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Biodegradable sol–gel coatings of waterborne polyurethane/gelatin chemical hybrids

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ABSTRACT

Gelatin from cold fish skin has strong mechanical properties and biodegradability. Cold fish gelatin was introduced into waterborne polyurethane (WPU) by covalent bonding to reinforce and render biodegradability of WPU. For this, gelatin was chemically modified with vinyltrimethoxysilane (VTMS) via the sol–gel type reactions and incorporated into hydroxyl ethyl acrylate (HEA) termini of WPU by UV curing. Covalent incorporations provided the hybrids with enhanced water resistance, hardness, glassy and rubbery state moduli, yield strength, and thermal resistance of soft segment along with significantly enhanced biodegradability both in trypsin solution and soil.

1. Introduction

Polyurethanes (PUs) are widely used in coatings, adhesives, sealants, elastomers, and medical materials as well as heat insulating foams. The world consumption of PU was over 12 million tons in 2012, and they are continuously expanding their usage as high performance and functional materials [1–4]. Among them, waterborne polyurethanes (WPUs) are environmentally friendly materials that are increasingly being used in coatings and adhesives for wood and automobiles, as well as for numerous flexible substrates, such as textiles, leather, paper, and rubber [5–9]. Generally, WPUs have inferior drying rates and water resistance due to the inclusion of ionic groups, and relatively poor hardness and modulus due to the limited usage of raw materials and crosslinking. However, problems related to their properties can largely be resolved by proper molecular designs and hybridization with other materials [10–14].

On the other hand, lack of landfill site has become problem with polymer wastes, which has led to a concern about biodegradation [15]. Though WPUs are synthesized in water with minimum pollution, they could be buried or burned once the life time is over. The biodegradability could be determined by many properties of polymer such as molecular orientation and crosslinking density as well as chain structures. The biodegradability of PU by microorganisms is mainly limited to polyester polyol based ones and it takes several days or weeks [16,17]. However, biodegradability of PU can significantly be improved by introducing appropriate biodegradable polymer fillers as physical and chemical hybrids.

Gelatin is hydrolysed form of collagens which are extracted from various animals. The gelatin films have strong mechanical properties due to the strong hydrogen bonding. Typical cold fish gelatin films show tensile modulus of about 2000 MPa, and strength of about 50 MPa with melting temperature of about 57 °C [18]. Even wider ranges of properties are obtained with plasticizer and crosslinking. They are biodegradaded in trypsin, a proteases in several hours [19].

Recently, combination of biocompatible PU with biodegradable gelatin finds new functional applications in medical areas. Using the electrospinning method PU/gelatin blend nanofiber scaffolds or meshes were prepared for wound dressing, blood vessels substitute [20,21]. Gelatin was used to synthesis urethane scaffolds for tissue engineering [22], or grafted onto PU dispersion using a grafting agent such as carbomoylonium [23].

In this study, we first time introduce gelatin molecules into the main chain WPU by covalent bonding via a sol–gel type reaction to reinforce and render biodegradability. For this, we chemically modified the cold fish gelatin with vinyltrimethoxysilane (VTMS), where the hydroxyl groups of gelatin are reacted with silanol groups of VTMS to form covalent bonds via sol–gel type reactions. Subsequently, the vinyl groups of VTMS attached to the gelatin were reacted with the acrylate termini of WPU by UV curing to obtain WPU/gelatin chemical hybrids. The gelatins are expected to provide the hybrids with crosslinks as well as biodegradable

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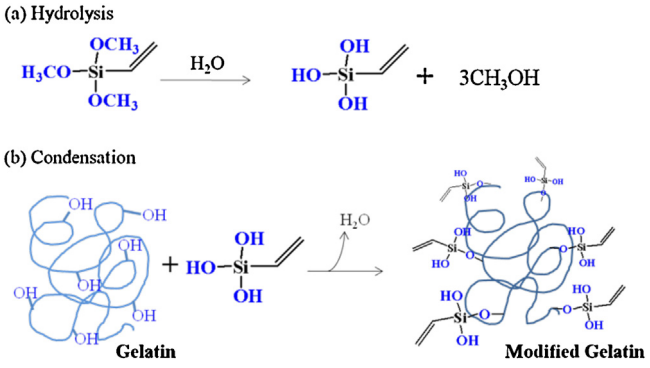


Scheme 1. Modification of gelatin using VTMS via sol–gel type reaction.

filler, and the effects have been analyzed in various ways. In addition, WPU/gelatin physical blend was also prepared and tested for comparison.

2. Experimental

2.1. Materials

Polycaprolactone diol (PCL diol, Mn = 530, Sigma–Aldrich) was degassed at 90 °C under vacuum for 3 h before use. Isophorone diisocyanate (IPDI, Sigma–Aldrich) was dried over 4 Å molecular sieves before use. Dimethylol butanoic acid (DMBA), 2-hydroxyethyl acrylate (HEA, Aldrich), α,α′-dimethoxy-α-hydroxy acetophenone (Darocur 1173, Ciba Specialty Chemicals), vinyltrimethoxysilane (VTMS, Sigma–Aldrich), phosphate buffered saline (PBS, Sigma–Aldrich), gelatin from cold water fish skin of molecular weight of about 60,000 g/mol (Sigma–Aldrich), trypsin from porcine pancreas (Sigma–Aldrich) were used as received.

2.2. Modification of gelatin

Four grams of gelatin and 1.085 g of VTMS were dissolved in 100 g of water at 40 °C, where hydrochloric acid was added to adjust the pH at 2.5 for the hydrolysis of VTMS. The vinyl modified gelatin was obtained as the condensation reactions between hydrolyzed VTMS and gelatin occur, where the modification procedure is described in Scheme 1.

2.3. Synthesis of WPU and UV cure

A 500-mL round-bottom, three-necked separable flask with a mechanical stirrer and dried N_2 inlet was used as reactor. The reaction temperature was kept at 70 °C in a constant temperature oil bath. DMBA and an excess amount of HDI were charged and reacted for about 4 h to obtain the NCO terminated potential ionomer segments. Then PCL and an additional amount of IPDI were added and reacted to make NCO terminated polyurethane prepolymers which were end capped with HEA to form acrylate termini. The theoretical molecular weight of PU acrylate prepolymer was about 3000 g/mol based on formulations. The prepolymer molecular weight corresponds to the molecular weight between crosslinks (Mc) for the unmodified WPU. Then the prepolymers were cooled to room temperature and neutralized with TEA for 45 min. The aqueous dispersion was obtained by adding water to the prepolymer solution with agitation for 1 h. Then the vinyl modified gelatin and the photoinitiator were added and stirred for the next 1 h to obtain the homogeneous mixture. The mixture was then cast onto a polyethylene plate and partially dried for about three days at 35 °C before it was cured by UV (254 nm). Finally the UV cured film was dried at 70 °C to a constant weight.

Table 1
Formulations to prepare WPU/Gelatin chemical hybrids (unit: g).

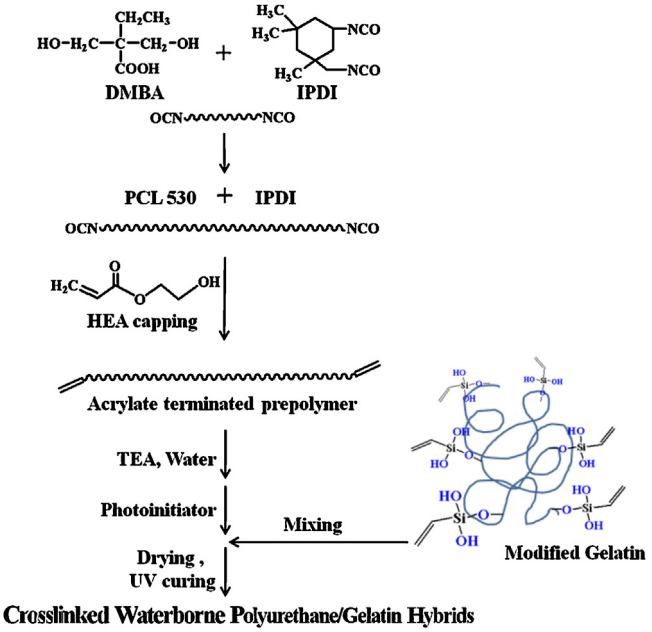
	Soft segment		Ionic group		HEA	VTMS	Gelatin (wt.%)
	PCL530	IPDI	DMBA	IPDI			
WPU	16.35	6.86	0.9	3.57	2.32	–	–
VG04						0.33	4
VG07						0.58	7
VG10						0.82	10
VG13						1.07	13
G10						–	10

Formulations and reaction scheme to synthesize the WPU/gelatin chemical hybrids are respectively shown in Table 1 and Scheme 2. On the other hand, WPU/gelatin blend was prepared by mixing WPU and water dissolved gelatin using a magnetic stirrer.

2.4. Characterizations

VTMS modification of gelatin (VG), end capping reaction of NCO terminated prepolymer with HEA, UV curing, and biodegradation in enzyme solution were followed by the IR measurements. IR spectra were taken on a Mattson Satellite Fourier transform infrared (FT-IR) spectrometer. Mechanical properties of the films were measured at 29 °C with a universal testing machine (Lloyd) at a crosshead of 500 mm/min using specimens prepared according to ASTM D-1822. Shore A hardness was measured using an indentation hardness tester according to ASTM D 2240-75. Ten sheets with 0.8 mm thickness were stacked to make 8 mm thickness film. The contact angle of the film surface was measured using a conventional contact angle goniometer (Theta lite100, KSV) with deionized water. Dynamic mechanical tests were performed using a dynamic mechanical analyzer (DMA Q800, TA Instrument) at 10 Hz, 5 °C/min, 0.2% strain. For thermogravimetric analysis (TGA Q50, TA Instruments,), ten mg of sample was charged and heated at 10 °C/min under N_2 condition. Biodegradations of the film were tested in a phosphate buffered saline (PBS) solution with trypsin (0.6%). Also, biodegradation in soil was performed at room temperature in humid condition.

The barrier/protective performance of the coating was tested according to a dc resistance/EIS/salt spray test with 5% NaCl solution at 35 °C. Sample was sprayed by the salt solution for 24 h, followed



Scheme 2. Reaction scheme to synthesize WPU/gelatin chemical hybrids.