



Chemical hybridization of waterborne polyurethane with β -cyclodextrin by sol-gel reaction



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ABSTRACT

A series of waterborne polyurethane (WPU)/ β -cyclodextrin (β -CD) chemical hybrids were synthesized from polypropylene glycol (PPG400), dicyclohexylmethane-4,4'-diisocyanate (H_{12} MDI), dimethylol butanoic acid (DMBA), 3-isocyanatepropyltriethoxysilane (ICPTES), and β -CD. The ICPTES-terminated WPU prepolymers were chain extended via a sol-gel reaction by using β -CD as a biodegradable multifunctional crosslinker at various β -CD equivalence ratios (ICPTES: β -CD = 1:0.5, 1:1, 1:1.5, and 1:2). The thermal, mechanical, and surface properties of the WPU/ β -CD dispersion cast film were investigated, with biodegradation experiments carried out in α -amylase enzyme solution. The glass transition temperature (T_g), particle size, Young's modulus, and hardness of the dispersion cast film increased up to an equivalence ratio of 1:1.5 owing to effective migration of β -CD molecules into WPU and crosslinking via the sol-gel reaction. However, at higher ratios, most of these parameters decreased owing to aggregation of β -CD.

1. Introduction

Polyurethanes (PUs) are versatile engineering materials that are synthesized by reaction of isocyanate, polyol, and various chain extenders. These polymers find broad industrial applications as elastomers, adhesives, coatings, sealants, and various foam products. The global consumption of PUs is continuously expanding with their usage as highly functional and high-performance materials [1–3]. Conventionally, PUs have been produced in organic solvents, including methyl ethyl ketone, acetone, and dimethyl formamide. Such solventborne PUs (SPUs) allow great freedom in molecular design and have processing advantages. However, owing to safety and environmental problems, waterborne PUs (WPUs) are steadily replacing SPUs, and are now applied in applications, including adhesives and coatings for numerous flexible substrates [4,5].

Generally, WPUs have slower adhesion development and drying rates than conventional SPUs. In addition, applications of WPUs have been limited by the type of raw materials required and the manufacturing process. However, problems related to properties and processing can be resolved by proper molecular design and hybridization with other materials [6–10]. On the other hand, growing land pollution and shortage of landfill sites with polymer wastes, led to concern about biodegradation [11]. Therefore, PUs have been molecularly designed to allow biodegradation by microorganisms [12]. Microbial degradation of PUs depends on various properties, such as functional groups in

molecular chains, orientation, and crosslink density, which determine degrading-enzyme systems. Biodegradation by microorganisms is mainly limited to polyester polyol-based PUs, with the process taking several days or weeks [13,14]. However, the biodegradability of PUs can be improved greatly by introducing appropriate biodegradable fillers as physical and chemical crosslinkers.

Among the available biodegradable fillers, cyclodextrins are produced from starch by means of enzymatic conversion. These molecules are used in food, pharmaceuticals, drug delivery, and chemical industries, as well as in agriculture and environmental engineering. In particular, β -cyclodextrin (β -CD) is composed of seven d-glucopyranose residues linked by α -1,4-glycosidic bonds. β -CD has both a hydrophobic internal cavity and a hydrophilic exterior owing to hydroxyl groups. A rotaxane, i.e., a mechanically interlocked topology consisting of a dumbbell shaped linear molecule threaded by a macrocycle, is formed between α -CD and polyethylene glycol. However, this is avoided with β - or γ -CD possessing larger cavities that cannot establish strong interactions with the linear guest chain. Also the pendant $-CH_3$ groups of PPG increase the cross section of the linear polymer which is too large to penetrate the narrow empty cavity of the cyclic host [15].

On the other hand, because of the external hydroxyl groups, β -CD has the ability to act as a multifunctional crosslinker and can be used for chemical reactions with appropriately modified organic polymers to form chemical hybrids. Typical cyclodextrins exhibit thermal stability, with degradation temperatures of about 300 °C, and are well known for

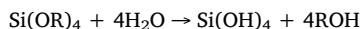
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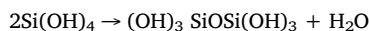
their ability to form inclusion complexes with a variety of components [16–19]. In addition, β -CD is degraded in α -amylase solution within several hours and has high solvent sorption properties [20–23].

The most commonly employed preparation procedure for hybrid materials is the sol-gel process, which can produce crosslinking at relatively low temperatures. This reaction involves two steps: hydrolysis and condensation. For example,

Hydrolysis:



Condensation:



where R is an alkyl group. These reactions depend on the concentration, type of solvent, and pH of the solution [23].

In this study, we introduced β -CD molecules into the main chain of WPU via a sol-gel type reaction to reinforce the chains and render biodegradability. For this, the silanol groups of WPU were reacted with the hydroxyl groups of β -CD at various ratios to examine the effects of β -CD as a multifunctional crosslinker and biodegradable filler.

The mechanical, thermal, surface and, solvent sorption properties, as well as the biodegradable properties, of the obtained polymers were carefully analyzed.

2. Experimental

2.1. Materials

Polypropylene glycol (PPG; Mn = 400, KPX, Korea) was dried and degassed at 80 °C under vacuum for 3 h prior to use. Dicyclohexylmethane-4,4'-diisocyanate (H_{12} MDI, Sejinci), dimethylol butanoic acid (DMBA, Aldrich), 3-isocyanatepropyltriethoxysilane (ICPTES, Acros), dibutyltin dilaurate (DBTDL, Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich), α -amylase (from *Bacillus amyloliquefaciens*, Aldrich), and β -cyclodextrin (β -CD, Aldrich) were used as received. Triethylamine (TEA, Aldrich) was dried over 4 Å molecular sieves before use. The formulation used to prepare the WPU is given in Table 1.

2.2. Synthesis of WPU/ β -CD chemical hybrids

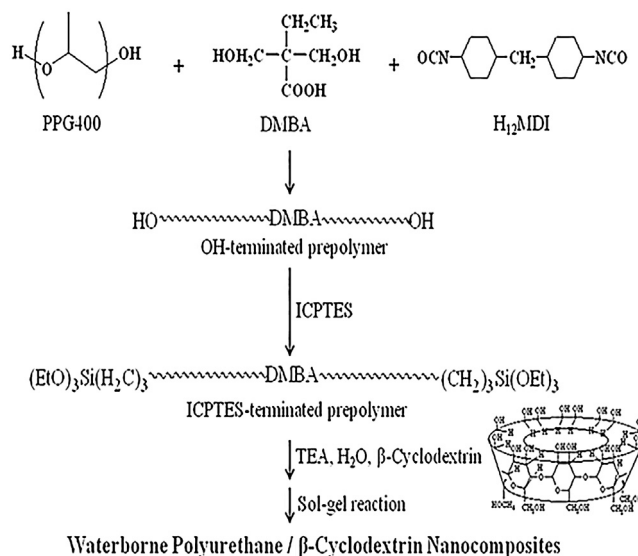
A 500 mL round-bottom, four-necked separable flask with a mechanical stirrer, thermometer, and condenser with a drying tube and N_2 inlet was used as the reactor. The reaction was carried out in a constant temperature oil bath. Molar excess PPG and DMBA as ionic center were first charged and H_{12} MDI added. The urethane reaction was carried out at 70 °C and a hydroxyl-terminated prepolymer was synthesized. Then, ICPTES was added and reacted with the terminal hydroxyl groups of the prepolymer to form silanized PU. Then, ICPTES-capped silanized PU

Table 1

Formulations to prepare WPU/ β -CD nanocomposites (number is the weight in grams, total solid = 30 g).

Series	Waterborne Polyurethane					β -Cyclo dextrin	[OEt]:[OH]*
	Ionic group		Soft segment		ICPTES		
	DMBA	H_{12} MDI	PPG400	H_{12} MDI			
PC00	0.9	0.61	16.08	10.55	1.86	–	–
PC05						0.975	1:0.5
PC10						1.950	1:1
PC15						2.925	1:1.5
PC20						3.90	1:2

[OEt]: [OH]* = Equivalence ratios of ICPTES-terminated prepolymer (OEt): β -cyclodextrin (OH).



Scheme 1. Reaction scheme for synthesizing WPU/ β -CD chemical hybrids.

was cooled down to 40 °C and DMBA as an ionic center was neutralized by TEA for 1 h. Then, β -CD dissolved in 70 mL of distilled water was added to the ICPTES-capped silanized PU and stirred at 1000 rpm using a mechanical stirrer to obtain an aqueous dispersion. Distilled water initiates hydrolysis of the ethoxy groups of ICPTES with DBU as a catalyst. Subsequently, the aqueous dispersion was cast onto a Teflon plate and dried for two days at 30 °C. Then, condensation reactions between the silanol groups of ICPTES and the hydroxyl groups of β -CD occurred during drying at 80 °C for two days. The reaction scheme is shown in Scheme 1.

2.3. Characterization

The formation of hydroxyl-terminated PU and ICPTES-capped prepolymer, and the condensation reactions between the silanol groups of ICPTES and the hydroxyl groups of β -CD were confirmed by Fourier transform infrared (FT-IR) spectroscopy (Mattson Satellite). The average diameters of particles in the dispersion were determined by photon correlation spectroscopy (Particle size analyzer N5, Beckmann Coulter). The gel fraction was determined from the weights of the samples before (W_{polymer}) and after (W_{network}) extraction in acetone using the following Eq. (1) [24].

$$\text{Gel fraction (\%)} = \frac{W_{\text{network}}}{W_{\text{polymer}}} \times 100 \quad (1)$$

The mechanical properties at 25 °C were examined using a universal testing machine (UTM, Lloyd) at a crosshead speed of 500 mm/min. Specimens for the tensile tests were prepared according to ASTM D 1822. Shore A hardness was determined using an indentation hardness tester according to ASTM D 2240-75. Eight sheets of 1 mm thickness were stacked to achieve a thickness of about 8 mm. The measurement was carried out by pressing the sample sheet on a type-A durometer at a load of 9.8 N.

The thermal properties were examined using differential scanning calorimetry (DSC, Seiko DSC 220) from –60 to 100 °C at a heating rate of 10 °C/min. About 8 mg of sample was placed in an alumina crucible and heated at 5 °C/min under a N_2 atmosphere. Thermal degradation was studied using thermogravimetric analysis (TA Instruments, TGA Q50) under such conditions.

The surface properties were analyzed by determining the contact angles of the dried films with deionized water using a conventional contact angle goniometer (Theta Lite100, KSV).

The biodegradation test was done in a phosphate buffer solution

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