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Covalent incorporation of starch derivative into waterborne polyurethane for biodegradability

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ABSTRACT

We introduced vinyltrimethoxysilane (VTMS) modified starch into the waterborne polyurethane (WPU) by covalent bond (hereafter called hybrids or chemical hybrids) to enhance the biodegradability of WPU. Effects of starch content on the biodegradation of the chemical hybrids in α-amylase solution and buffer solution were evaluated in terms of weight loss and tensile property change with incubation time, contact angle, Shore A hardness, and scanning electron microscopy morphology. The VTMS modified starch provided the chemical hybrids with multifunctional crosslinks and significantly enhanced tensile modulus and strength of the hybrids. When the hybrids were incubated in α-amylase solution, maximum weight loss of 15% and tensile strength decrease of 60% were noted in 10 days with 10% starch incorporation. Notably, these property changes were much smaller with physical blend of WPU and unmodified starch than those of chemical hybrids.

1. Introduction

Polyurethanes (PUs) are a most versatile engineering material which is synthesized by a simple polyaddition reaction of polyol, isocyanate, and chain extender. They find a variety of industrial applications including coatings, adhesives, sealants, elastomers (abbreviated by CASE), primer, sports goods, medical devices, textile finish aside from the various foam products (Barikani, Zia, Bhatti, Zuber, & Bhatti, 2008; Kim & Kim, 2005; Zia, Barikani, Zuber, Bhatti, & Sheikh, 2008). The worldwide annual production of PU in 2010 is over twelve million tons, and ever increasing by about 5% annually.

Conventionally PU was produced in solvent typically in acetone, dimethyl formamide (DMF) and methyl ethyl ketone (MEK). The solventborne PU (SPU) has great freedoms in molecular design and advantages in 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 much faster with SPU than WPU where water molecules are tightly bounded to the ionic species which, on the other hand, is essential for dispersion in water. Due to the safety and environmental consideration, WPU is steadily replacing SPU since late 1960s, and it is now legislated in many countries in many areas of applications including primers, adhesives, and coatings industries (Jung, Kim, Kang, & Kim, 2010; Lamba, Woodhouse, & Cooper, 1998; Lu & Larock, 2008; Park et al., 2009; Petrie, 2000).

However, lack of degradability and growing land pollution have become serious with polymeric materials and led to concern about biodegradation. Polyurethane has been found to be susceptible to biodegradation by naturally occurring microorganisms (Howard, 2002). Microbial degradation of polyurethanes depends on the many properties of the polymer such as molecular orientation, crystallinity, cross-linking and chemical groups present in the molecular chains which determine the accessibility to degrading-enzyme systems. However, microbial degradation of polyurethane is mainly limited to polyester type, which is hypothesized to be mainly due to the hydrolysis of ester bonds by the esterase enzymes.

On the other hand, starch is a most promising material for biodegradable plastics because of the abundant supply, low cost, renewability, and ease of chemical modifications (Cao, Chang, & Huneault, 2008; Galliard, 1987; Mathew & Dufresne, 2002; Whistler & Bemiller, 2009). However, compared to conventional synthetic thermoplastics, starch based biodegradable products exhibit water sensitivity, brittleness, and poor mechanical properties (Santayanon & Wootthikanokkhan, 2003). Consequently, a number of physical and chemical methods have been used to solve this problem. Among them blending with biodegradable synthetic polymers offers a relative simple and effective route to enhance the properties of starch based biodegradable materials. These include starch blends with WPU from poly(ε-caprolactone) (Cao et al., 2008; Zou et al., 2011), castor oil (Lu, Tighzert, Dole, & Erre, 2005; Wu, Wu, Tian, Zhang, & Cai, 2008) and rapeseed oil (Lu, Tighzert,

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Table 1
Formulations to prepare WPU/starch chemical hybrids (number is the weight in grams, total solid = 30 g).

	Soft segment		Hard segment		Ionic group		HEA	VTMS	Starch (wt%)
	PTMG650	HDI	1,4-BD	IPDI	DMBA (wt%)	HDI			
WPU	16.55	4.28	2.60	0.64	3	2.70	2.32	–	–
BS05									5
VS02								0.51	2
VS05								1.29	5
VS10								2.64	10

Berzin, & Rondot, 2005). The blends were miscible at low WPU content (<20%) via the hydrogen bonding between the hydroxyl group of starch and urethane group of WPU. The environmentally friendly nature of WPU and biodegradability of ester type polyol were considered in these works.As far as the present authors are concerned, direct incorporation of starch into the WPU chain by covalent bonding is sparse in the open literature. In this work we introduced vinyltrimethoxysilane (VTMS) modified starch into the WPU by covalent bond to enhance the miscibility and biodegradability of WPU. Effects of starch content on the biodegradation in α-amylase solution, an enzyme that catalyses the breakdown of starch into sugars and buffer solution were evaluated in terms of weight loss and tensile property change as a function of incubation time, contact angle, hardness and scanning electron microscopy morphology of the cast films. In this way, starch molecules act as multifunctional crosslinks to bridge the polyurethane molecules in the networked structure. Simple blend of WPU and starch was also prepared for comparison.

2. Experimental

2.1. Materials

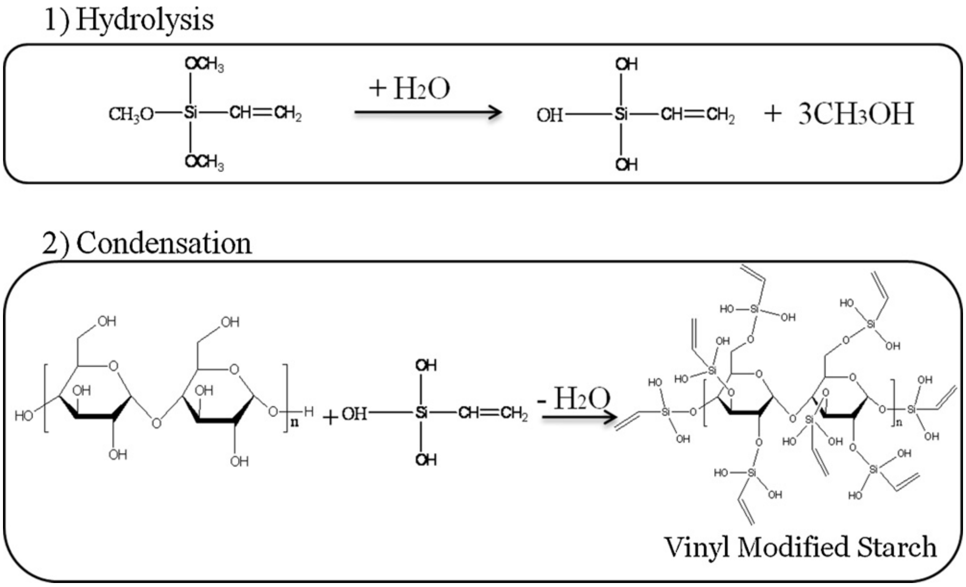
Poly(tetramethylene adipate) glycol (Mn = 650 g/mol, Union Chemicals) and 1,4-butanediol (BD; Aldrich) were dried and degassed at 80 °C, 1–2 mm Hg, for 3 h before use. Dimethylol butanoic acid (DMBA; Aldrich) was dried at 50 °C for 48 h *in vacuo*. Isophorondiisocyanate (IPDI, TCI), 1,6-hexamethylene diisocyanate (HDI; Aldrich), dibutyltin dilaurate (DBTDL; Aldrich), starch (Aldrich), vinyltrimethoxysilane (VTMS; Aldrich), buffer solution (pH 7, Aldrich), α-amylase (*Bacillus amyloliquefaciens*, Aldrich) were used as received. Triethylamine (TEA; Aldrich) was dried over 4 Å molecular sieves before use. The formulation to prepare the WPU is given in Table 1.

2.2. Modification of starch

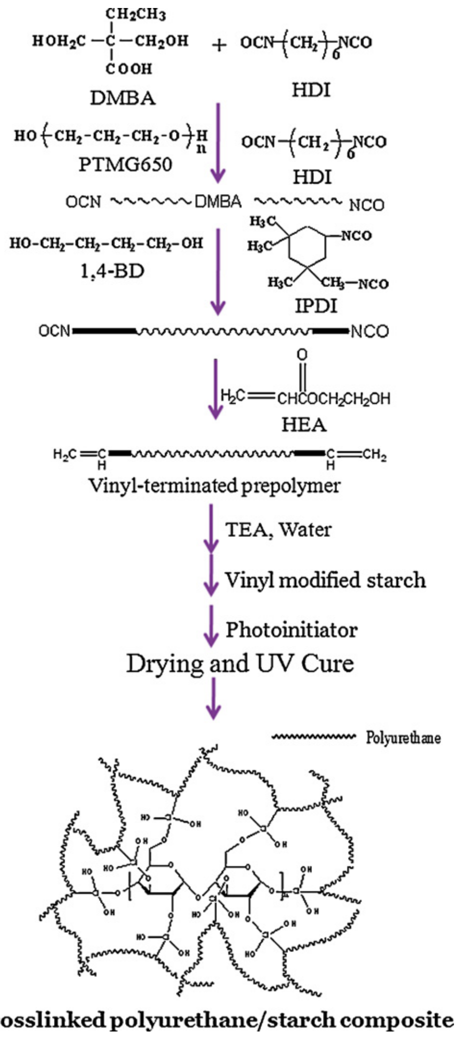
The desired amount of starch was dissolved in 70 g of water at 120 °C. Subsequently it was cooled down to 60 °C and hydrochloric acid was added to adjust pH 2 for the hydrolysis of VTMS, followed by condensation between the VTMS and starch to obtain vinyl modified starch (Prachayawarakorn, Sangnitidej, & Boonpasith, 2010). Modification is illustrated in Scheme 1.

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 N_2 inlet was used as reactor. The reaction was carried out in a constant temperature oil bath. DMBA and HDI were first charged and reacted for about 3 h at 70 °C to obtain NCO terminated ionomer segments. Then 1, 4-BD and an excess amount of IPDI were added and adducted at the chain termini 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 with agitation using a tubing pump. Then the modified starch was added and stirred for about one hour to homogenize the mixture. Subsequently, a photoinitiator was added and stirred for the next one hour. The mixture was cast onto a Teflon plate and partially dried for two days at 35 °C before it was cured



Scheme 1. Schematic representation of vinyl modified starch.



Scheme 2. Synthetic route to prepare WPU/starch chemical hybrids.

by an UV lamp. Finally the UV cured film was dried for two days at 70 °C (Scheme 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 (FT-IR) spectrometer. The sample was obtained by casting films on the KBr pellet. Surface morphology of the films, which were incubated in α-amylase for 10 days, was examined under the scanning electron microscopy (SEM, Hitachi S430, Japan).

Particle size of the dispersion was determined by a particle size analyzer (Beckman Coulter, N5).

Biodegradation was tested in a buffer solution and in α-amylase solution which expedites degradation. Mechanical properties were measured with a universal testing machine (Lloyd) at a crosshead of 500 mm/min. Microtensile test specimens were prepared according to ASTM D 1822. Tests were made at room temperature and at least five runs were made to report the average. Shore A hardness was measured using an indentation hardness tester according to ASTM D 2240–75. Eight sheets with 1 mm thickness were stacked to about 8 mm thickness. The measurement was carried out by pressing the sample sheet on a type-A durometer at a load of 9.8 N.

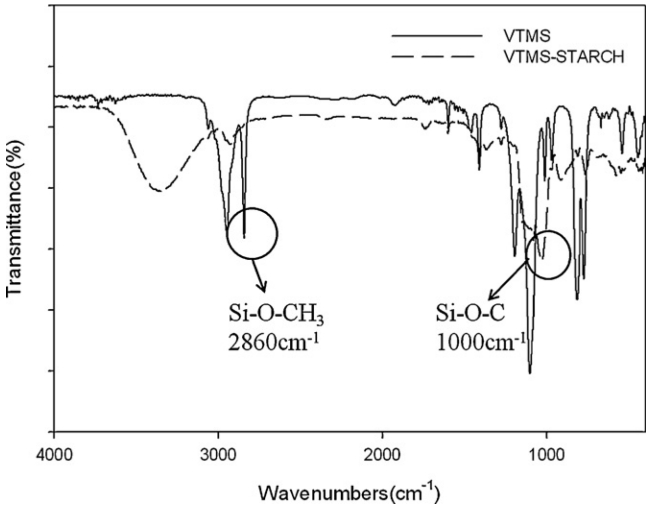


Fig. 1. FTIR spectra of virgin VTMS and after condensation reaction with starch.

3. Results and discussion

3.1. Vinyl modification and HEA capping

Fig. 1 shows the characteristic absorption peak of Si–O–CH_3 has completely disappeared upon hydrolysis reaction of VTMS at the prevailing experimental conditions. Upon the condensation reaction between the hydrolyzed VTMS and starch, Si–O–C peak appears at around 1000 cm^{-1}.

Fig. 2 shows that the NCO absorption peak at 2270 cm^{-1} disappears upon capping the NCO terminated prepolymers with HEA, while the vinyl peak at 807 cm^{-1} disappears upon UV curing (Jung, Jeong, & Kim, 2010).

3.2. Particle size and surface properties

The particle sizes increases with the addition and increasing amount of starch (Table 2) (Lu, Tighzert, Berzin, et al., 2005). This implies that the starch solution added to the dispersion is preferentially migrated into the WPU particles due to the concentration gradient. At the same content of starch, modified starch gives greater particle size than the blend with virgin starch due both

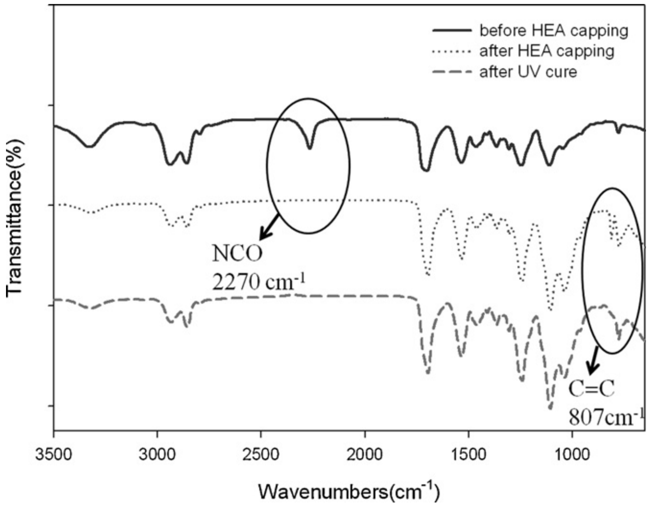


Fig. 2. FTIR spectra of NCO terminated prepolymer, after HEA capping, and after UV cure.

Table 2
Particle size of the dispersion, contact angle and Shore A hardness of the cast film.

	Particle size (nm)		Contact angle (°)	Hardness (Shore A)
	Before starch addition	After starch addition		
WPU	104.40	106.11	65	65
BS05	104.40	118.47	62	67
VS02	104.40	127.76	68	71
VS05	104.40	142.60	72	76
VS10	104.40	144.67	80	82

to the enhanced miscibility with WPU and enlarged size of vinyl modified starch. Contact angle of the blend cast film decreases below WPU due to the increased hydrophilicity of the film (Table 2). However, contact angle increases with the addition and increasing amount of modified starch. This implies that crosslink effect is more significant than hydrophilicity increase. Hardness is an important property of coating which finds an ample application of WPU. Hardness of the cast film increases with the addition and increasing amount of modified starch (Table 2). This again is due to the increased crosslink density of the film. A small increase with blend seems due to the strong hydrogen bond between WPU and starch.

3.3. Biodegradation

Fig. 3 shows the weight loss of film vs. incubation time in a buffer solution. About 5% of the original weight is lost in about five days for the chemical hybrids and blend, with a slight difference depending on the amount of starch. Degradation of the hybrids in α-amylase is expedited by about three times as compared with that of buffer solution (Fig. 4). The weight loss of VS05 in α-amylase solution is approximately 2.5 times of the starch added. α-Amylase is a calcium metalloenzyme that catalyses the breakdown of starch into sugars at random locations along the starch chain, and hence much great weight loss is expected. The weight loss of the hybrids is greater than the amount of starch incorporated into the hybrids. This means that the WPU segments crosslinked by the VTMS modified starch are removed from the network along with the starch. To verify this, we measured the IR spectra of the precipitates which show the characteristic urethane peak at 1720 cm^{-1} (Fig. 5). Among the hydrolysis products, glucose is dissolved in solution while the urethane segments are precipitated as shown in the figure. The weight loss of WPU and blend in α-amylase is essentially the same with the buffer solution. Result for WPU is expected since α-amylase selectively hydrolyses starch chains. Also, the weight loss for the blend is essentially the same with the amount of starch blended to the WPU (5%). This implies that the starch molecules in blend are independently degraded and do not interact with the WPU in the process of degradation.

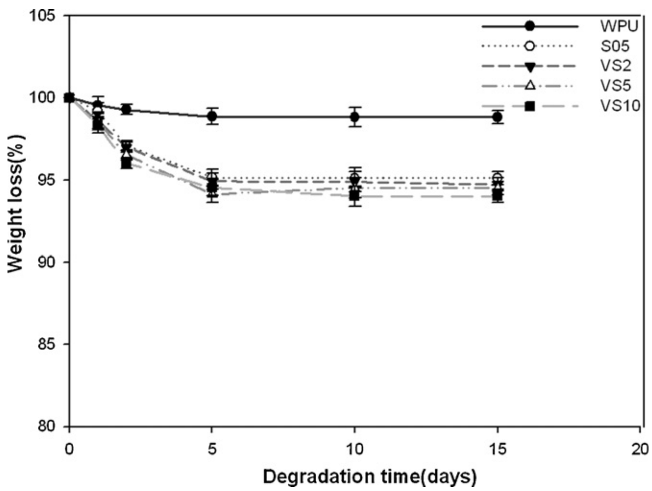


Fig. 3. Weight loss of the film vs incubation time in a buffer solution.

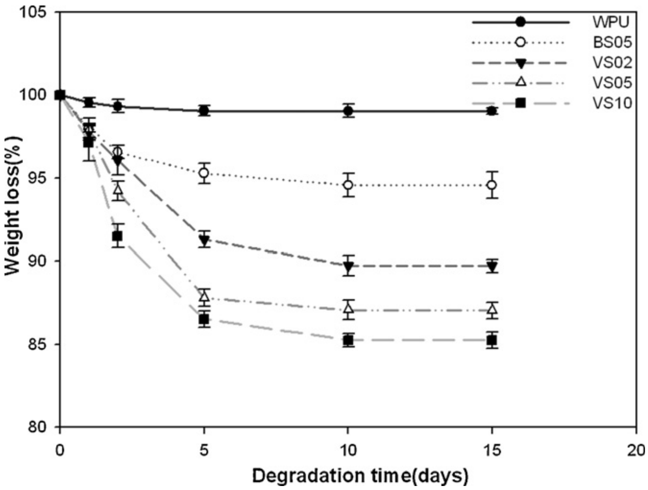


Fig. 4. Weight loss of the film vs incubation time in α-amylase solution.

3.4. Mechanical properties

Fig. 6 shows the tensile behavior of the films with different incubation times with the detailed data in Table 3. The as cured films show that initial modulus and break strength monotonically

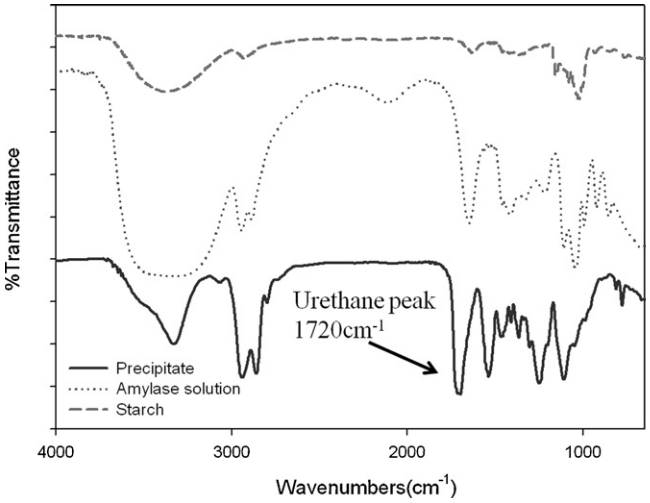


Fig. 5. FTIR spectra of precipitates after hydrolysis of starch chains.

Table 3
Initial modulus break stress and strain of the cast film at different incubation times.

	Incubation time								
	0 day			3 days			10 days		
	Initial modulus [MPa]	Break strength [MPa]	Break strain [%]	Initial modulus [MPa]	Break strength [MPa]	Break strain [%]	Initial modulus [MPa]	Break strength [MPa]	Break strain [%]
WPU	20.1	23.3	379.4	19.5	20.7	363.1	18.0	20.2	363.4
BS05	23.6	24.2	386.7	22.8	20.0	363.9	20.5	20.1	363.2
VS02	40.2	26.9	375.9	39.0	20.7	338.8	22.1	17.9	322.8
VS05	51.1	39.4	365.1	46.5	28.4	305.3	38.9	19.5	236.1
VS10	65.7	43.1	351.5	52.1	32.1	290.5	40.2	17.5	175.6

increase with the addition and increasing amount of modified starch accompanied by a marginal decrease of elongation at break. This indicates that the starch molecules provide the hybrids with multifunctional crosslinks connecting the WPU segments. Effect of crosslink is obvious by comparing the hybrids with the simple blend which shows a marginal increase in modulus and strength over the WPU. Upon incubation in the α-amylase, modulus and strength of the hybrids are significantly decreased in proportion to the amount of starch incorporated, a verification of biodegradation. Consequently, break strengths of the hybrids are almost reversed in ten days of incubation. Notably, these properties are not changed with the blend as well as the WPU, indicating that these materials are not vulnerable to the hydrolysis reaction catalysed by the enzyme.

3.5. Morphology

SEM morphology (Fig. 7) shows that the film surfaces of WPU and blend are not damaged in the α-amylase solution, while those of hybrids are seriously damaged in proportion to the starch content.

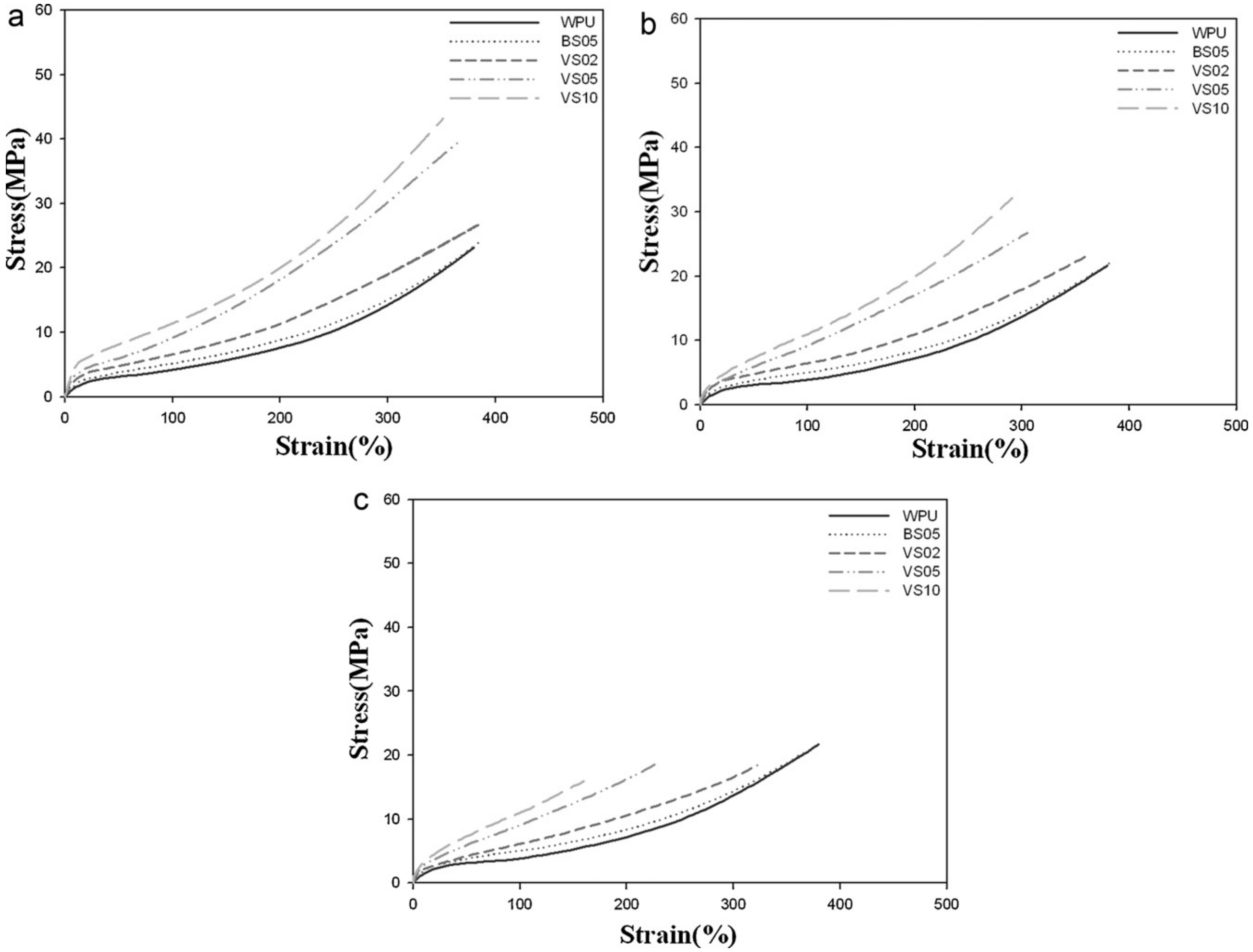


Fig. 6. Tensile behaviors of the hybrid cast films vs incubation time: 0 day (a), 3 days (b), and 10 days (c).

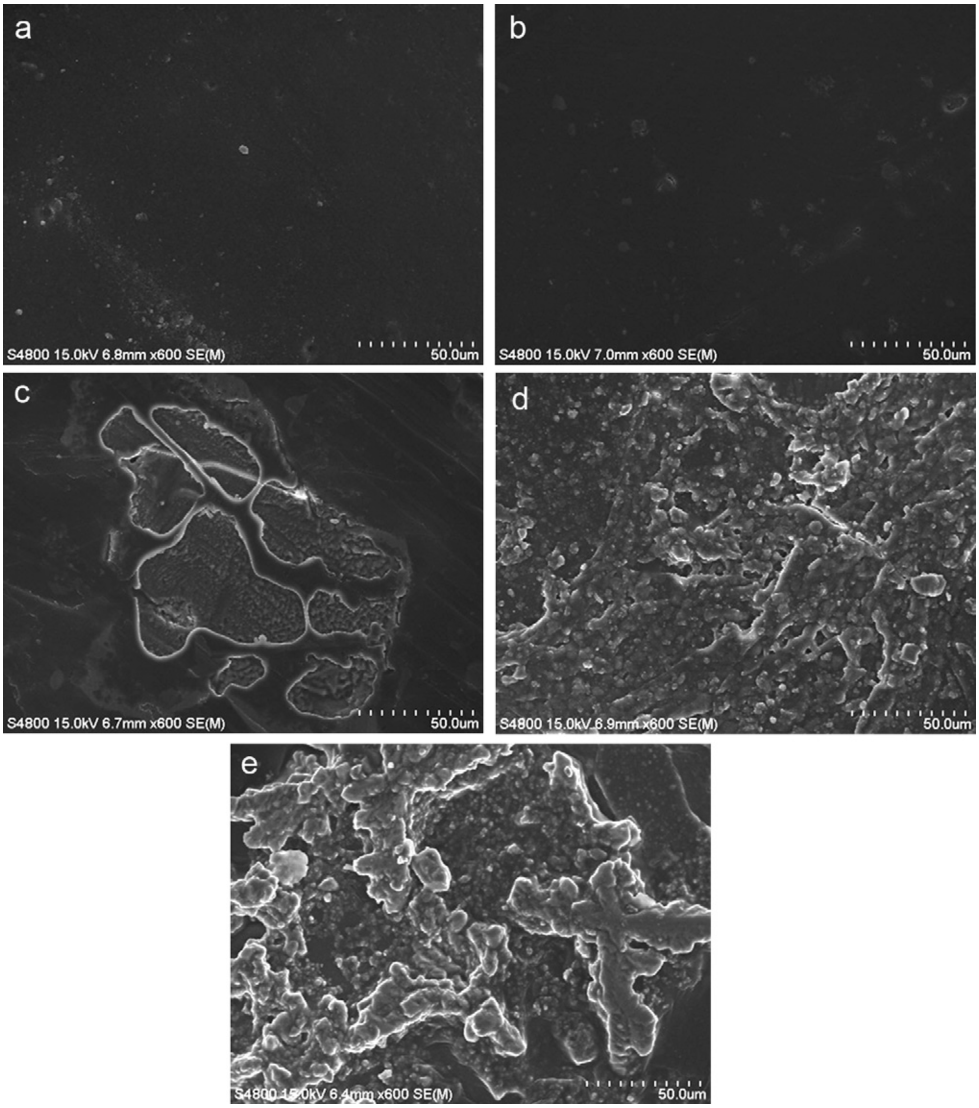


Fig. 7. SEM morphology of the film surface incubated 10 days in α-amylase solution. (a) WPU, (b) BS05, (c) VS02, (d) VS05, (e) VS10.

4. Conclusions

Chemical incorporation of vinyltrimethoxysilane (VTMS) modified starch molecules into the waterborne polyurethane (WPU) by covalent bond showed a significantly enhanced biodegradability of WPU hybrids in terms of weight loss in α-amylase solution, decreased tensile properties, and roughened film surfaces from SEM. Tensile modulus and strength of the WPU increased with the addition and increasing amount of starch content. This demonstrates the role of starch molecules as multifunctional crosslinks bridging the polyurethane molecules in network structure.

When the hybrids were incubated in α-amylase solution, maximum weight loss was greater than the amount of starch which was incorporated into the hybrid. This implies that when the starch molecules are degraded, polyurethane segments are also degraded from the networks. The maximum weight loss of the blend was the same with the amount of starch blended confirming that the starch is independently degraded in blend.

The particle size increased with the addition and increasing amount of starch to the dispersion. This indicates that the starch molecules effectively migrated into the WPU particle, followed by casting and drying while UV cure occurs to form covalent bonding with the modified starch and WPU.

Contact angle decreased with blend due to the increased hydrophilicity and increased with chemical hybrids, implying that crosslink effect is more significant than hydrophilicity. Hardness increased with the modified starch due to the increased crosslink density. A small increase of hardness with blend seems due to the strong hydrogen bond between WPU and starch.

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