[25-26]

Morphological analyses

SEM micrographs of the surface of PUEs with various contents of β-CD are shown in **Fig 3.2**. The PUE$_0$ presents a rougher surface compared to the others and phase separation is not very clear due to fewer agglomerates of hard domains. The size of the low intensity regions range from 0.1–0.5 μm, which correspond to hard domains. In case of PUE$_1$, PUE$_2$, and PUE$_3$, phase separation is not obvious, either. This may be the result of cross-linking, which could increase the compatibility

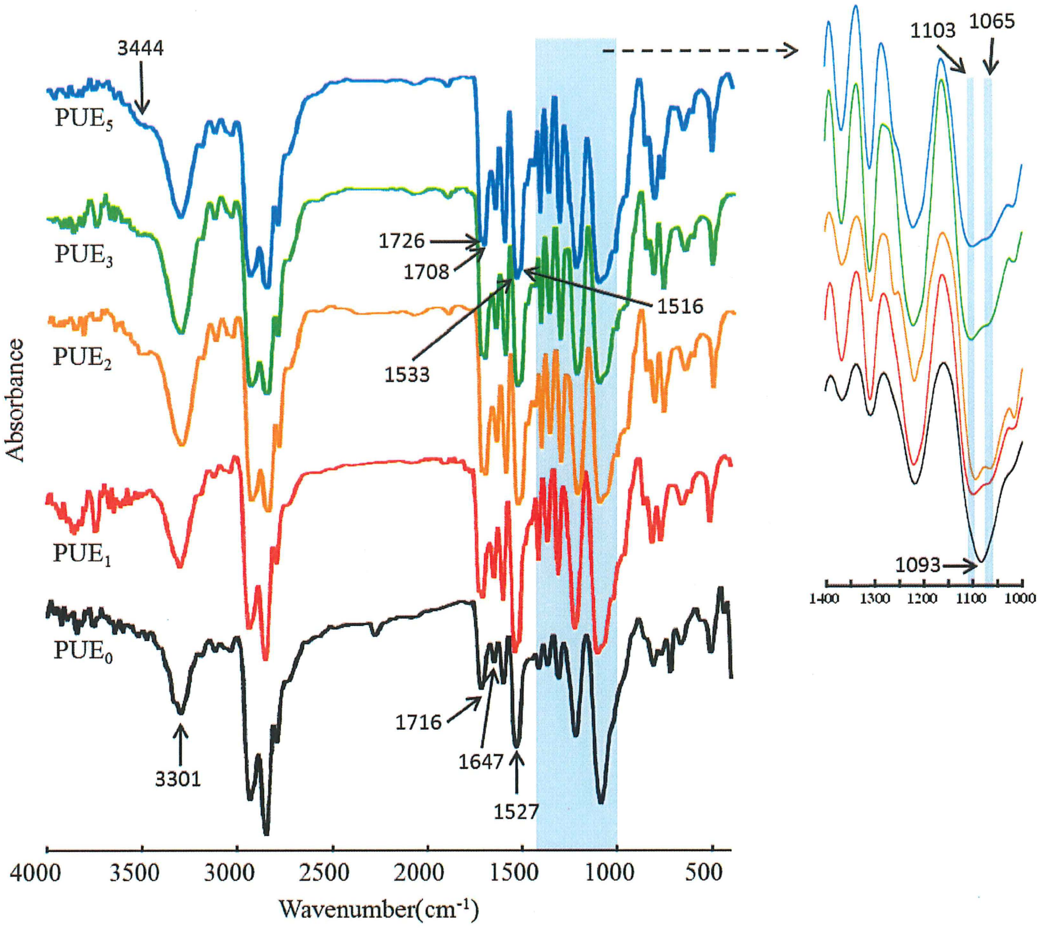


Fig 3.1 FTIR spectrum of PUE_0, PUE_1, PUE_2, PUE_3 and PUE_5

between hard segments (HS) and soft segments (SS) and thus reduces the degree of phase separation.[27-29] However, this nanoscale phase separation is also observed in PUE_5, wherein the low intensity regions are brighter and a little larger compared to PUE_0. We consider it as the enlargement of the hard domains caused by the size of the cross-linker (β-CD) itself.

The SEM micrographs at 100 μm scale, shown in **Fig 3.3**, indicate a microscale phase separation phenomenon in PUE_4 and PUE_5 and the size of the low intensity regions, which correspond to hard domains, is approximately 10–50 μm in length. In contrast, phase separation is unclear in PUE_0, PUE_1, and PUE_2. This phase separation is quite different from that of normal PU materials in size. It is considered that the hard domains observed here correspond to the highly cross-linked regions generated by β-CD.

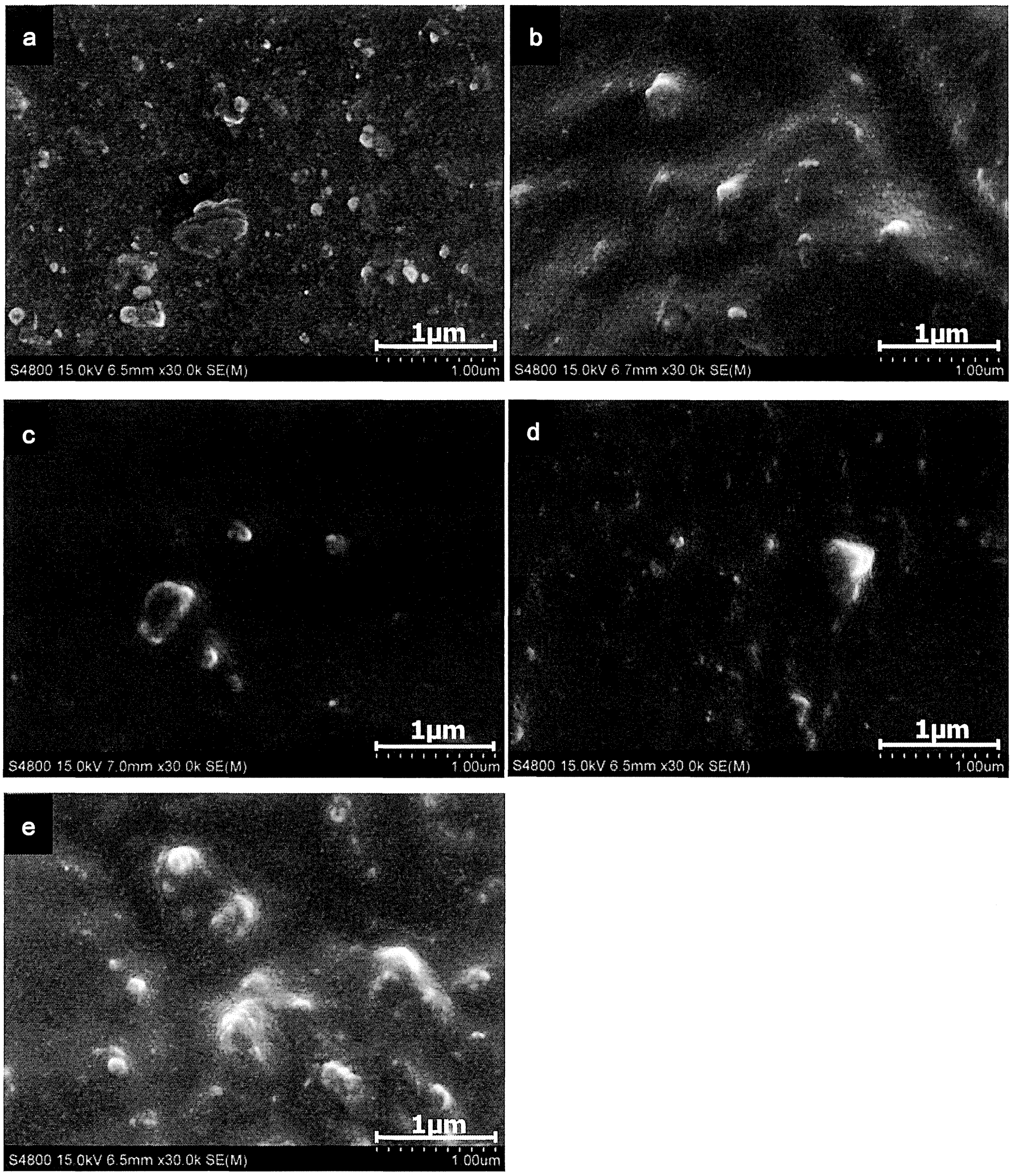


Fig 3.2 SEM micrographs of (a)PUE_0 (b)PUE_1 (c)PUE_2 (d)PUE_3 and (e)PUE_5 on 1μm scale

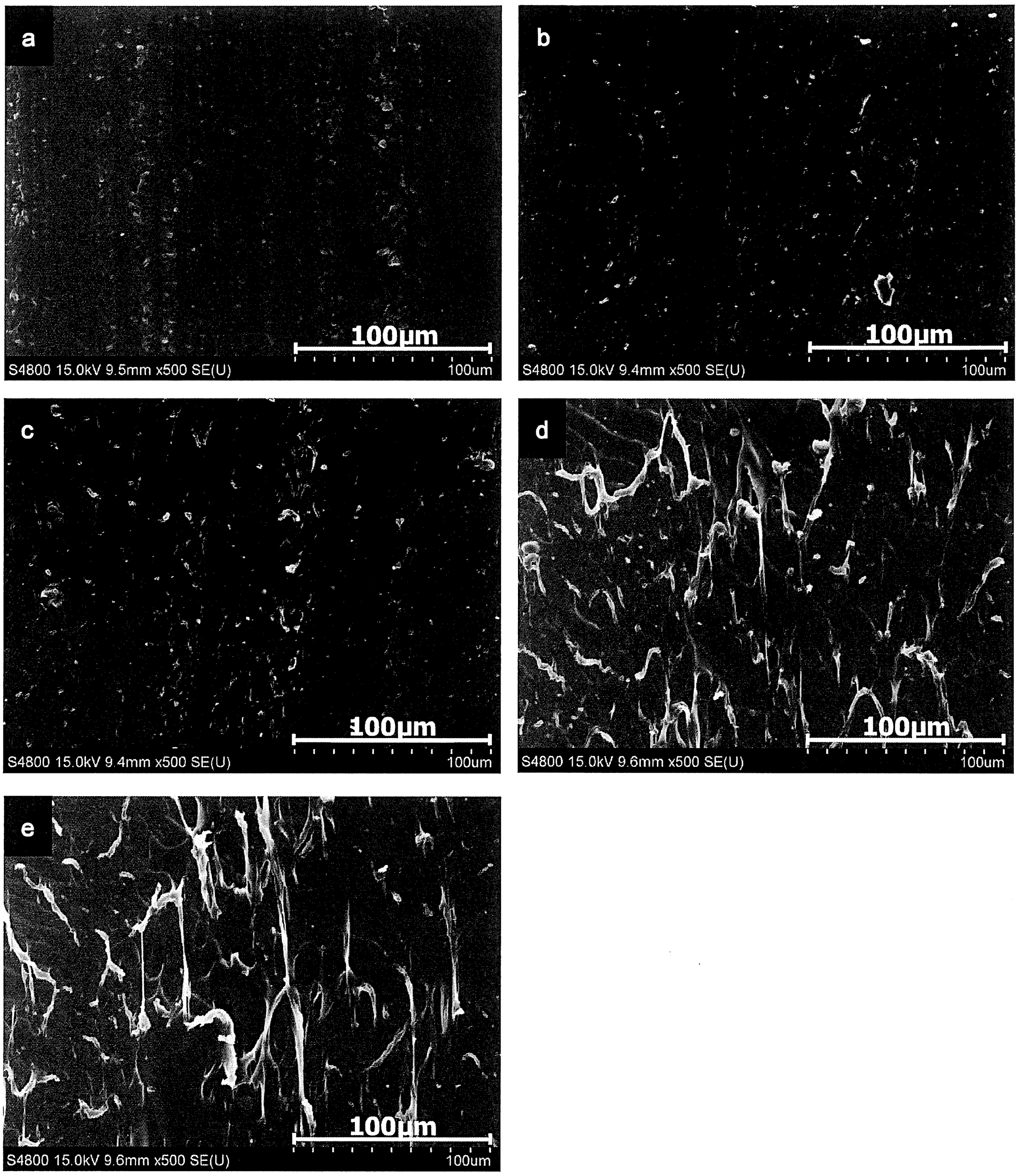
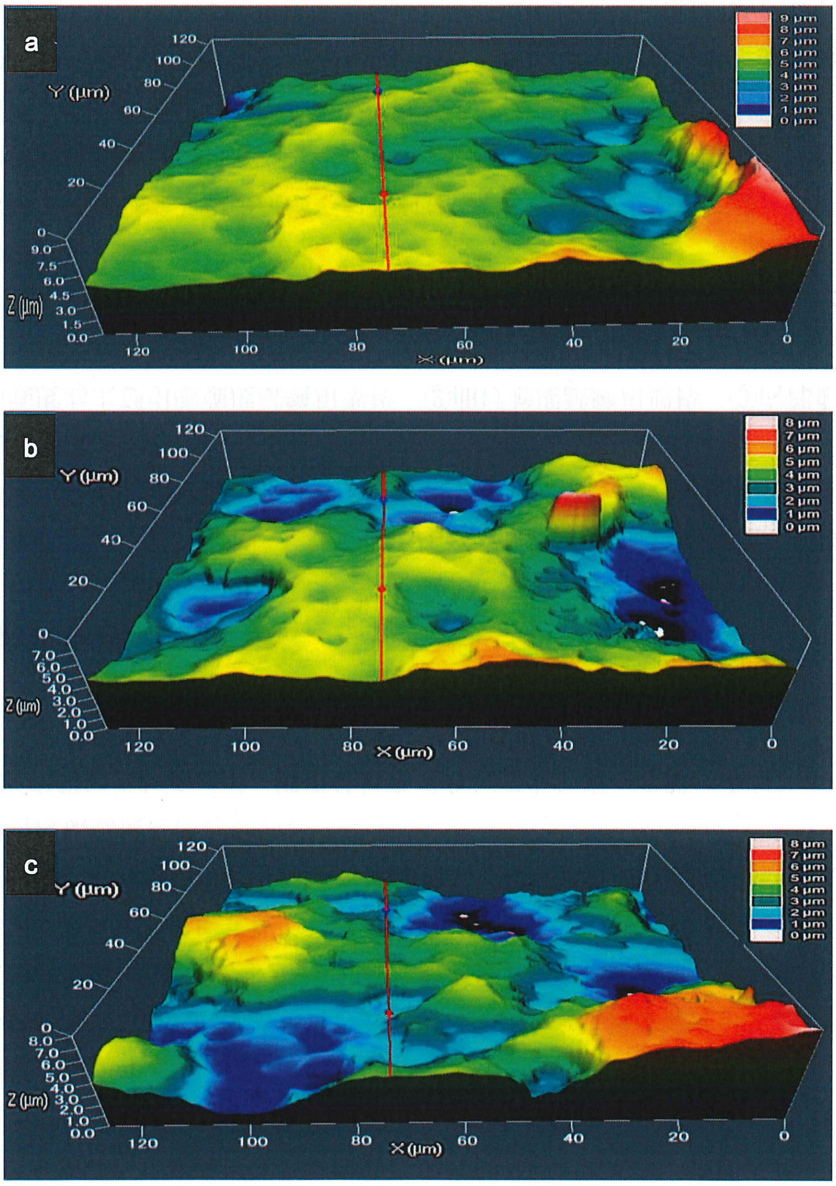


Fig 3.3 SEM micrographs of (a)PUE$_0$ (b)PUE$_1$ (c)PUE$_2$ (d)PUE$_3$ and (e)PUE$_5$ on 100μm scale

The same phenomenon was also observed in the CLSM 3D images (**Fig 3.4**). PUEs with β-CD show a lumpier surface than PUE_0. Additional island-like regions were observed in the PUEs with β-CD, particularly in PUE_4 and PUE_5. These regions are square-shaped with a 20–40 µm side, which is in agreement with the results from the SEM micrographs. It is obvious that β-CDs have been incorporated into the PUEs and contribute to microscale phase separation. The differences between the hard domains are shown in **Fig 3.5**.



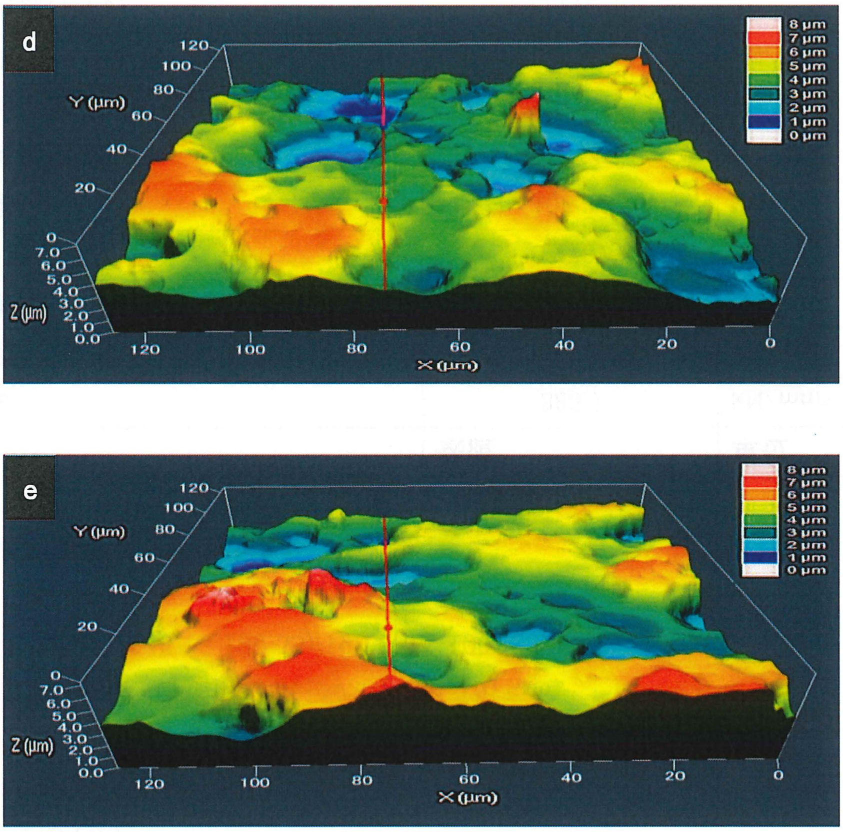


Fig 3.4 CLSM images of (a)PUE_0 (b)PUE_1 (c)PUE_2 (d)PUE_3 and (e)PUE_5

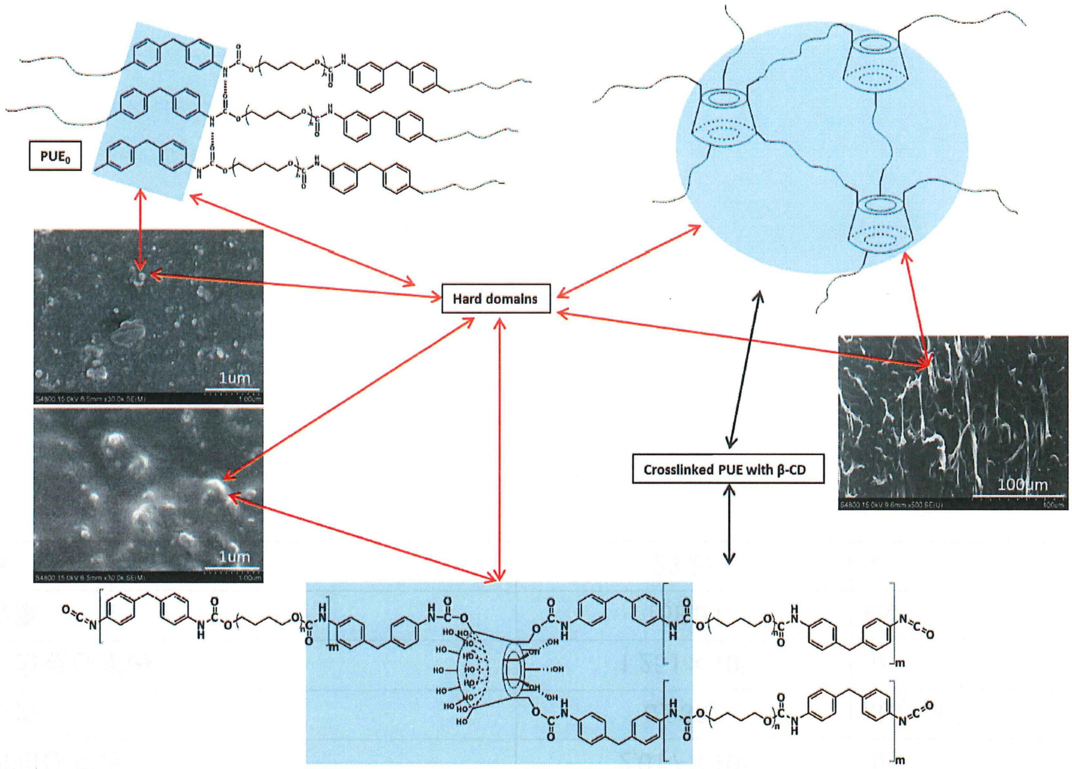


Fig 3.5 Diagrammatic sketch of phase separation on different scales

Swelling property and hardness

Swelling tests were performed to confirm the addition of β-CD as a cross-linker. As evident from **Table 3.2**, PUE$_0$ is soluble, and therefore, indicates a less cross-linked structure. However, the addition of β-CD leads to the formation of insoluble PUEs and the swelling rate increases as the content of β-CD increases. Due to the size effect of the CD ring, the distance between the molecular chains of PUE will be increased when CD acts as a cross-linker. Thus, the molecular density decreases, which also explains the decrease in the hardness of PUE$_1$. However, hardness increase from PUE$_2$ to PUE$_5$ indicates that the increase in theβ-CD content leads to an increase in chemical cross-link density. The regularity in the molecular chain increases again, which was related to the increase of crosslinked structure in the SEM observations presented above.

Table 3.2 Hardness and swelling rate of PUE_0, PUE_1, PUE_2, PUE_3 and PUE_5

Sample	Thickness (mm)	Hardness (JIS K)	Swelling rate (%)
PUE_0	0.76	80	soluble
PUE_1	0.68	78	283
PUE_2	0.67	83	312
PUE_3	0.80	83	407
PUE_5	0.83	89	417

Mechanical properties

Tensile tests were performed to evaluate the influence of the additive of β-CD on the mechanical properties of PUEs. The stress–strain curves are shown in **Fig 3.6**.

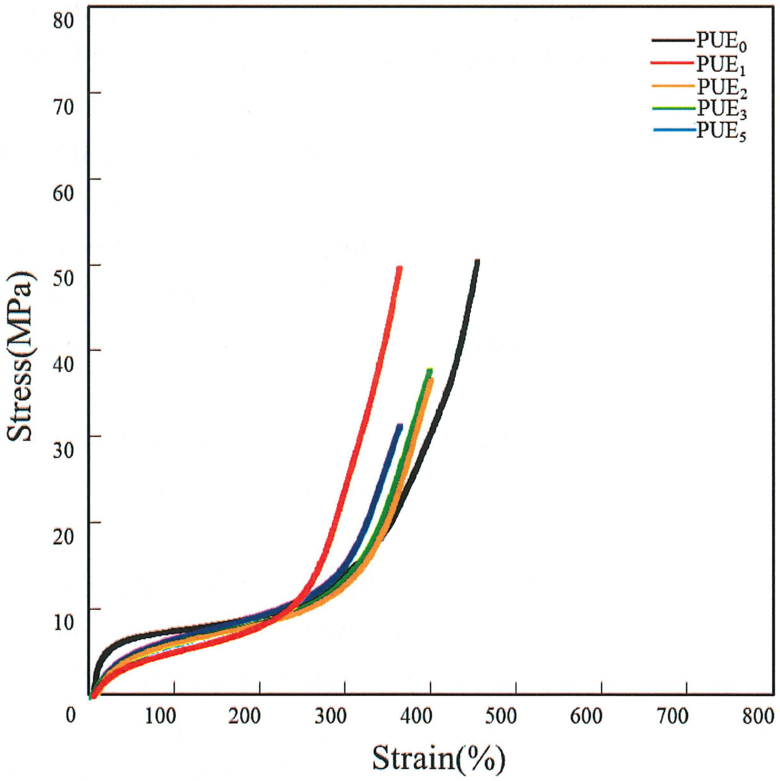


Fig 3.6 Stress-strain curve of PUE_0, PUE_1, PUE_2, PUE_3 and PUE_5

Although without a chain extender, PUE_0 shows comparatively acceptable mechanical property, which may due to the comparatively satisfactory regularity of MDI and PTMG.[30-32] The tensile strength and elongation at break of PUE_0 is 50.55 MPa and 449%, respectively. However, as seen from the curves for PUE_1–PUE_5, the cross-linking caused by the addition of β-CD did not increase the strength as a normal cross-linker would. As widely accepted, the formation of cross-linking prevents the slippage of neighboring chains in polymers under stress, thereby increasing strength.[33] The results here appear to be contradictory, which actually are in agreement with the results from the other tests above. It is considered that the decrease of tensile strength caused by the addition of β-CD is not the result of a simple process. It is a balance between the formation of chemical cross-links and destruction of physical cross-links, of which the latter is dominant here. Moreover, the PUEs retain their elasticity. The tensile strength and elongation at break are shown in **Table 3.3**.

Table 3.3 Parts of mechanical properties of PUE_0, PUE_1, PUE_2, PUE_3 and PUE_5

Sample	σ100% (Mpa)	σ200% (Mpa)	σ300% (Mpa)	σ (Mpa)	EB (%)
PUE_0	7.69	9.46	14.62	50.55	449
PUE_1	5.30	8.40	25.81	49.80	359
PUE_2	6.17	8.40	13.73	36.50	389
PUE_3	6.37	8.76	14.13	38.08	395
PUE_5	6.82	9.58	16.12	31.32	358

σ: strength

EB: elongation at break

Thermal properties

Fig 3.7 shows the viscoelastic behavior of PUEs through the storage modulus (E′) and tan δ (tan δ = E″/E′). The glass transition temperature (Tg) of PUE_0 was observed at −53.4 °C. As the β-CD content increases, the Tg of PUE_1, PUE_2, PUE_3 and PUE_5 increases to −35.5 °C, −31.5 °C, −33.7 °C and −36.9 °C, respectively. All PUEs display a long rubbery plateau up to approximately 150 °C. However, PUE_0 has a higher modulus value of approximately 1×10^8 Pa compared to the other PUEs (3×10^7–6×10^7 Pa). After 150 °C, the modulus value of PUE_0 rapidly decreases and is similar to the values of the other PUEs at 200 °C. These results suggest that the PUEs with β-CD comparatively have much more crosslinked structure to compare to PUE_0; however, the molecular chains in them can move more easily above Tg. Although it appears to be contradictory, this is in agreement with the balance phenomenon mentioned previously. It is also supported by a previous study, which shows that hydrogen bonding begins to vanish as the temperature increases and is related to the glass transition of the hard segments.[34] Only 35%–40% of hydrogen bonding persists at 200 °C.

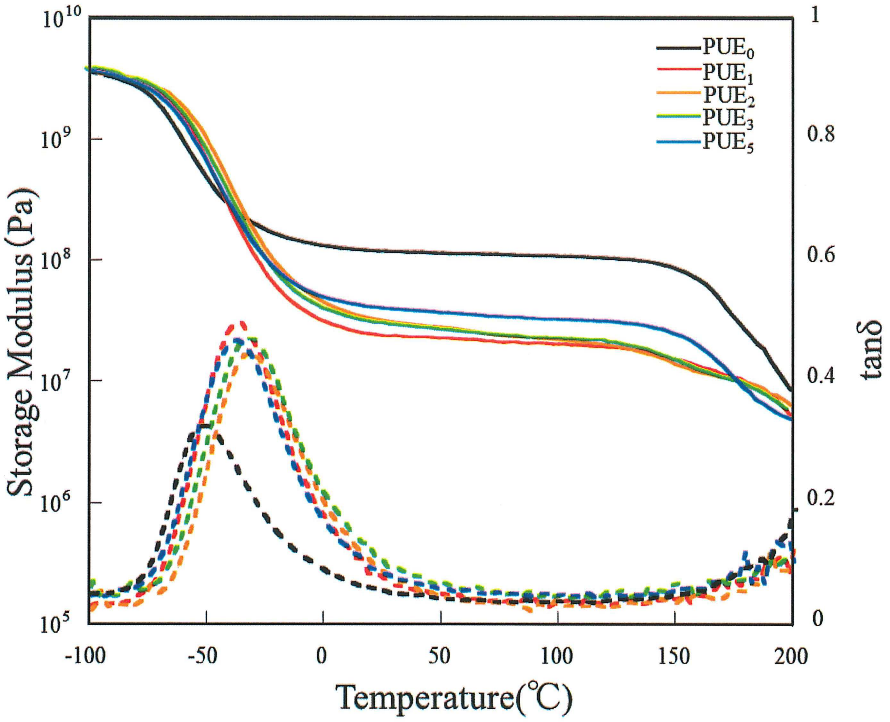


Fig 3.7 Storage modulus and tanδ of PUEs as a function of temperature

The TGA curves are shown in **Fig 3.8**: all the PUEs are thermally stable up to around 280 °C and begin to lose weight at higher temperatures. The 10% weight loss temperature ($T_{10\%}$) of PUEs with β-CD is almost the same as PUE$_0$ and 50% weight loss temperature ($T_{50\%}$) is higher than PUE$_0$. The decomposition of PUE is believed to occur in two main steps: urethane linkage dissociates to isocyanate and alcohol at 200 °C–300 °C and polyol degradation occurs at above 350 °C. Therefore, it is obvious that PUEs with higher β-CD content are more thermally stable.

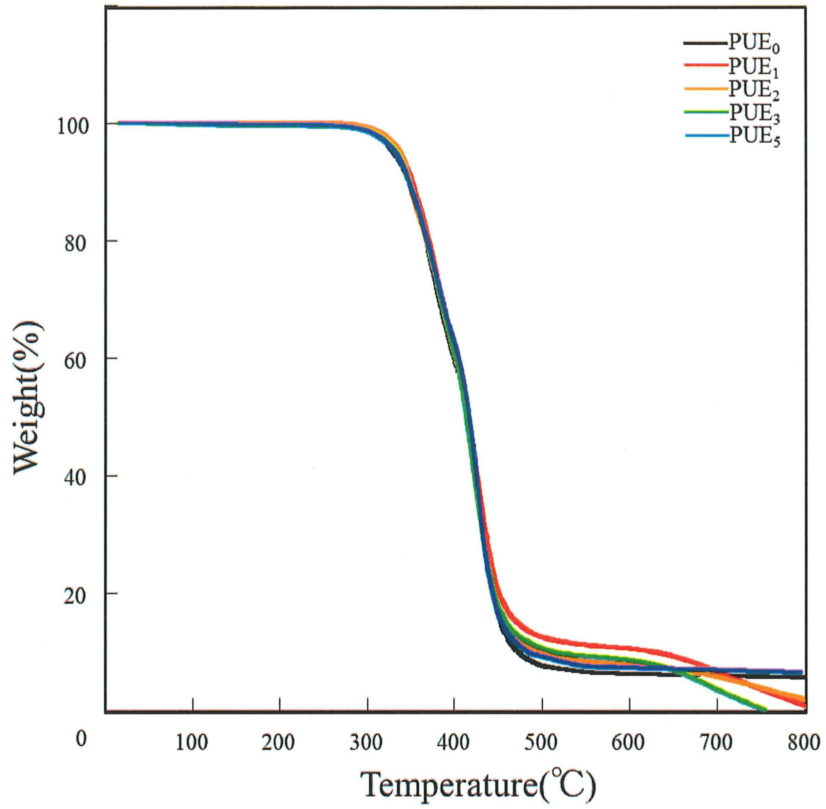


Fig 3.8 TG thermograms of PUE$_0$, PUE$_1$, PUE$_2$, PUE$_3$ and PUE$_5$

3.3 Conclusions

A series of PUEs, which contain β-CD as the cross-linker, were synthesized. The influence of β-CD on the chemical, mechanical, and thermal properties and the surface morphology of PUEs were investigated through DSC, DMA, TGA, SEM, and CLSM. The results prove the existence of β-CD in the molecular structure and that it contributes to the phase separation. However, the degree of phase separation is not proportional to the properties of PUEs. In addition, the mechanical properties demonstrate the elasticity of PUEs.

Based on the swelling rate and tensile tests, we confirmed that both chemical cross-linking (β-CD structure) as well as physical cross-linking (hydrogen bonds) exist in these PUEs and a dynamic balance is obtained between them. At <5% of the additive amounts of β-CD, PUEs retained their elasticity. The decrease in tensile strength and elongation at the break shown in tensile test is not a simple process. It indicates that existence of extensive hydrogen bonding in MDI–PTMG-based PUs and the destruction of regularity of PUE chains contributes much more to tensile strength than the cross-linking arising due to the addition of β-CD.

Although the tensile strength of PUEs did not improve, due to the introduction of elasticity, the results of our study will broaden the application areas of CD-based PUs.

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Chapter 4 Influence of diisocyanate on PUEs which crosslinked by β-CD

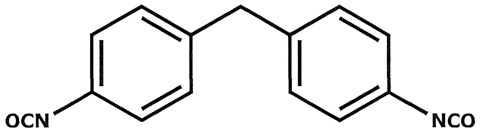
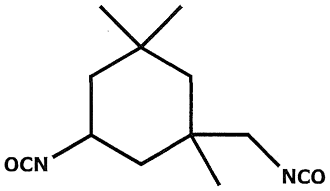
In PUEs, HS are dissolved in SS matrix. The agglomerate of HS and hydrogen bonding between HS lead to the physical crosslinks. Thus, the structure and reactivity of isocyanates play an important role in affecting properties of PUEs.

4.1 Experimental

4.1.1 Materials

4,4'-Diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) was supplied by Tosoh Industry, Tokyo, Japan and was purified by distillation under reduced pressure (267-400 Pa) at 100 °C before use. The diisocyanates used are shown as **Table 4.1**. 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 267-400Pa/80℃ before use. Tetrahydrofuran (THF) was purchased from Nacalai and distilled over calcium hydride under an Ar atmosphere. 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. The following compounds were purchased from commercial suppliers and used as received: hexane (Nacalai), and acetone (Nacalai).

Table 4.1 structure of diisocyanates used

Isocyanate		Chemical structural formula
Hexamethylene diisocyanate	HDI	
4,4'-Diphenylmethane diisocyanate	MDI	
Isophorone diisocyanate	IPDI	

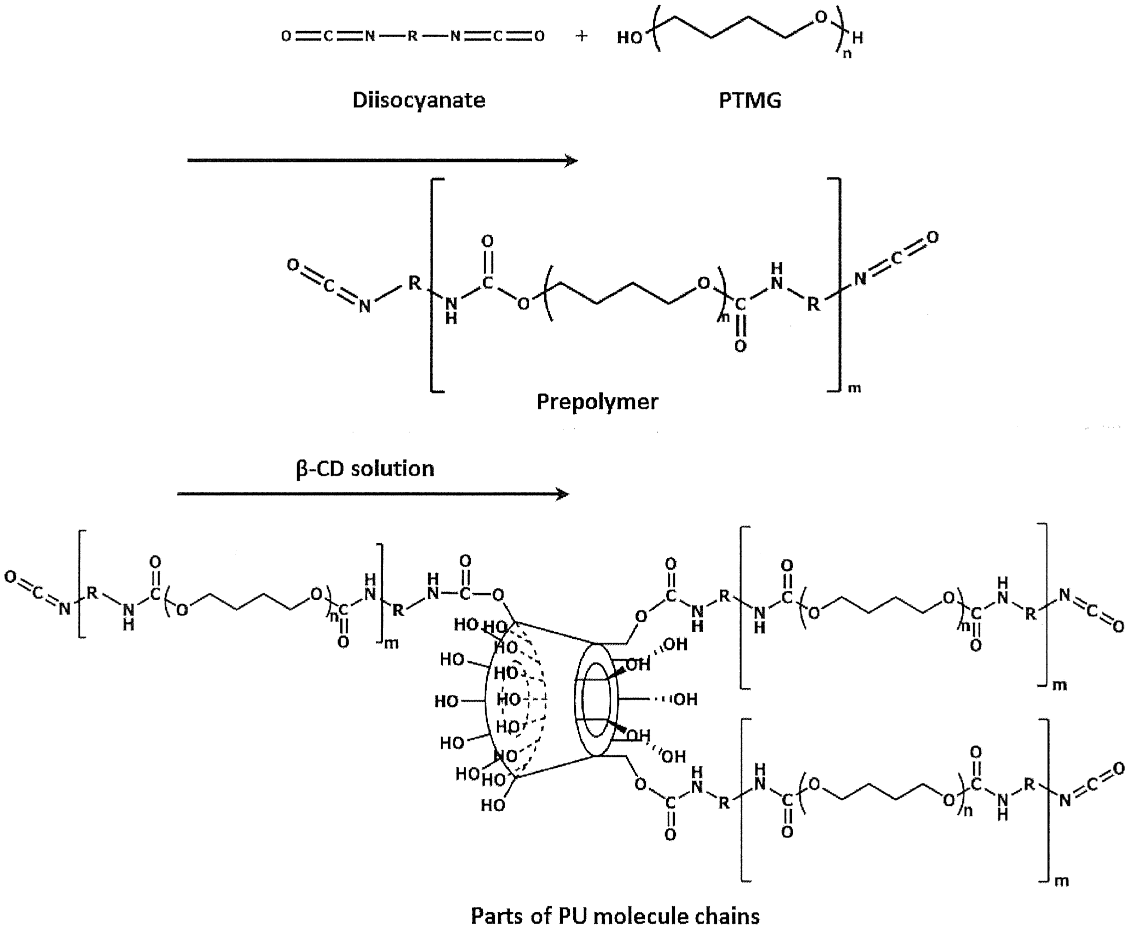
4.1.2 Synthesis

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

The synthesis was performed as follows: β-CD was initially dissolved in DMF (10 mL) at 80 °C for 20 min under an Ar atmosphere to reach a solution. Disocyanate (0.020 mol) and PTMG1000 (10 g, 0.010 mol) were added into a 100-mL four-necked separable reaction 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 used. The route is shown as **Scheme 4.1**.

The thin PUE sheets were obtained by casting the resulting PUE solution at room temperature(23 ±

2° C) for 24 h, at 50 °C for 24 h and at 100 °C for 24 h. The DMF residues in sheet were removed at 80 °C under vacuum for 6 h.



Scheme 4.1 Synthesis of PUEs crosslinked by β-CD

4.1.3 Characterization

4.1.3.1 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of PUE sheets were recorded on a JASCO (Tokyo, Japan) FTIR-5300 spectrometer equipped with an attenuated total reflection (ATR) system, which used an ATR500/M with an ATR prism KRS-5.

4.1.3.2. Scanning electron microscopy (SEM)

SEM was used to observe the surface morphology of PUEs by using S-4800(Hitachi High-Technologies Corporation, Japan), all micrographs were taken at magnification of 30k×.

4.1.3.3. Differential scanning calorimetry (DSC)

The thermal phase behavior of these PUEs was investigated using a Rigaku Thermo-Plus DSC-8230 differential scanning calorimeter, operated at a heating rate of 10°C/min under N2 atmosphere. Samples were heated from -100°C to 250°C.

4.1.3.4. Dynamic mechanical analysis (DMA)

DMA was performed on a dynamic mechanical analyzer (Seiko Instruments DMS 6100) at frequency of 20 Hz under an N2 atmosphere. The heating rate was 5 °C/min and heat from −100 to 200 °C.

4.1.3.5. Swelling test

Swelling tests were carried out in THF. PUE sheets were cut into 10 × 20 mm samples. After testing their weight, they were put into THF solution in test tube to keep 24h.Removed the THF on the surface, the weight of samples would be tested again. The degree of swelling (Rs) was calculated using the formula Rs (%) = W'-W/W × 100, where W, W' are the weight of samples before and after swelling.

4.1.3.6. Hardness

Hardness was tested by using a Asker Durometer(Kobunshi Keiki Corporation, Japan) with the A scale, which is used for rubbers in the normal hardness range. The test procedure follows JIS K 6253.

4.1.3.7. Tensile test

Tensile test was measured by RTC-1225A Universal Tensile Testing Instruments (ORIENTEC Corporation, Japan) equipped with a U-4300 extensometer. Samples were cut into dumbbell strip followed JIS K 6251-3 standard. Tensile test was performed at a crosshead speed of 100mm/min at room temperature (23±2 °C).

4.2 Results and Discussion

IR measurements were utilized to investigate the microphase separation of PUEs. Carbonyl C=O group absorptions were shown as **Figure 4.1**. Two peaks were observed clearly at around 1700 and 1720cm^{-1}, which respond to hydrogen-bonded carbonyl stretching $\upsilon(C{=}O_{bonded})$ and free one $\upsilon(C{=}O_{free})$, respectively. In addition, in HDI-PUEs, one more peaks were also observed at around 1680cm^{-1}, which could be assigned to ordered carbonyl stretching $\upsilon(C{=}O_{ordered})$ in urethane linkage. No peak around 1680cm^{-1} appeared for MDI- and IPDI-PUEs. It is considered as the symmetry of diisocyanates used.[18]-[20] Symmetrical HDI results in ordered hard segments, which may cause agglomerate and crystallization of hard segments and thus lead to better microphase separation. On the other hand, axisymmetrical MDI and unsymmetrical IPDI will result in no or only a few well-ordered hard segments. The PUEs have weaker intermolecular hydrogen bonding and small sized hard domains, which may lead to weak microphase separation or no phase separation.

It is also observed clearly that the ratio of $\upsilon(C{=}O_{ordered})$ to $\upsilon(C{=}O_{bonded(disordered)})$ for HDI-PUE$_0$ was much greater than the crosslinked ones caused by β-CD. We considered it as the disordering of hard segments caused by β-CD molecules because of the truncated cone shape. It will also disable parts of the formation of hydrogen bonding, which will reduce the size of hard domains and thus lead to weaker microphase separation.

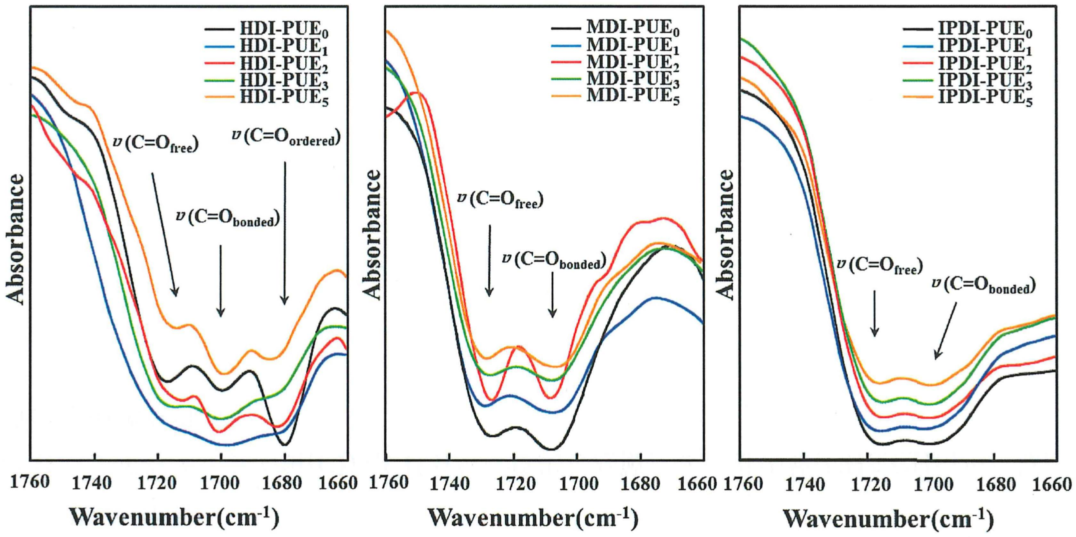


Figure 4.1 FTIR spectra of C=O region of PUEs

Figure 4.2 shows the DSC curves for HDI-PUEs, MDI-PUEs and IPDI-PUEs. Glass transition temperature(Tg) of soft segment were observed around -70°C for HDI-PUEs, -50°C for MDI-PUEs and -60°C for IPDI-PUEs. Peaks of crystallization of hard segments were observed at 167.5°C and 159.4°C in HDI-PUE$_0$ and HDI-PUE$_1$. In HDI-PUE$_2$ and HDI-PUE$_3$, only peaks of melting of hard segments were observed at 182.4°C and 178.8°C and HDI-PUE$_5$ exhibit no clear thermal transitions in this area. It can be easily found that addition of β-CD has destroyed the regularity of hard segments. Similarly, peak of melting of hard segments could be found in MDI-PUE$_0$ at 170.7°C which could not be found in other MDI-PUEs. In addition, peaks of melting of soft segments were also observed in HDI-PUE$_0$, MDI-PUE$_0$ and MDI-PUE$_1$ at 50.1°C, 70.8°C and 52.8°C, respectively, which could not be found in PUEs with higher β-CD content. In these PUEs with higher β-CD content, regularity of soft segments was also destroyed. However, IPDI-PUEs exhibit quite different thermal behaviors. As β-CD content increase, peak of melting of hard segments disappeared and crystallization of soft segments appeared at around 20°C. Thermal behaviors of these PUEs crosslinked by β-CD have a high correlation with the symmetry of diisocyanates used.

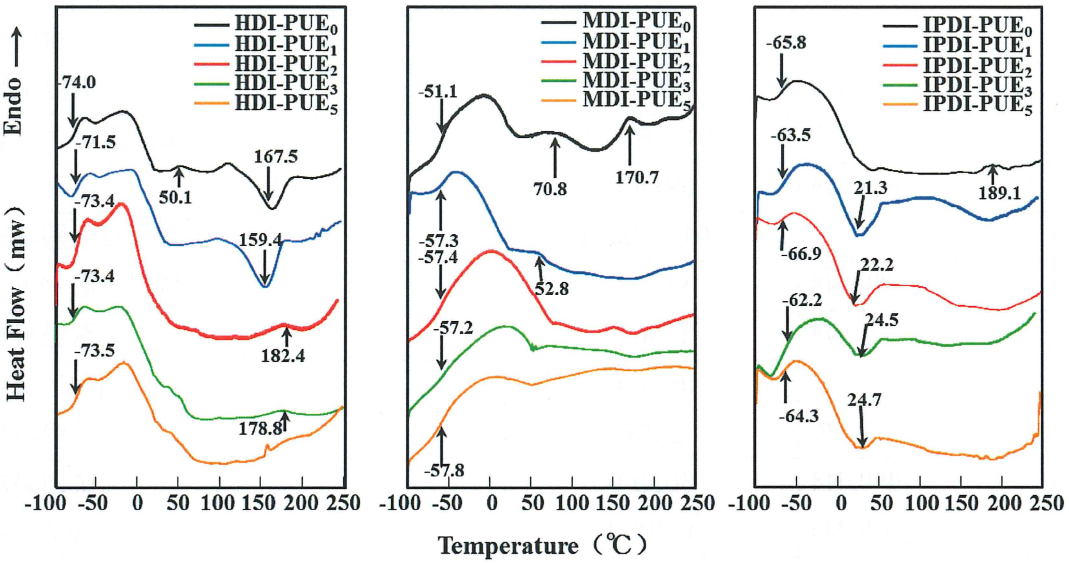


Figure 4.2 DSC thermographs of PUEs

To confirm the microphase separation mentioned above, we took the SEM micrographs of each PUE films. **Figure 4.3**, **Figure 4.4** and **Figure 4.5** shows the surface features of HDI-PUEs, MDI-PUEs and IPDI-PUEs, respectively. In HDI-PUEs, phase separation is quite clear that the brighter parts response to hard domains while darker parts response to soft domains. The morphology of HDI-PUE$_0$ is unique that the brighter parts are so ordered. It may result from the crystallization of hard segments. The other HDI-PUEs do not show any ordered structure as the big sized β-CD molecule have destroyed it. In HDI-PUE$_5$, we could find much smaller hard domains with a particle size of about 200nm to compare with other HDI-PUEs. These hard domains are considered to form with absolutely different structure. On the contrary, microphase separation phonomenon was not clear in MDI-PUE$_0$ and IPDI-PUE$_0$. However, the degree of phase separation increased as the β-CD content increase and the hard domains are quite different from the ones observed in HDI-PUEs.

Schematic representation of structure of IPDI-PUEs is shown as **Figure 4.6**. It is obvious that β-CD contribute to the microphase separation of PUEs especially in those ones with unsymmetrical diisocyanates.

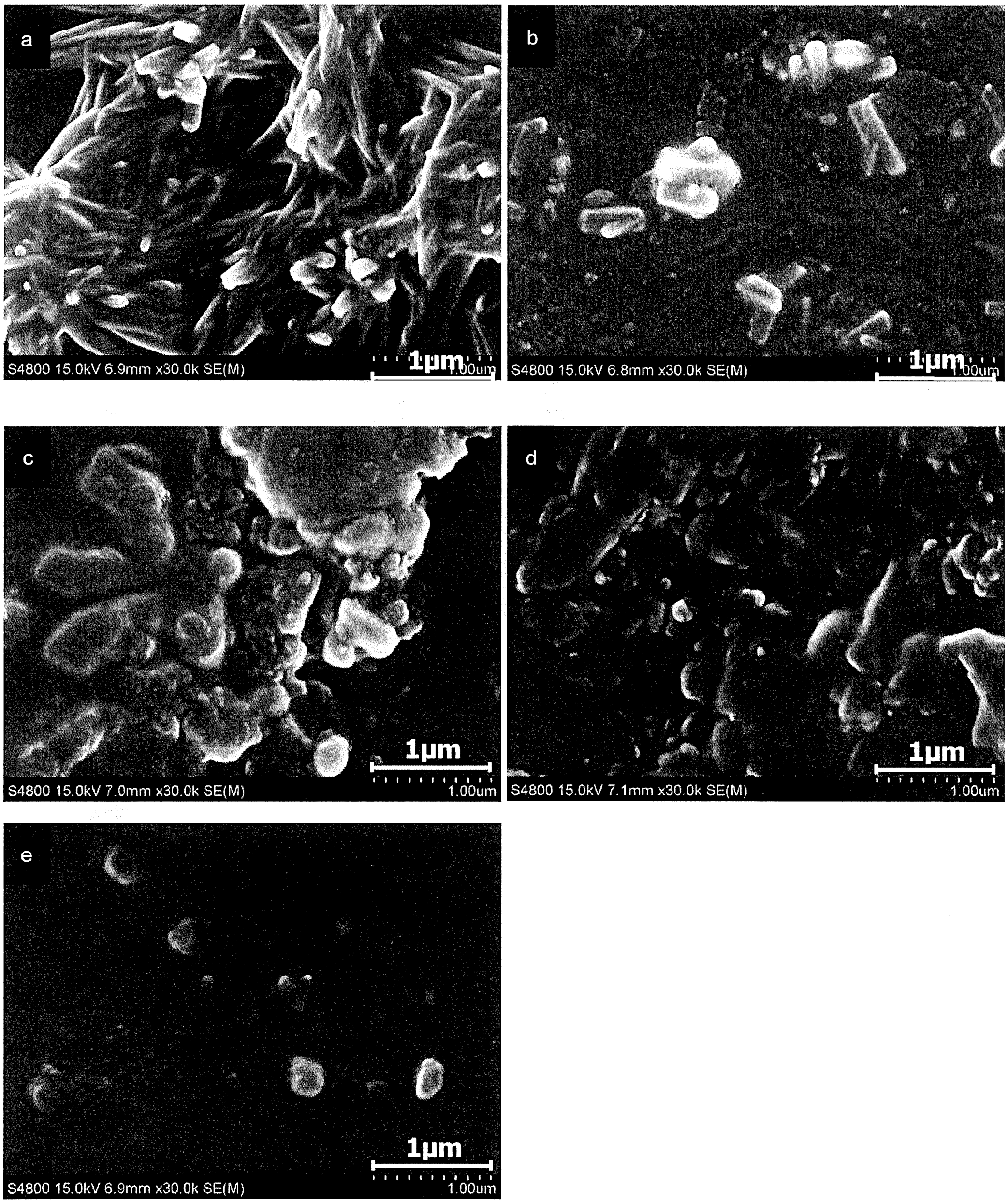


Figure 4.3 SEM micrographs of HDI-PUEs,(a)HDI-PUE$_0$ (b)HDI-PUE$_1$ (c)HDI-PUE$_2$ (d)HDI-PUE$_3$ (e)HDI-PUE$_5$

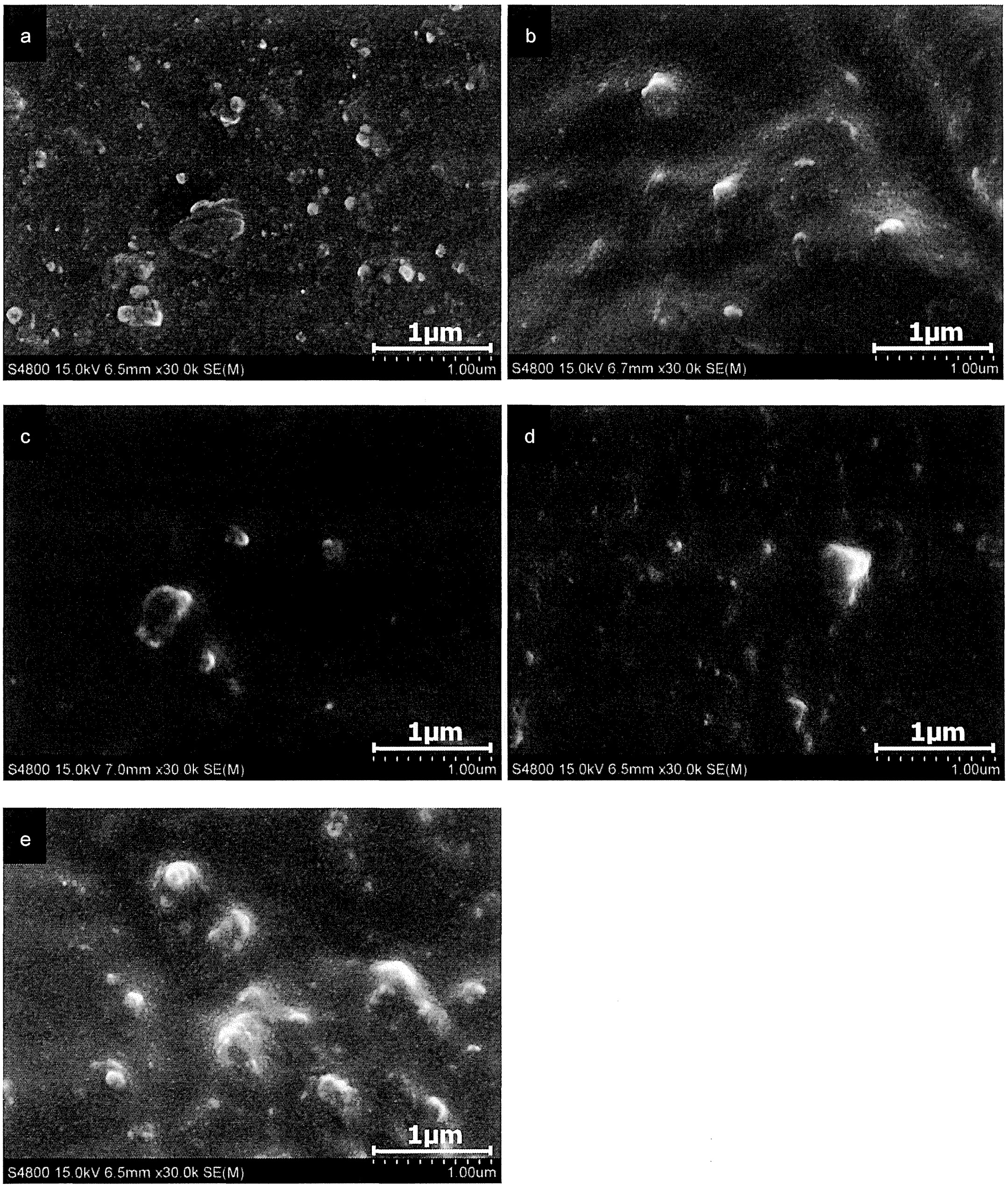


Figure 4.4 SEM micrographs of MDI-PUEs (a)MDI-PUE$_0$ (b)MDI-PUE$_1$ (c)MDI-PUE$_2$ (d)MDI-PUE$_3$ (e)MDI-PUE$_5$

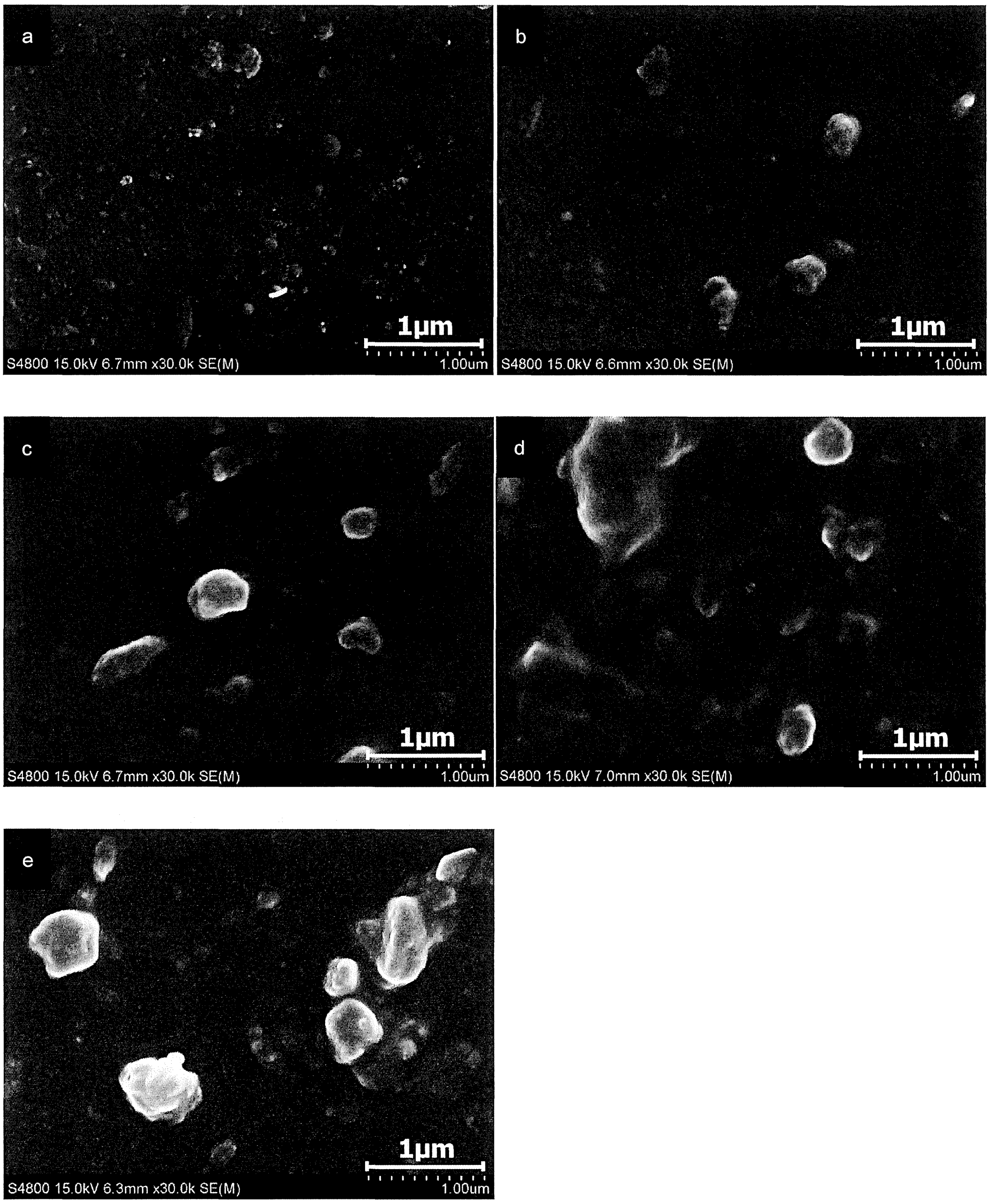


Figure 4.5 SEM micrographs of IPDI-PUEs (a)IPDI-PUE$_0$ (b)IPDI-PUE$_1$ (c)IPDI-PUE$_2$ (d)IPDI-PUE$_3$ (e)IPDI-PUE$_5$

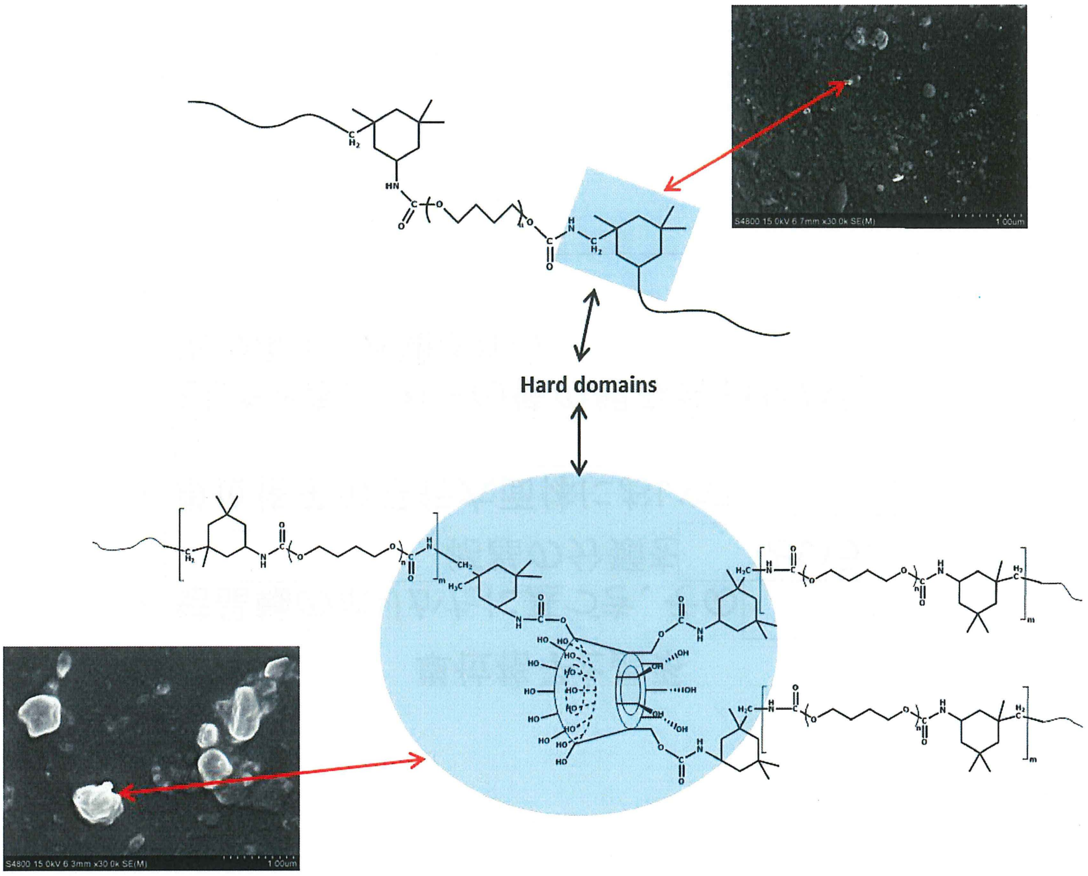


Figure 4.6 Schematic representation of hard domains of IPDI-PUEs with and without β-CD

The viscoelastic behaviors of PUEs through the Storage Modulus (E') and tan δ (tan δ= E"/E') are shown as **Figure 4.7**. All PUEs display a sharp glass transition of PTMG soft segments. The Tg of soft segments of PUEs with β-CD are higher than that of PUE$_0$s due to the crosslink structure. In HDI-PUEs, HDI-PUE$_0$ has a much higher Storage Modulus until a sharp around about 150°C, which corresponds to the melting of crystalline that also proved by DSC. The other HDI-PUEs with β-CD are less thermal sensitive because of the crosslink introduced. All MDI-PUEs display a long rubbery plateau up to about 150°C and MDI-PUE$_0$ has higher module value. No rubbery plateau is found in IPDI-PUE$_0$. However, the addition of β-CD increased the thermal stability and mechanical property of PUEs.

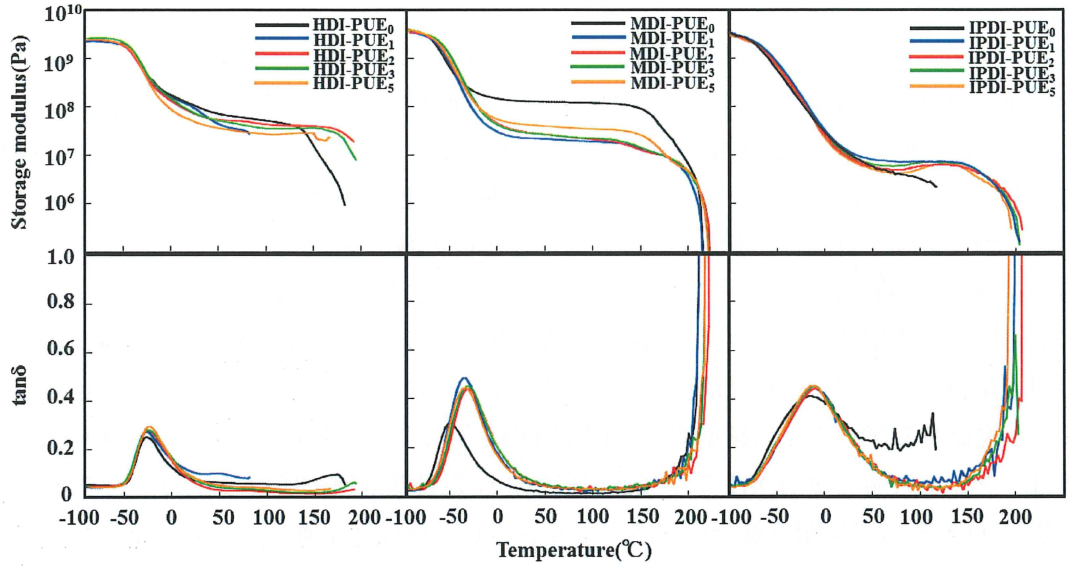


Figure 4.7 Storage modules-temperature and tan δ-temperature curves of PUEs

Table 4.2 shows the hardness and swelling rate of PUEs. Highest hardness of 87A appeared on HDI-PUE$_0$ and hardness of HDI-PUEs reduced as the β-CD content increase. On the contrary, lowest hardness of 62A appeared on IPDI-PUE$_0$ and hardness of IPDI-PUEs increased as the β-CD content increase. It may attribute to the regularity of molecule chains. In HDI-PUE$_0$, the symmetrical HDI lead to the crystallization of parts of hard segment in PUEs and thus increase the hardness. However, although introduce new chemical crosslinks by β-CD, the regularity of main-chain of PUE is broken by β-CD and this damage is in advantage here. Unlike this, the situation in IPDI-PUEs is exactly opposite. Hardness of IPDI-PUE$_0$ is low as the irregularity of molecular chains caused by unsymmetrical IPDI. Moreover, crosslinks caused by β-CD resulted in the increase of hardness of PUEs. The situation of MDI-PUEs is between the HDI- and IPDI-PUEs due to the axisymmetrical structure of MDI.

Table 4.2 Hardness and swelling rate of PUEs

Sample	Hardness (JIS A)	Swelling rate (%)
HDI-PUE$_0$	87	110
HDI-PUE$_1$	82	111
HDI-PUE$_2$	83	127
HDI-PUE$_3$	82	143
HDI-PUE$_5$	78	159
MDI-PUE$_0$	80	nearly soluble
MDI-PUE$_1$	78	283
MDI-PUE$_2$	83	312
MDI-PUE$_3$	83	407
MDI-PUE$_5$	89	417
IPDI-PUE$_0$	62	soluble
IPDI-PUE$_1$	66	243
IPDI-PUE$_2$	66	230
IPDI-PUE$_3$	67	216
IPDI-PUE$_5$	67	211

The results of swelling tests indicated the packing state of molecular chains because the small solvent molecules can enter the space between the molecular chains of PUEs. As we can see clearly, HDI-PUEs are little swelled and the swelling rate increased from 110% to 159% as β-CD content increases. IPDI-PUE$_0$ is soluble for the reason that few ordered structure and chemical crosslink exist in these PUEs. The swelling rate decreased from 243% to 211% as β-CD content increase because the crosslink density increased. The results are quite agreed with the IR and hardness results mentioned above. However, remarkable results appeared in MDI-PUEs. MDI-PUE$_0$ is nearly soluble and swelling rate increased as β-CD content increases while hardness also increased as β-CD content increases. It indicates the small amount of ordered structure in MDI-PUEs and the damage of ordered structure caused by β-CD is stronger than the crosslink introduced. Moreover, steric hindrance is also considered to be one factor to influence hardness. Aromatic ring and cyclodextrin ring will reduce the flexibility of molecular chains and increase hardness.

Tensile tests are also undertaken to study microphase separation-mechanical properties relationship. Stress-Strain (S-S) curves are shown as **Figure 4.8**. Elongation at break (EB) and tensile strength are shown as **Table 4.3**. Although the HDI-, MDI- and IPDI-PUEs were synthesized with the same mole ratio, their performance in S-S curves are quite different. In HDI-PUEs, HDI-PUE$_0$ has superior appearance both at EB of 616% and extreme tensile strength of 74.14Mpa. As β-CD content increases, both EB and tensile strength decreased. It is worth mentioning that HDI-PUE$_3$ and HDI-PUE$_5$ even lose elasticity. It can be concluded that the ordered structure is main factor to influence the mechanical property of PUEs when symmetrical diisocyanate is used. In IPDI-PUEs, EB decreased and tensile strength increased as β-CD content increases. The crosslink effect of β-CD is similar to normal cross-linker. In MDI-PUEs, comparatively optimum property appeared in MDI-PUE$_1$. We consider it as a balance between damage of ordered structure and formation of chemical crosslinks which agreed with the other tests proved above.

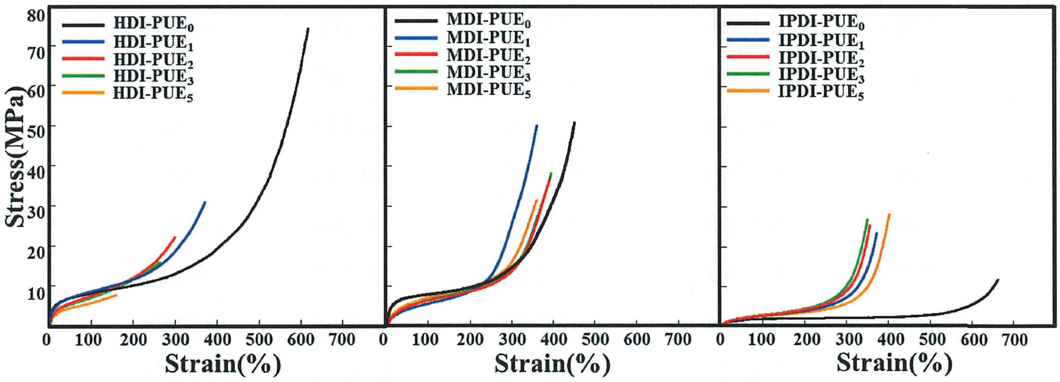


Figure 4.8 Stress-Strain curves of PUEs

Table 4.3 EB and tensile strength of PUEs

sample	σ100% (Mpa)	σ 200% (Mpa)	σ 300% (Mpa)	σ (Mpa)	EB (%)
HDI-PUE$_0$	8.05	9.99	12.96	74.14	616
HDI-PUE$_1$	8.36	11.41	18.59	30.86	370
HDI-PUE$_2$	7.22	11.81	12.40	21.84	297
HDI-PUE$_3$	6.82	11.42	-	15.72	263
HDI-PUE$_5$	5.62	-	-	7.60	156
MDI-PUE$_0$	7.69	9.46	14.62	50.55	449
MDI-PUE$_1$	5.30	8.40	25.81	49.80	359
MDI-PUE$_2$	6.17	8.40	13.73	36.50	389
MDI-PUE$_3$	6.37	8.76	14.13	38.08	395
MDI-PUE$_5$	6.82	9.58	16.12	31.32	358
IPDI-PUE$_0$	1.49	1.63	1.80	11.55	662
IPDI-PUE$_1$	2.45	3.63	7.14	23.17	370
IPDI-PUE$_2$	2.59	4.00	8.87	23.34	354
IPDI-PUE$_3$	2.69	4.26	10.30	26.83	348
IPDI-PUE$_5$	2.30	3.23	5.59	27.92	402

σ: strength

EB: elongation at break

4.3 Conclusion

The effects of diisocyanate on PUEs which synthesized by using β-CD as cross-linker were evaluated. Differ from common low-molecular weight cross-linkers, the size of β-CD influence the crosslink effect. β-CD molecules enlarged the distance between molecular chains of PUEs in some areas which will destroy the ordered structure. Thus, on symmetrical diisocyanate based PUEs, the crosslink effect will be blocked. In addition, high β-CD content will lead to the disappearing of elasticity of PUEs.

On the contrary, crosslink effect is well reflected in unsymmetrical diisocyanate based PUEs. As same as normal chemical crosslinks, the crosslinks caused by β-CD increase the strength and hardness of these PUEs. Moreover, β-CD contributes to the microphase separation of PUEs and form different hard domains.

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Chapter 5 Influence of polyol on β-CD crosslinked PUEs

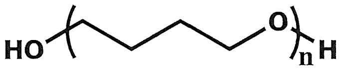
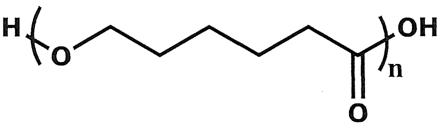
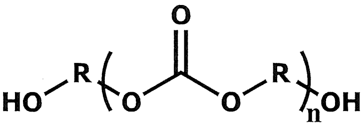
In PUEs, soft segments (SS) are only provided by polyols which have long chain molecular structure. Therefore, the kinds of polyols and their structure play an important role in affecting properties of PUEs, especially in flexibility and low-temperature property. In this chapter, the influence of polyol on β-CD crosslinked PUEs was discussed.

5.1 Experimental

5.1.1 Materials

PTMG (molecular weight=1000) (PTMG1000), PCL (molecular weight=1000) (PCL1000), PCD (molecular weight=1000) (PCD1000) were supplied by Invista Industry, Texas, USA. 4,4'-Diphenylmethane diisocyanate (MDI) was supplied by Tosoh Industry, Tokyo, Japan and was purified by distillation under reduced pressure (267-400Pa) at 100°C before use. β-cyclodextrin (β-CD) was purchased from Nacalai Tesque, Inc., Kyoto, Japan (Nacalai) and was dried for 24 hours under a condition of 267-400Pa/80°C before use. Tetrahydrofuran (THF) and benzene were purchased from Nacalai and distilled over calcium hydride under an Ar atmosphere. N, N-Dimethylformamide (DMF) was purchased from Nacalai and stored over 4 Å molecular sieves before use. The following compounds were purchased from commercial suppliers and used as received: hexane (Nacalai) and acetone (Nacalai).

Table 5.1 structure of polyols used

Polyol		Chemical structural formula
polytetrahydrofuran	PTMG	
polycaprolactone diol	PCL	
polycarbonate diol	PCD	

5.1.2 Synthesis

A series of PUEs with β-CDs were synthesized from different kinds of polyols, MDI and β-CD via prepolymer method, named Y-PUEy. (Y=kind of polyol, y=weight percent (%) of β-CD)

The synthesis was performed as follows: β-CD was initially dissolved in DMF (10 mL) at 80 °C for 20 min under an Ar atmosphere to reach a solution. MDI (0.020 mol) and polyol (10 g, 0.010 mol) were added into a 100-mL four-necked separable reaction 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. 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. The thin PUE sheets were obtained by casting the resulting PUE solution at room temperature(23±2°C) for 24 h, at 50 °C for 24 h and at 100 °C for 24 h. The DMF residues in sheet were removed at 80 °C under vacuum for 6 h.

5.1.3 Characterization

5.1.3.1 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of PUE sheets were recorded on a JASCO (Tokyo, Japan) FTIR-5300 spectrometer equipped with an attenuated total reflection (ATR) system, which used an ATR500/M with an ATR prism KRS-5.

5.1.3.2. Scanning electron microscopy (SEM)

SEM was used to observe the surface morphology of PUEs by using S-4800(Hitachi High-Technologies Corporation, Japan), all micrographs were taken at magnification of 30k×.

5.1.3.3. Swelling test

Swelling tests were carried out in THF. PUE sheets were cut into 10 × 20 mm samples. After testing their weight, they were put into THF solution in test tube to keep 24h.Removed the THF on the surface, the weight of samples would be tested again. The degree of swelling (Rs) was calculated using the formula Rs (%) = W'-W/W × 100, where W, W' are the weight of samples before and after swelling.

5.1.3.4. Hardness

Hardness was tested by using a Asker Durometer(Kobunshi Keiki Corporation, Japan) with the A scale, which is used for rubbers in the normal hardness range. The test procedure follows JIS K 6253.

5.1.3.5. Tensile test

Tensile test was measured by RTC-1225A Universal Tensile Testing Instruments (ORIENTEC Corporation, Japan) equipped with a U-4300 extensometer. Samples were cut into dumbbell strip followed JIS K 6251-3 standard. Tensile test was performed at a crosshead speed of 100mm/min at room temperature (23±2 °C).

5.2 Results and Discussion

IR measurements were utilized to ensure the structure of PUEs. Carbonyl C=O group absorptions are shown as **Figure 5.1**. In PTMG-PUEs, as C=O groups only exist in urethane linkage, only the peak around 1708 cm^{-1} and 1726 cm^{-1} appear, which correspond to hydrogen-bonded carbonyl stretching $\upsilon(C=O_{bonded})$ and free one $\upsilon(C=O_{free})$, respectively. In PCL-PUEs, one more peak around 1721 cm^{-1} was observed. It responds to the acid C=O group in PCL molecule. In PCD-PUEs, peak at 1737 cm^{-1} proved the existence of carbonate C=O group in PCD. It is obvious that PTMG, PCL and PCD have successfully been introduced to PUE molecular chains.

The morphology of PUEs were characterized by SEM. The images of PTMG-PUEs, PCL-PUEs and PCD-PUEs are shown as **Figure 5.2**, **Figure 5.3** and **Figure 5.4**, respectively. Phase separation is observed in all images. As the β-CD content increases, the size of hard domain get bigger. In PCL-PUEs and PCD-PUEs, especially in PCL-PUE_3, PCL-PUE_5 and PCD-PUE_5, the agglomerate of hard domains are very notable. It may relate to the structure of polyol used. It can be easily concluded that PTMG has a more regular structure than PCL and PCD, thus to possesses greater flexibility. When introduced into PUE molecular chains, PTMG moves more easily than PCL and PCD. Therefore, when crosslinks formed by β-CD, the flexibility of molecular chain decrease and the molecular chains of PUEs synthesized from less flexible polyols like PCL and PCD will get harder to move.

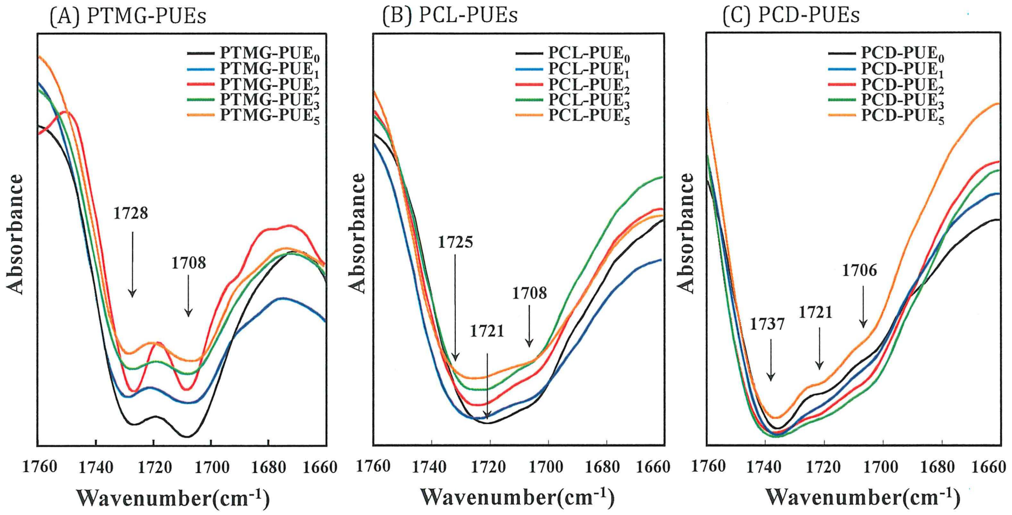


Figure 5.1 FTIR spectra of C=O region of PTMG-PUEs, PCL-PUEs and PCD-PUEs

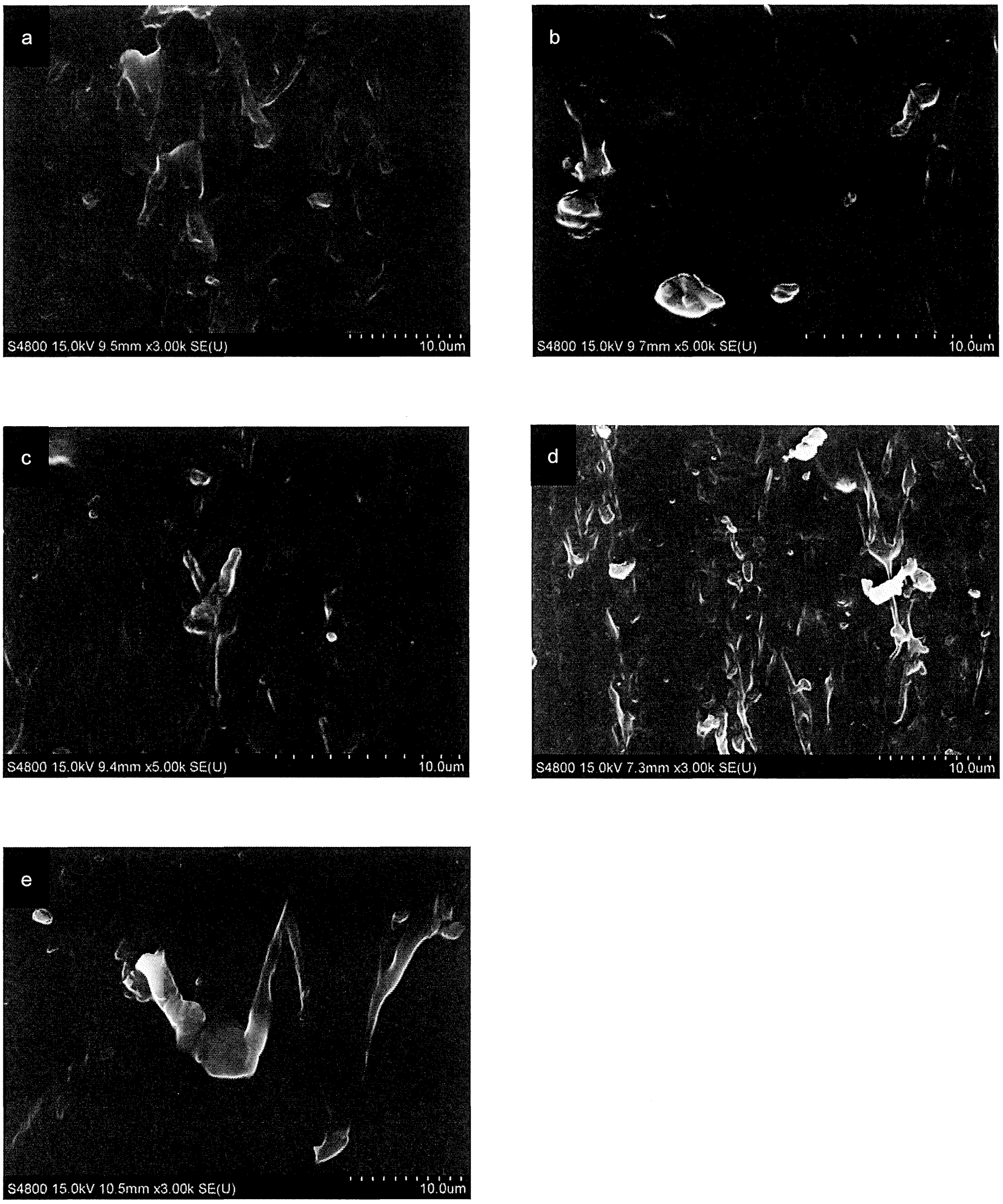


Figure 5.2 SEM micrographs of PTMG-PUEs,(a)PTMG-PUE$_0$ (b)PTMG-PUE$_1$ (c)PTMG-PUE$_2$ (d)PTMG-PUE$_3$ (e)PTMG-PUE$_5$

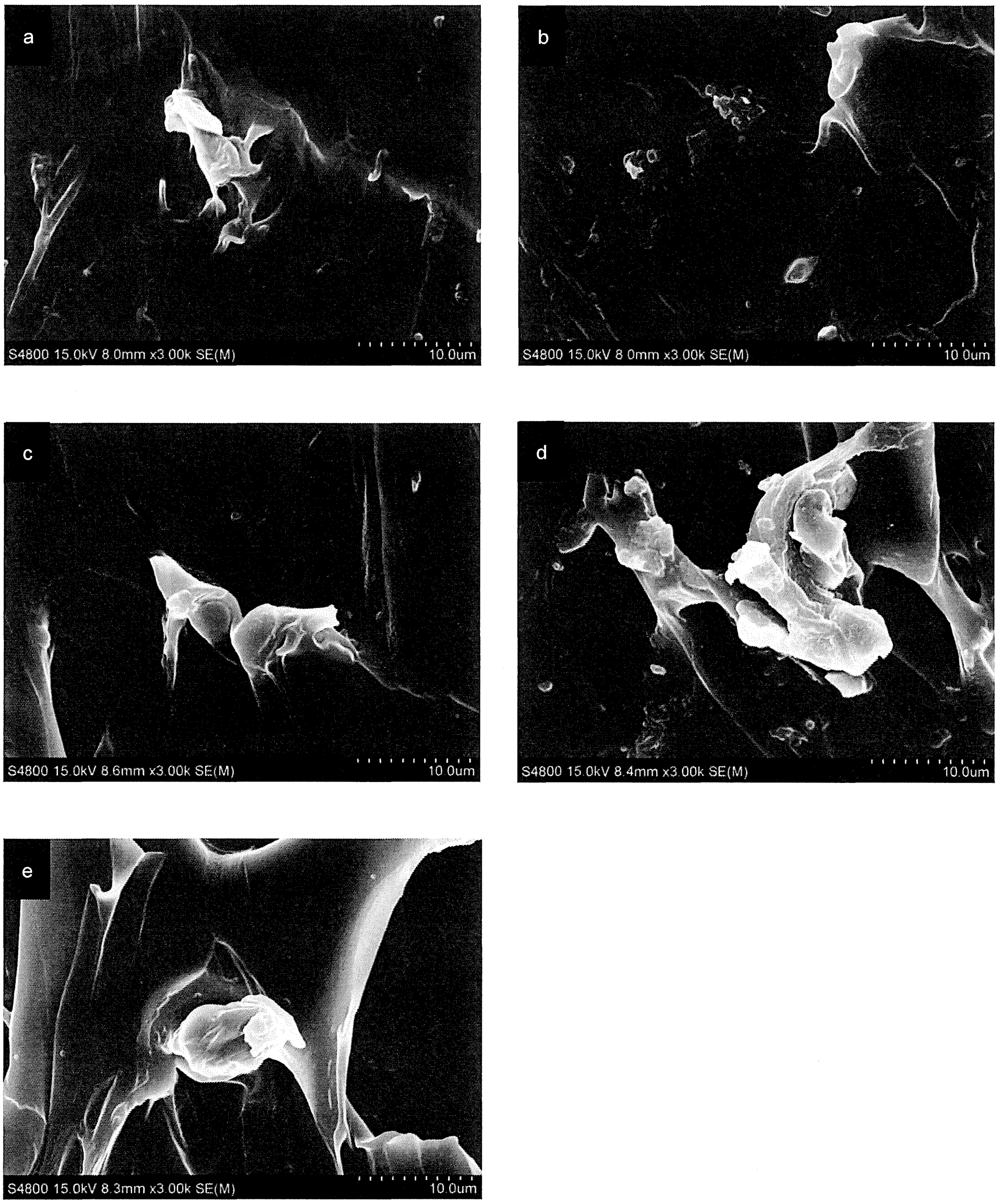


Figure 5.3 SEM micrographs of PCL-PUEs,(a)PCL-PUE$_0$ (b)PCL-PUE$_1$ (c)PCL-PUE$_2$ (d)PCL-PUE$_3$ (e)PCL-PUE$_5$

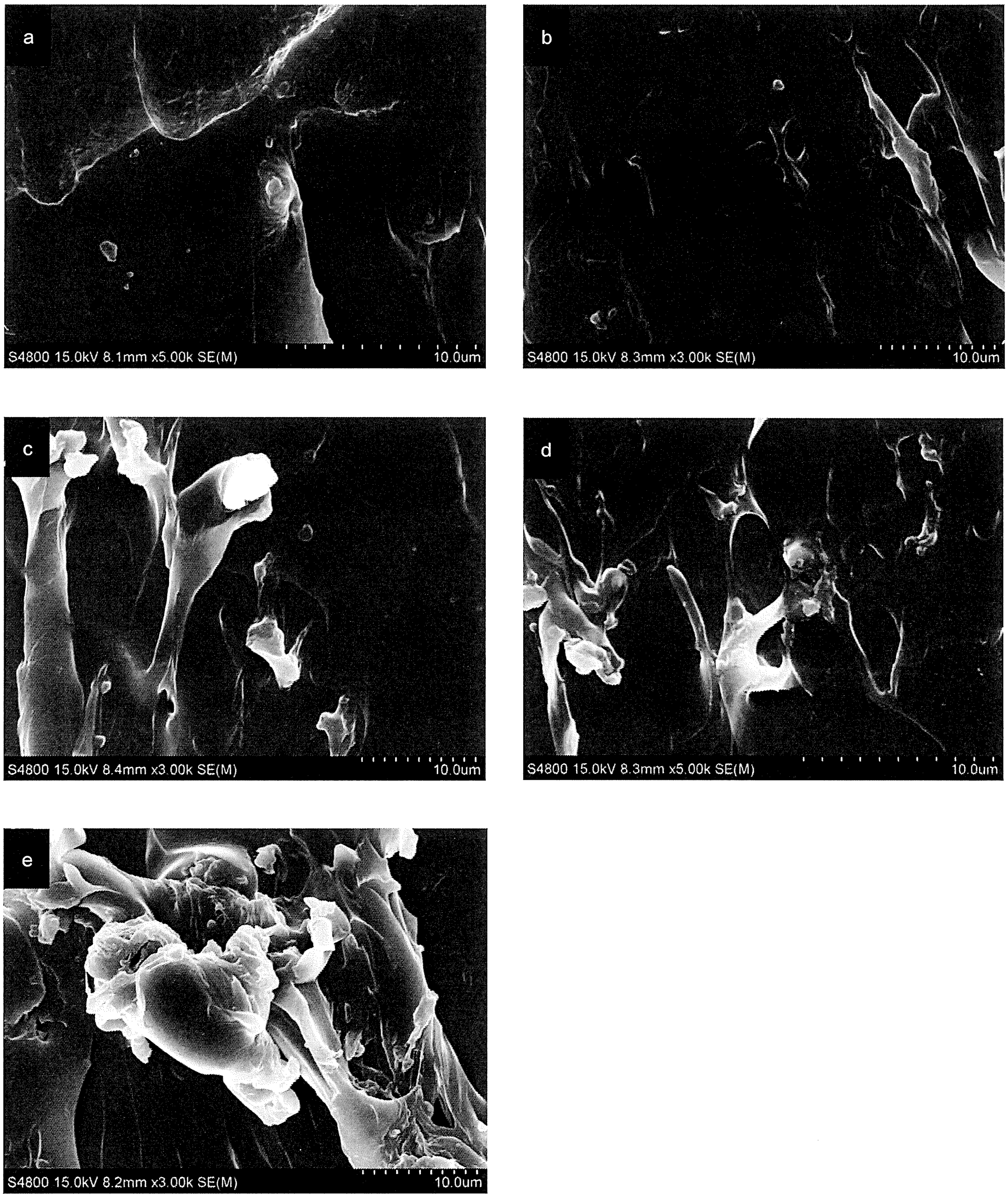


Figure 5.4 SEM micrographs of PCD-PUEs,(a)PCD-PUE$_0$ (b)PCD-PUE$_1$ (c)PCD-PUE$_2$ (d)PCD-PUE$_3$ (e)PCD-PUE$_5$

In order to clarify the relationship between the phenomenon and properties of PUEs, swelling tests, tensile tests and hardness tests were measured. **Table 5.2** shows the hardness and swelling rate of PUEs. It can be seen that the crosslink caused by β-CD increased the hardness of PUEs and the hardness of PCD-PUEs are apparently higher than that of PTMG-PUEs and PCL-PUEs. It is because sterically hinder of PCD-PUE molecular chains which reduced the mobility of molecular chains and make PUEs get harder and tougher.

Swelling rates of PCL-PUEs and PCD-PUEs decrease as the β-CD content increases. It proves the increase of density of crosslink. However, different results appear in PTMG-PUEs that PTMG-PUE$_0$ is nearly soluble and swelling rates of PTMG-PUEs increase as the β-CD content increases. It relates to the solvent used. Due to the similar dissolve mutually theory, PTMG-PUEs are easier to dissolve in THF solvent. Structure of THF and PTMG are shown as **Figure 5.5**.

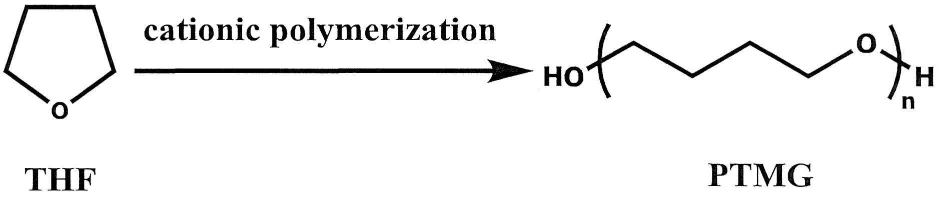


Figure 5.5 Schematic manufacture of PTMG

Table 5.2 Hardness and Swelling rate of PTMG-PUEs, PCL-PUEs and PCD-PUEs

Sample	Hardness (JIS A)	Swelling rate (%)
PTMG-PUE_0	80	nearly soluble
PTMG-PUE_1	78	283
PTMG-PUE_2	83	312
PTMG-PUE_3	83	407
PTMG-PUE_5	89	417
PCL-PUE_0	78	626
PCL-PUE_1	82	409
PCL-PUE_2	83	393
PCL-PUE_3	84	377
PCL-PUE_5	87	370
PCD-PUE_0	85	705
PCD-PUE_1	89	331
PCD-PUE_2	89	370
PCD-PUE_3	91	320
PCD-PUE_5	91	310

Stress-strain curves of PUEs are shown as **Figure 5.6**. The tensile strength and elongation at break were shown as **Table 5.3**. To compare with PTMG-PUEs, PCL-PUEs and PCD-PUEs have much lower elongation at break which is correspond to worse elasticity of PUEs. However, there is only little difference between the strength of PTMG-PUEs and PCL-, PCD-PUEs when with the same β-CD content. It proves that influences of polyols on PUEs are mainly on flexibility. It also agrees with the results of hardness and swelling rate above. It needs to mention that PCD-PUEs almost lose elasticity, especially with high β-CD content. Not only the ratio of HS/SS or HD/SD, but also the balance between stiffness and flexibility need to be controlled in synthesis of PUE.

Table 5.3 EB and tensile strength of PTMG-PUEs, PCL-PUEs and PCD-PUEs

sample	σ100% (Mpa)	σ200% (Mpa)	σ300% (Mpa)	σ (Mpa)	EB (%)
PTMG-PUE$_0$	7.69	9.46	14.62	50.55	449
PTMG-PUE$_1$	5.30	8.40	25.81	49.80	359
PTMG-PUE$_2$	6.17	8.40	13.73	36.50	389
PTMG-PUE$_3$	6.37	8.76	14.13	38.08	395
PTMG-PUE$_5$	6.82	9.58	16.12	31.32	358
PCL-PUE$_0$	7.15	12.40	35.02	45.81	376
PCL-PUE$_1$	5.63	9.81	31.17	59.22	369
PCL-PUE$_2$	7.50	13.16	39.25	52.80	332
PCL-PUE$_3$	6.10	10.02	24.91	38.70	344
PCL-PUE$_5$	5.75	10.32	28.60	34.22	317
PCD-PUE$_0$	6.85	9.87	21.24	35.87	376
PCD-PUE$_1$	13.42	48.02	-	64.32	231
PCD-PUE$_2$	11.51	39.20	-	51.88	234
PCD-PUE$_3$	16.17	-	-	47.30	183
PCD-PUE$_5$	14.92	-	-	30.12	166

σ: strength

EB: elongation at break

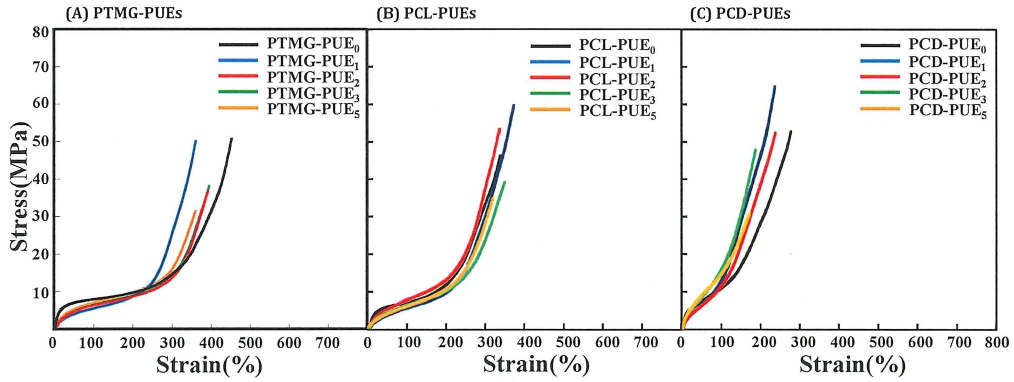


Figure 5.5 Stress-strain curve of PUEs, (A)PTMG-PUEs (B)PCL-PUEs (C)PCD-PUEs

5.3 Conclusion

A series of β-CD crosslinked PUEs from different polyols were synthesized. Polyols affect properties of PUEs to a large extent. The polyol with comparatively regular molecular chains, like PTMG, results in acceptable properties of PUEs. In contrast, the polyol with low regularity, like PCD, leads to the worse elasticity of PUEs.

In addition, as β-CDs cause crosslinks in PUE molecular chains, the PUEs synthesized from polyols with low regularity will get harder and firmer.

Chapter 6 Contact mechanics of PUEs which crosslinked by β-CD

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 rigidty to molecular chains and called HS, while polyol give flexibility to chains and are called SS.[1-2] Due to the imcompatibility 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 also proved by images of Atomic Force Microscope (AFM)[4-5] that hard domains (HD) consist of agglomerate of hard segments and soft domains (SD) consist of 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 attracted 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 made 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.

6.1 Experimental

6.1.1 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.

6.1.2. Synthesis of PUEs crosslinked by β-cyclodextrin

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

The thin PUE films (0.5-0.8mm) were obtained by casting the resulting PUE solution at room temperature (23 ± 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.

6.1.3. 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 (nanoDMA) were undertook. In nanoDMA tests, surface images were also took during the tests, the tested areas were marked in the images. A Berkovich tip is used in all nanoindentation experiments. All measurements are performed at room temperature. In Load and depth sensing indentation mode, indentation area of specimens were selected randomly. Each sample was test for 5 to 7 times.

6.1.4. Theory

Some parameters in indentation with Berkovich tip are illustrated in Figure 6.1. Load-depth curves produced by instrumented indentation systems is often based on Oliver and Pharr[12]. As Figure 6.2 shown, several important parameters are illustrated. The hardness H is an important parameter to evaluate mechanical property of materials. H=Pmax/A, where Pmax is the peak indentation load and A is projected area of the hardness impression[13-14].

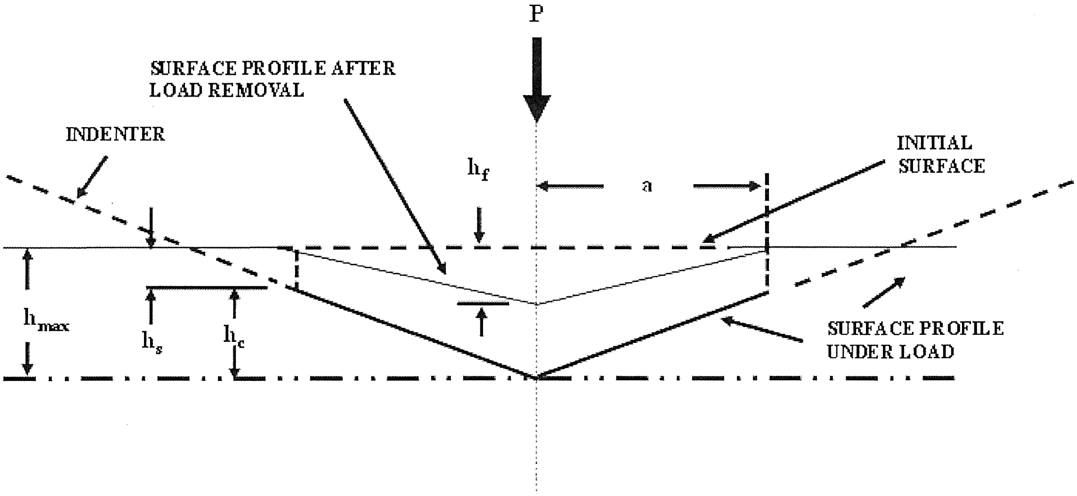


Figure 6.1 A schematic representation of the indentation

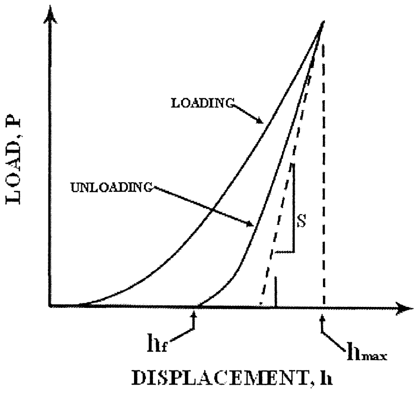


Figure 6.2 A schematic representation of Load-depth curve

6.2 Results and Discussion

The Load-depth curves of PUEs are shown as **Figure 6.3**. In MDI-PUEs and HDI-PUEs, hmax of MDI-PUE$_0$ and HDI-PUE$_0$ are greater than the PUEs with β-CD. In contrast, IPDI-PUEs that contain β-CD have much lower hmax than IPDI-PUE$_0$. The calculated hardness of these PUEs is shown as **Table 6.1**. It is concluded that addition of β-CD reduce the hardness of MDI-PUE$_0$ and HDI-PUE$_0$. Whereas, increase the hardness of IPDI-PUE$_0$. 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 the results in Chapter 4.

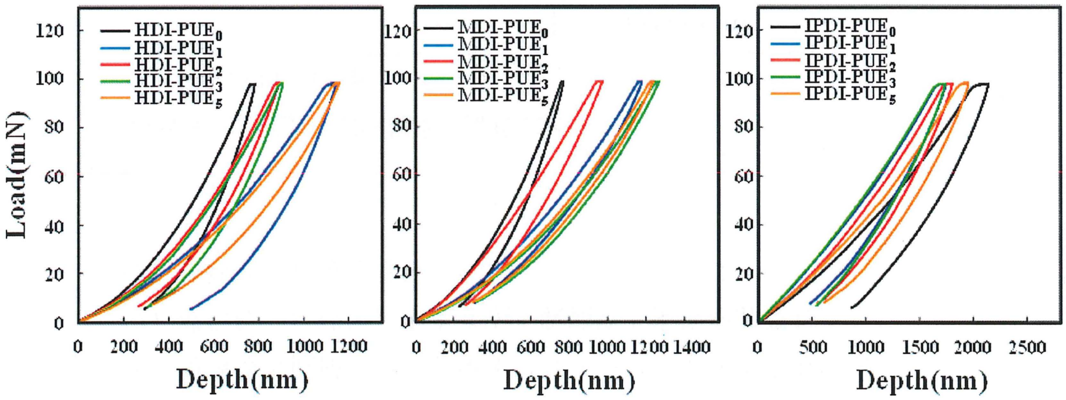


Figure 6.3 Load-depth curves of HDI-PUEs, MDI-PUEs and IPDI-PUEs

Table 6.1 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

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, nanoDMA mode was used. As **Figure 6.4**, **Figure 6.5** and **Figure 6.6** 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-PUE$_1$, MDI-PUE$_3$, IPDI-PUE$_1$ and IPDI-PUE$_5$, 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.

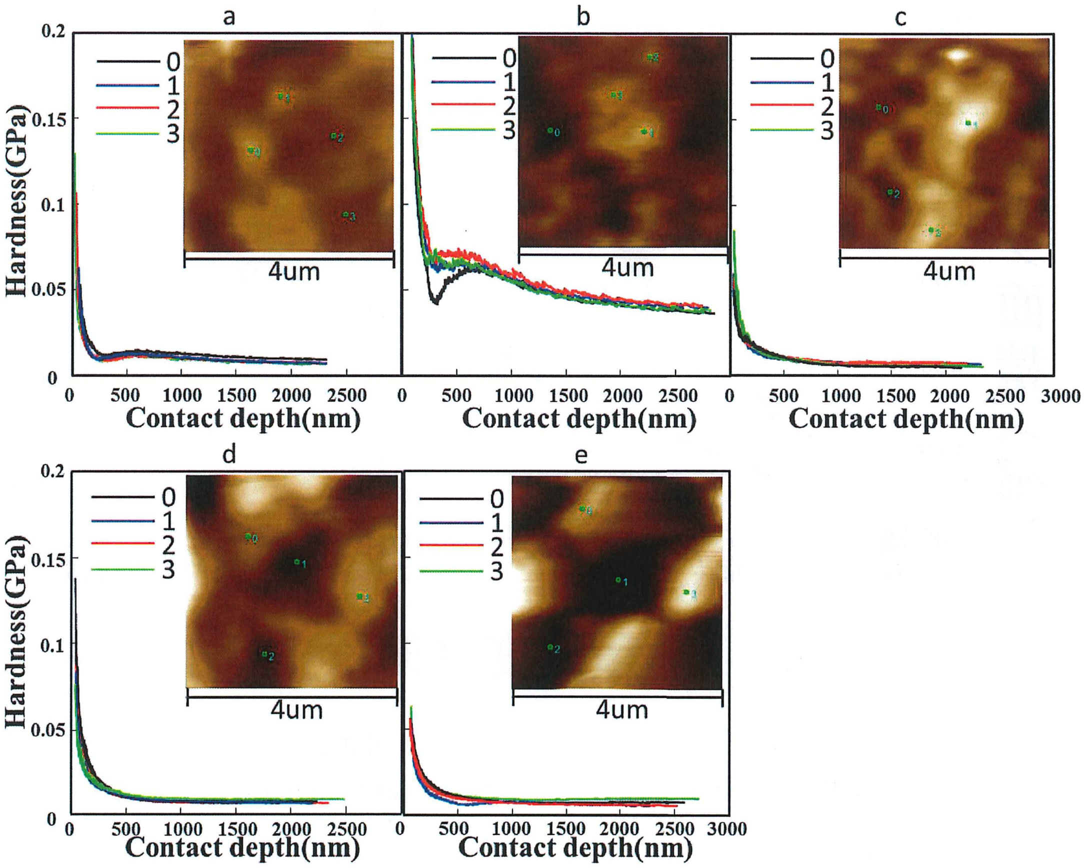


Figure 6.4 Hardness-depth curves of HDI-PUEs, (a)HDI-PUE$_0$ (b)HDI-PUE$_1$ (c)HDI-PUE$_2$ (d)HDI-PUE$_3$ (e)HDI-PUE$_5$

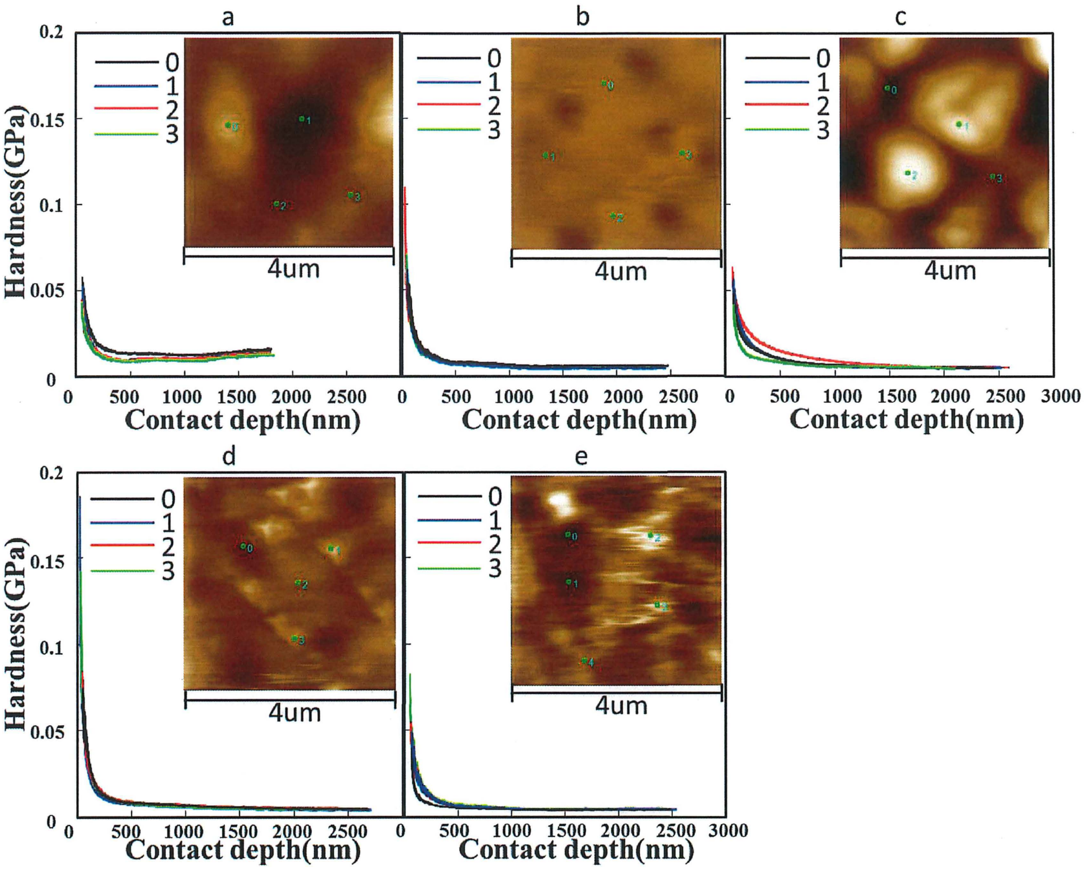


Figure 6.5 Hardness-depth curves of MDI-PUEs, (a)MDI-PUE$_0$ (b)MDI-PUE$_1$ (c)MDI-PUE$_2$ (d)MDI-PUE$_3$ (e)MDI-PUE$_5$

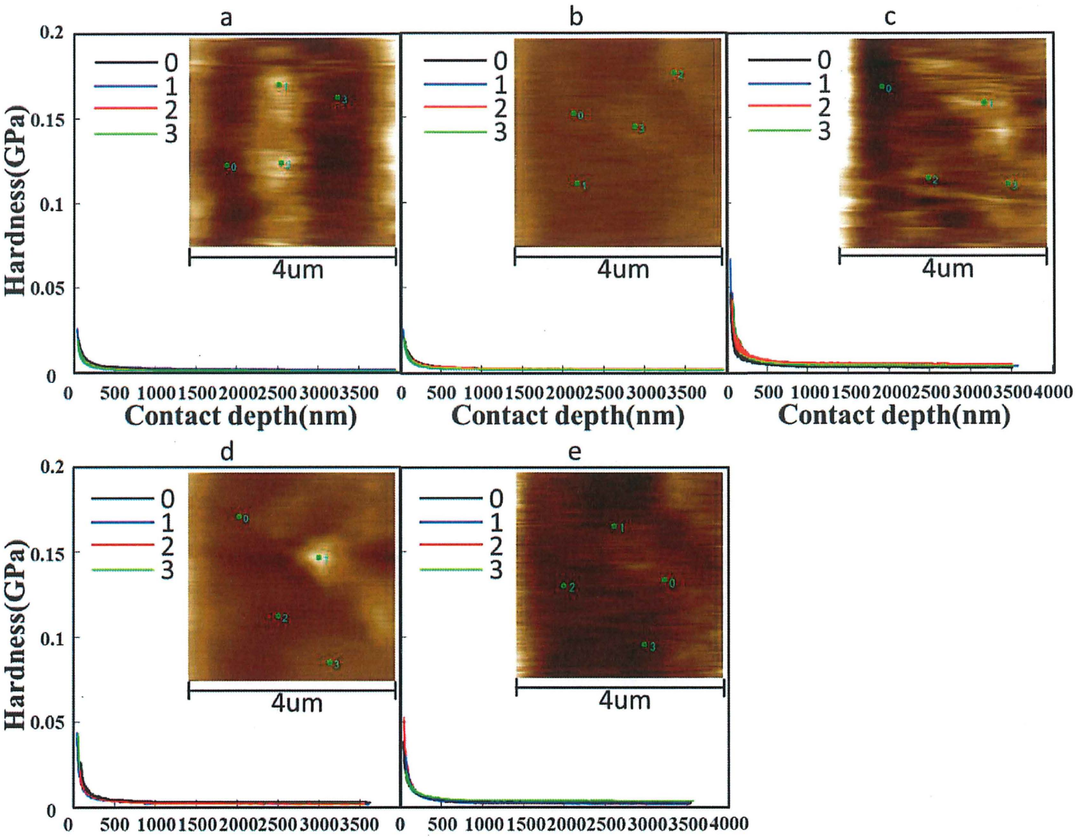


Figure 6.6 Hardness-depth curves of IPDI-PUEs, (a)IPDI-PUE$_0$ (b)IPDI-PUE$_1$ (c)IPDI-PUE$_2$ (d)IPDI-PUE$_3$ (e)IPDI-PUE$_5$

6.3 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 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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Chapter 7 Conclusions

A series of PUEs using β-CD as cross-linker were synthesized and characterized. The influences of β-CD content, symmetry of diisocyanates, regularity of polyol molecules on properties of PUEs were investigated. In addition, the mechanical properties of PUEs were also measured on hard domain/ soft domain scale by nanoindentation. The conclusions are shown as follows:

1.Within 5% of the additive amounts of β-CD, PUEs kept elasticity. The decrease of tensile strength and elongation at break indicates that the exist of large quantities of hydrogen bonds in MDI-PTMG based polyurethanes and the destruction of regularity of PUE chains is much more contribute to tensile strength than the formation of crosslinks by addition of β-CD.

2. β-CD molecules enlarged the distance between molecular chains of PUEs in some areas which will destroy the ordered structure. Thus, on symmetrical diisocyanate based PUEs, the crosslink effect will be blocked. In addition, high β-CD content will lead to the disappearing of elasticity of PUEs. On the contrary, crosslink effect is well reflected in unsymmetrical diisocyanate based PUEs. As same as normal chemical crosslinks, the crosslinks caused by β-CD increase the strength and hardness of these PUEs. Moreover, β-CD contributes to the microphase separation of PUEs and form different hard domains.

3. The polyol with comparatively regular molecular chains, like PTMG, results in acceptable properties of PUEs. In contrast, the polyol with low regularity, like PCD, leads to the worse elasticity of PUEs. Kinds of polyols do not affect the crosslink effect of β-CD.

The structure and properties of PUEs which using β-CD as cross-linker, also the structure-property relationship was investigated systematically. The results show the possibility of using β-CD as replacement to cross-linker in synthesis of PUE.

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

As most β-CD based PUs have bad elasticity, the results of this research will broaden the application areas of β-CD based PUs.

In the future, the cavity of β-CD is expected to utilize to develop functional PUEs. This work can be regarded as a fundamental. In addition, the degradation experiments will be undertook to evaluate the function in biochemistry area.