Biodegradable waterborne polyurethane with modified hydroxyethylcellulose

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Abstract. The waterborne polyurethane (WPU)/hydroxyethyl cellulose (HEC) chemical hybrids were synthesized by incorporating vinyltrimethoxysilane (VTMS) modified HEC (VC) into the WPU. Effects of VC on the contact angle, gel content, thermal and mechanical properties of the cast films, and biodegradation in cellulase solution were evaluated. It was found that the VTMS modified HEC provided the WPU with multifunctional crosslinks as well as conventional reinforcing fillers and biodegradability.

Keywords: mechanical properties, waterborne polyurethane, hydroxyethylcellulose (HEC), chemical hybrids, biodegradation

1. Introduction

Polyurethanes (PUs) are versatile engineering materials which are synthesized by a simple polyaddition reaction of isocyanate, polyol, and chain extender. They have widely been used as elastomers, adhesives, coatings, sealants, primer, sports goods, medical devices, textile finish aside from the various foam products [1]. The worldwide consumption of PU is over 13 million tons per annum and steadily their usage as high functional and performance materials [2].

Conventionally PU was produced in organic solvent including methyl ethyl ketone, acetone, dimethyl formamide. The solventborne PU (SPU) has great freedoms in molecular design and advantages in properties and processing. For example, aromatic as well as aliphatic isocyanates are used in SPU, while waterborne PU (WPU) is vulnerable to aromatic type due to its fast reaction with water. Drying is also faster with SPU than WPU since water molecules are tightly bound to the ionic species which, on the other hand, is essential for dispersion in water [3–5]. How-

ever, due to the safety and environmental problems, WPU is steadily replacing SPU and it is now applied in many areas of application including numerous flexible substrates, adhesives, and coating industries [6, 7]. Also problems related to WPU can be resolved greatly by proper molecular designs and hybridization with other materials [8–11].

On the other hand, growing land pollution and shortage of landfill sites with polymer wastes led to concern about biodegradation [12]. Therefore, PU has been found to be allowed to biodegradation by microorganisms. Microbial degradation of PU depends on chemical groups in molecular chains, orientation, and crosslink density etc. The biodegradability of PU by microorganisms is mainly limited to ester and lactone type polyol based PU [13, 14]. However, biodegradability of polyether based PU can be improved greatly by introducing proper biodegradable fillers. However, cases where fillers are chemically incorporated into WPU as chemical crosslink are sparse. Among the biodegradable fillers, starch has widely used as an additive to prepare disintegration plastic

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since it is thermally stable and causes minimum melt viscosity increases [15–17]. However, starch based biodegradable products generally exhibit water sensitivity and poor mechanical properties. Cellulose is a most abundant naturally occurring polymer of glucose, found as the main constituent of plants and natural fibers such as cotton and linen. In addition, chemical modification of cellulose, usually involving esterification or etherification of the hydroxyl groups, is easily performed to produce cellulose derivatives, named cellulose derivatives, which are easily processed and find large application in the industry. Cellulose and its derivatives are environmentally friendly, as they are degradable by several bacteria and fungi present in air, water and soil [18, 19], which are able to synthesize cellulose-specific enzymes i.e. cellulases. The biodegradation of cellulose has been widely investigated, and progressively leads to decreased molecular weight, lower mechanical strength and increased solubility. Moreover, higher biodegradation rates of cellulose are likely yielded by lower degrees of crystallinity and improved water solubility [20].

Hydroxyethylcellulose (HEC) is a promising material for biodegradation because of the abundant supply, low cost, renewability, and ease of chemical modifications. HEC is a cellulose derivate that is obtained via etherification of cellulose, which involves the reaction of the hydroxyl group of cellulose. So, HEC has water-solubility [19]. It should be mentioned that polyurethanes are not completely degraded with only biodegradable fillers in laboratory time frame as far as the soft segments are not from ester or lactone type polyols.

In this work HEC was for the first time chemically modified by using vinyltrimethoxysilane (VTMS) to form VTMS modified HEC (hereafter called VC) via the sol-gel reaction route. VC was then incorporated into the WPU by covalent bonding. The effects are

twofold, i.e., to provide PU with multiple crosslinks and biodegradability via HEC molecules. Multiple crosslinks enhance thermal and mechanical properties via the ideal rubber theory [21]. In addition enhanced HEC/WPU miscibility as compared with simple blend should also contribute to the enhanced properties. Effects of cellulose content on the contact angle, gel content, thermal, and mechanical properties of the cast films as well as the biodegradation of the films in cellulase solution, an enzyme that catalyzes the breakdown of cellulose into sugars, were evaluated in terms of weight loss and tensile property change as a function of incubation time.

2. Experimental

2.1. Materials

Polypropylene glycol ($M_n = 600$ g/mol, KPX Chemicals, Ulsan, Korea) and 1,4-butanediol (BD; Aldrich, St Louis, USA) were dried and degassed at 80 °C, 1–2 mm Hg, for 3 h before use. Dimethylol butanoic acid (DMBA; Aldrich, St Louis, USA) was dried at 50 °C for 48 h in a vacuum oven. Isophorondiisocyanate (IPDI, TCI, Fukaya, Japan), dibutyltin dilaurate (DBTDL; Aldrich, St Louis, USA), HEC (Aldrich, St Louis, USA), vinyltrimethoxysilane (VTMS; Aldrich, St Louis, USA), acetate buffer solution (pH 5, Aldrich, St Louis, USA), cellulase (Bacillus amyloliquefaciens, Aldrich, St Louis, USA) were used as received. Triethylamine (TEA; Aldrich, St Louis, USA) was dried over 4 Å molecular sieves before use. The formulation to prepare the WPU is given in Table 1.

2.2. Modification of HEC

The desired amount of HEC was dissolved in 70 g of water at 70 °C. Subsequently it was cooled down to 60 °C and hydrochloric acid was added to adjust pH 2 for the hydrolysis of VTMS, followed by condensation

Table 1. Formulations to prepare WPU/VC chemical hybrids.

Series	Polyurethane							VTMS modified HEC [wt%]
	Ionic group		Soft segment		Hard segment		HEA	
	DMBA	IPDI	PPG600	IPDI	1.4BD	IPDI		
WPU	0.9	2.68	11.69	4.33	2.60	6.40	1.39	—
VC01								1
VC02								2
VC03								3
VC04								4
VC05								5

(Prepolymer molecular weight = 5000 g/mole, number is the weight in grams, total solid = 30 g)

Figure 1. Modification of HEC using VTMS via sol-gel type reaction.

between the hydrolyzed VTMS and HEC to obtain vinyl modified HEC. The modification procedure is illustrated in Figure 1 [22].

2.3. Synthesis of WPU and UV cure

A 500 mL round-bottom, four-necked separable flask with a mechanical stirrer, thermometer, and condenser with drying tube and nitrogen inlet was used as reactor. The reaction was carried out in a constant temperature oil bath. DMBA, PPG and IPDI were first charged and reacted for about 3 h at 70 °C to obtain NCO terminated ionomer segments. In this way, ionic groups are located in soft segments of PU, which give much finer and stable dispersion as compared with the conventional ionic groups in hard segments [21]. Then 1,4-BD and an excess amount of IPDI were added to build up hard segments with isocyanate termini which were subsequently capped with HEA. Then the prepolymers were cooled to 60 °C and neutralized with TEA for 1 h. An aqueous dispersion was obtained by adding water (35 °C) to the mixture. Then the modified HEC was added and stirred for about one hour to homogenize the mixture. Subsequently, a photoinitiator was added and stirred for the next one hour. Then the mixture was cast onto a Teflon plate and partially dried for two days at 35 °C before it was cured by an UV lamp. Finally the UV cured film was dried for two days at 70 °C. The reaction procedure is shown in Figure 2.

2.4. Characterizations

The hydrolysis reaction of VTMS, and condensation reaction between VTMS and starch, and end capping reaction of NCO terminated prepolymer with HEA, and the UV cure reaction were followed by the IR measurements. IR spectra were measured on a Mattson Satellite Fourier transform infrared spectrometer (FT-IR, Bosque, USA). The sample was obtained by

Figure 2. Reaction scheme to synthesize WPU/VC chemical hybrids.

casting films on the KBr pellet. Particle size of the dispersion was measured by particle size analyzer (Beckman Coulter N5, Indianapolis, USA), using a He-Ne laser (633 nm). The contact angles of the dispersion cast films with a deionized water drop at room temperature were measured using a conventional contract angle goniometer (G-1, Erma, Tokyo, Japan) [23].

To measure the gel content of film, film of known weight (W_0) was put in DMF for 24 h, dried for 48 h and weighed as the network weight (W_n). The gel content [%] (Equation (1)) was calculated according to [24]:

$$\text{Gel contents [\%]} = \frac{W_n}{W_0} \cdot 100 \quad (1)$$

Thermal analyses were carried out with differential scanning calorimetry (DSC, Seiko DSC 220, Tokyo, Japan) at a heating rate of 10 °C/min. For thermogravimetric analysis (TA Instruments, TGA Q50, New Castle, USA), 8–10 mg of sample was put in an alumina crucible and heated at 5 °C/min under nitrogen atmosphere. Mechanical properties were measured with a universal testing machine (UTM, Lloyd, London, England) at a crosshead speed of 500 mm/min. Tensile test specimens were prepared according to ASTM D 1822. Tests were made at room temperature (20 °C) and at least five runs were made to report the average. Biodegradations of the film were tested in a sodium-phosphate buffered solution (pH 5, 37 °C) with cellulase (0.5 wt%).

3. Results and discussion

3.1. FT-IR spectra analysis

Figure 3 shows the characteristic absorption peak of Si–O–CH₃ of VTMS has completely disappeared upon hydrolysis reaction at the prevailing experimental conditions. Upon the condensation reaction between the hydrolyzed VTMS and HEC, characteristic vinyl peaks appeared at 1410 and 810 cm⁻¹.

Figure 4 shows that the NCO absorption peak at 2270 cm⁻¹ disappeared and vinyl peak at 807 cm⁻¹ newly appeared upon capping the NCO terminated

Figure 3. FT-IR spectra for virgin and VTMS modified HEC.

Figure 4. FT-IR spectra for NCO terminated prepolymer, HEA capped prepolymer, and UV cured WPU/VC chemical hybrid.

prepolymers with HEA, while the vinyl peak disappears upon UV curing.

3.2. Particle size of dispersion and contact angle of the cast film

The particle size of the dispersion increases with the addition of VC up to 2%, beyond which it decreases (Table 2). This implies that the VTMS modified cellulose (VC) which was added to the aqueous phase of WPU preferentially migrates into the particles due to the concentration gradient. On the other hand, the decreased particle size of dispersion at high VC contents implies that VC molecules are subject to aggregation in aqueous phase. Aggregation in aqueous phase gives rise to a decreased concentration gradient and decreased penetration of VC molecules into the PU particles as well.

The contact angle of cast film decreased from 78 to 66° with 1% VC due to the great hydrophilicity of VC over WPU (Figure 5, Table 2). However, with 2% VC contact angle increased over the WPU, implying that crosslink effect is rather more pronounced than the hydrophilicity. As the VC content further increases

Table 2. Particle size, contact angle, gel fraction of WPU/VC hybrid cast films.

Series	Particle size [nm]	Contact angle [°]	Gel fraction [%]
WPU	72.4	78.0	76.45
VC01	80.3	66.0	78.93
VC02	84.7	79.5	85.42
VC03	80.1	77.5	81.35
VC04	78.7	61.5	77.62
VC05	76.4	49.5	74.41

Figure 5. Contact angle of WPU/VC hybrids.

contact angle significantly decreases down to 49.5° at 5% VC. This implies that the crosslinking reaction becomes less significant at high VC contents to be seen from the gel content measurements to follow. Contact angle of a solid surface depends on the chemical composition and surface morphology. The crosslink generally reduces spreading of liquid molecules on the substrate surfaces [25].

3.3. Gel contents

Gel content is directly related to the crosslinking density. According to a classical theory of French, the crosslink density is directly proportional to the square of the gel fraction based on an empirical correlation [26]. With the addition of VC, gel content of the cast film increases from about 76% (virgin) to a maximum of 85% at 2% VC, implying that crosslinking density of the hybrids is maximum at this composition. Beyond 2%, gel content decreases to 74% at 5% VC (Table 2), accompanied by crosslinking density. Virgin WPU is crosslinked by the UV cure of HEA termini, which contributes to gel content. On the other hand in hybrids, many vinyl groups of VC molecule act as multifunctional crosslinks upon UV cure, which augment gel content further (2–4% VC). However, at 5% VC, VC molecules are vulnerable to aggregation in aqueous phase and reduce crosslinking reactions between PU and VC molecules.

3.4. Thermal properties

WPU synthesized in this work is amorphous where soft segments and hard segments are phase mixed due to the asymmetric molecular structures of polyol (PPG) and diisocyanate (IPDI). This gives a single glass transition temperature (T_g) of the polymer. T_g of the cast film increases with VC content up to 2%, beyond which it decreases (Figure 6, Table 3). The increase in T_g is related primarily to the crosslinking density of the polymer as described by the DiBenedetto's equation (Equation (2)) [27]:

$$T_g = K \cdot T_{g,0} \frac{X_c}{1 - X_c} + T_{g,0} \quad (2)$$

where $T_{g,0}$ is the T_g of the uncrosslinked polymer, X_c is the mole fraction of crosslinker, and K is a constant. The VC provides the materials with multifunctional crosslinks and the effect was most pronounced with 2% VC (VC02). High VC contents (VC04, VC05) are most vulnerable to particle aggregation, which decrease the crosslinking sites of PU to keep T_g at the level of virgin WPU in spite of filler loadings. TGA data are shown in Table 3 and Figure 7 where 10% weight loss temperature is decreased and the 90% weight loss temperature is increased with the addition of VC, and the effect is most pronounced

Table 3. Glass transition temperature and thermal degradation of WPU/VC hybrid cast films.

Series	T_g [°C]	10% weight [°C]	90% weight [°C]	Residue [wt%]
WPU	22.33	283.65	342.05	0.15
VC01	23.16	281.41	342.26	0.65
VC02	26.95	280.44	344.73	0.93
VC03	23.24	278.62	347.14	0.95
VC04	22.89	278.41	347.36	1.36
VC05	20.02	267.89	373.04	2.93

Figure 6. Glass transition temperature of WPU/VC hybrids.

Figure 7. Thermal degradation of WPU/VC hybrids.

with 5% VC. On the other hand, it is expected that crosslinking retards burning due at least to the compact structure, and this is not seen from the data. It seems that VC dominates burning rate of the chemical hybrids. The bulky structure of VC accelerates the early burning while the less flammable nature of VC retards complete burning, leaving more residues at 700 °C, and the effect seems to be most pronounced with 5% VC where 10% weight loss temperature is decreased by about 16 °C and 90% weight loss temperature increased over 31 °C.

3.5. Mechanical properties

Figure 8 and Table 4 show the stress–strain behavior of the hybrids at 24 °C. The Young’s modulus and break strength of the hybrids increased up to 2 wt% VC beyond which they decreased. At high contents, aggregation of VC reduced crosslinking density and mechanical properties of amorphous polymers. According to the ideal rubber theory modulus (E) is given by Equation (3) [28]:

Figure 8. Stress-strain behaviors of WPU/VC hybrids.

Table 4. Mechanical properties of WPU/VC hybrid cast films.

Series	E [MPa]	σ_b [MPa]	ε_b [%]
WPU	65.28	4.16	281.2
VC01	105.65	6.28	222.6
VC02	138.40	7.54	187.5
VC03	117.42	6.67	202.0
VC04	98.60	6.03	230.6
VC05	89.65	5.66	238.2

$$E = 3NkT \quad (3)$$

where T , N , and k are absolute temperature, number of subchains bridging the crosslinking points per volume, and the Boltzmann constant. As expected, variation of modulus is the same with gel fraction, viz., the crosslinking density. On the other hand, elongation at break shows exactly the opposite tendency to the modulus and strength. It seems that the mechanical behavior of the amorphous polymers mainly depends on the crosslinking density which is shown in terms of gel content.

3.6. Biodegradation

Figure 9 shows the weight loss of the dried film vs. incubation time in a buffer solution with cellulase (0.5%). The weight loss of virgin WPU is negligible since cellulase selectively hydrolyzes HEC chains and ether type polyol (PPG) is virtually insensitive to hydrolysis. The amount of hybrid weight loss increases with the amount of VC incorporated, implying that particle aggregation is immaterial regarding biodegradation. It is also noted that the amount of weight loss is much greater than the amount of VC

Figure 9. Biodegradation of WPU/VC hybrids.

incorporated. This implies that WPU segments between VC molecules as well as the VC species are also degraded and removed from the networks.

4. Conclusions

VTMS modified HEC (VC) molecules are chemically incorporated into WPU by covalent bond and provided the materials with increased particle size, contact angle, tensile modulus and strength, and glass transition temperature (T_g) with maxima at 2% VC due to the multifunctional crosslinking effect VC. The increased crosslinking density was verified by the increased gel fraction. Beyond 2% VC, the effects were less pronounced due presumably to the aggregations of VC molecules. Aggregations in aqueous phase were indirectly seen from the decreased particle size of dispersion, implying less of VC molecules were migrated into the WPU particle. On the other hand, biodegradation of the hybrids in buffer solution of cellulase was evident and the effect was more pronounced with more VC, regardless of the particle aggregation. The fact that the amount of weight loss was much great than the amount of VC added indicates that WPU segments have also been biodegraded and removed from the networks.

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