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Silk-Inspired Polyurethane Containing GlyAlaGlyAla Tetrapeptide. III. Morphological, Thermal, and Mechanical Features of Electrosprayed and Electrospun Deposition

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ABSTRACT: Morphological, thermal, and mechanical features of electrosprayed and electrospun deposition of the silk-inspired polyurethane (PU) containing GlycineAlanineGlycineAlanine (GlyAlaGlyAla, the featured peptide sequence of silkworm silk fibroin) tetrapeptide, which was synthesized by the traditional liquid-phase peptide synthesis method and the classical two-step polymerization method using Boc-protected amino acids and diisocyanates as starting materials, were characterized. The results show that the synthesized silk-inspired PU dissolved in tetrahydrofuran (THF) can be easily electrosprayed or electrospun into the film form, although its molecular weight ranging from 13,000 to 15,000 is quite low. Elastomeric fibrous membranes with surface morphologies of "droplets," "bead-on-string," and "nonwoven fibers" have been obtained by electrospraying and electrospinning the silk-inspired PU/THF solution of varying concentrations. The thermograms confirm high thermostability of the silk-inspired PU between 350 and 400°C due to the polar peptide linkages. The tanδ peak of dynamic mechanical analysis curve corresponding to its glass transition temperatures is detected at −34.3°C. Its elongation at break is about 140–150%, and the breaking tensile strength ranges from 22 to 27 MPa, which is consistent with the data of other PUs containing L-alanine residue. Information provided by this study can be used to better understand the correlation between the natural and man-made silk polymers. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40245.

KEYWORDS: fibers; polyurethanes; properties and characterization

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INTRODUCTION

Thermoplastic linear polyurethanes (PU) were usually synthesized by using diisocyanates, bi-functional polyols with terminal hydroxyl groups and chain extenders (glycols or diamines) as basic raw materials.[1] The PU chain is composed of hard segments and soft segments arranged alternately. The hard segments are most frequently derived from diisocyanates and low-molecular weight chain extenders, while the soft segments are normally composed of poly(oxyethylene)s, which make linear PU even more flexible. The interactions through hydrogen bonds can separate hard domains within the soft phase or separate soft domains within the hard phase. Miscibility can be improved by increased polarity of structural fragments within macromolecules.[2]

Naturally, occurring silkworm silk fiber, on the other hand, has a core-shell type structure (twin fibroin filaments sticked by sericin). The amino acid composition of silk fibroin consists primarily of glycine (Gly; 43%), alanine (Ala; 30%), and serine (Ser; 12%), and the GlyAlaGlyAla tetrapeptide is its featured peptide sequence.[3] In a simplified way, it can be described as an all-protein nanocomposite consisting of Ala-rich β-sheet crystalline domains dispersed in a Gly-rich unordered matrix, whereas the matrix is responsible for the toughness.[4]

To achieve the artificial production of high performance and mimetic structure of silk-like fibers, a variety of poly(amino acid)s (known as polypeptides or proteins) and polymers based on silk fibroin model have been explored by chemical method or genetic bioengineering.[5–16] PU and silk fibroin have similarly molecular architecture in their primary and aggregate structure, both of which have amide bonds and microphase separation, and they have been employed as scaffold materials for biomedical applications.[3,17] This inspires us to develop a novel synthetic PU containing polypeptides composed of amino acid residues of silk fibroin. In our previous work, we presented silk-inspired

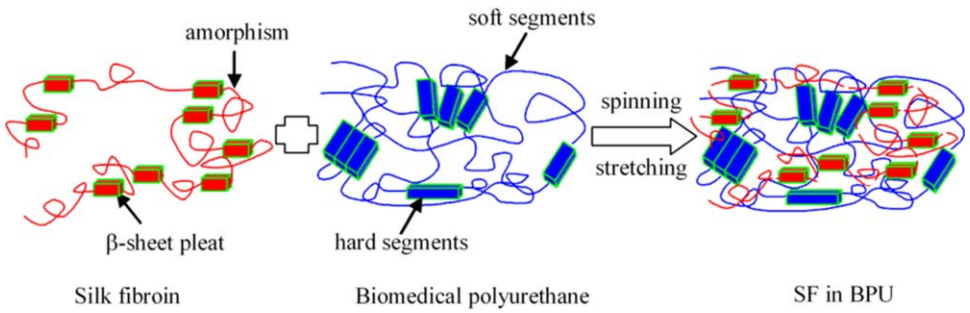

Figure 1. Hypothetic possible alignment of silk fibroin in segmented PU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PU biofiber by wet-spinning of biomedical PU/superfine silk protein powder blends.[18,19] Figure 1 is the hypothetic possible alignment of silk fibroin in segmented PU.

In our recent work,[20,21] the silk-inspired PU containing GlyAla-GlyAla tetrapeptide was synthesized and its physical properties and structure were quantitatively or qualitatively identified by means of elemental analysis (EA), ^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy, pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), intrinsic viscosity ([η]), gel permeation chromatography, Fourier transform infrared, Raman spectroscopy, and ultraviolet-visible (UV–vis) spectroscopy. We have found GlyAlaGlyAla tetrapeptide within the chain extender is partially incorporated into the PU chain, and the PU molecular weight ranged from 13,000 to 15,000, which is quite low and is hard to be improved as reported in literatures.[12,22] However, it is soluble in a variety of ordinary solvents (such as THF, DMF) facilitating processing into fibers or other forms. Currently, in the end part of a series of reports, we describe herein our efforts in investigating the morphological, thermal, and mechanical features of its electrosprayed and electrospun deposition for potential applications.

EXPERIMENTAL

Starting Materials

Chloroform (Sinopharm Chemical Reagent, China, abbreviated as SCRC, 99.0%) and *N*-methylmorpholine (SCRC, 98.0%) were distilled under atmospheric pressure prior to use. Tetrahydrofuran (THF; SCRC, 99.9%) was dried using sodium wire and distilled over sodium/benzophenone ketyl under an atmosphere of nitrogen before use. *N, N′*-dimethylformamide (DMF; SCRC, 99.5%) and dimethyl sulfoxide (DMSO; SCRC, 99.0%) were used after dehydration with 4 Å molecular sieves (SCRC, Φ 3–5 mm) for 2 days. Polytetrahydrofuran (PTHF, $M_W = 2000$, Aladdin Reagent, China) was dried under vacuum at 60°C for 9 h before use. *N-tert*-butoxycarboxyl-L-alanine (Boc-Ala-OH; Yangzhou Baosheng Biochemical, China, 98.0%), *N-tert*-butoxycarboxyl-glycine (Boc-Gly-OH; Yangzhou Baosheng Biochemical, China, 98.0%), *N*-hydroxysuccinimide (HOSu; SCRC, 97.0%), 1,6-hexamethylene diisocyanate (Alfa Aesar, 98.0%), 4,4′-diphenylmethane diisocyanate (Alfa Aesar, 98.0%), *N,N′*-dicyclohexyl carbodiimide (SCRC, 95.0%) were used without further purification. Other chemicals (toluene, sodium hydrate, and citric acid) were analytical grade. Natural silk fiber was provided by Luotian Silk Incorporation of Hubei Province, China.

Synthesis, Electrospraying, and Electrospinning of Silk-Inspired PU

The silk-inspired PU containing GlyAlaGlyAla tetrapeptide in this study was obtained by a two-step polymerization method. The detailed synthesis procedures and the chemical composition (Figure 2) of the final PU were illustrated in previous articles.[20,21] The PU products were made into granules by being dripped into a mixture of methanol-water (3/1, v/v) and then coagulated.[23] The granules were further purified by extraction in toluene, dried, and stored in granular or flaky forms.

For comparison, two related control specimens were employed. One PU with a classical 1,4-butanediol (BDO; Aladdin Reagent, China) chain extender was also synthesized in the same condition, which was denoted as BDO-extended PU. The silk-inspired PU was a poly(urethane urea), while BDO-extended PU was a poly(urethane ether). The other PU was commercially available Pellethane® 2363-80AE (biomedical grade) from Dow Chemical, which was denoted as Dow BPU in this article.

THF was used as the solvent to prepare the silk-inspired PU solutions at different concentrations (10, 20, and 30 w/v %, respectively) for electrospraying and electrospinning. Each of

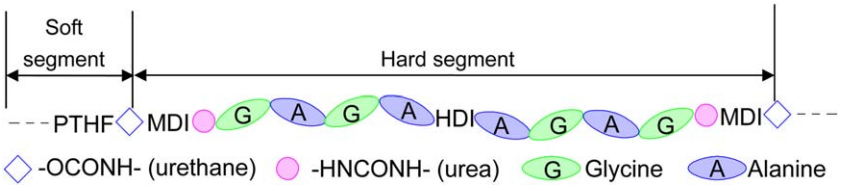

Figure 2. Chemical structure for the silk-inspired PU containing GlyAlaGlyAla tetrapeptide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the PU solutions was loaded into a 10 mL plastic syringe capped with a blunt 9-gauge stainless steel hypodermic needle (I. D. = 0.9 mm) and delivered by a programmable syringe pump (Cole-Parmer® Instrument Company, Vernon Hills, IL) to the exit hole. The electrode of a positive high-voltage DC power supply (EST705-60 Static Generator, Beijing EST S & T, China) was connected via an electrical alligator clip onto the external surface of the needle. Aluminum foil was used as a static collector and grounded. The voltage was changed from 0 to 30 kV until the formation of a stable Taylor cone. The flow rate of the PU solution was fixed at 0.8 mL/h, the distance between the spinneret and the collector was 15 cm, and the applied electric field was 1 kV/cm. The electrosprayed or electrospun mesh was prepared on to the foil through continuous deposition at room temperature in a chamber having a ventilation system. For morphology analysis, the collection time was about 1–2 h, while it took 24 h to obtain a thick enough mat for mechanical measurement and dynamic mechanical analysis (DMA) testing.

Polymer Characterizations

Scanning Electron Microscopy (SEM). The morphology of the electrosprayed or electrospun mesh samples of silk-inspired PU/THF with varying concentrations (10, 20, and 30 w/v%) was observed with scanning electron microscopy (SEM, JSM-5610LV, JEOL, Japan) at an accelerating voltage of 25 kV after sputtering a very thin layer of gold.

Thermal Property Measurements. Thermogravimetric analysis (TGA) of each sample (as-obtained Dow BPU, as-synthesized BDO-extended PU, as-synthesized silk-inspired PU, and as-obtained natural silk fiber) in an alumina crucible with about 10 mg mass was carried out on a TG 209 F1 thermogravimetric analyzer (Netzsch, Germany). The experiment was performed under dry nitrogen (N_2) gas atmosphere (flow of 60 mL/min) and the profiles were recorded at a heating rate of 10°C/min from 30 to 600°C.

DMA was evaluated in the tension mode under a nitrogen flow of 50 mL/min using a DMA 242 dynamic mechanical thermal analyzer (Netzsch, Germany) over a temperature range of −150–250°C at a frequency of 1 Hz, a ramp rate of 5°C/min, and an initial strain of ~0.2%. DMA was conducted on films cast from PU solutions (30 w/v % silk-inspired PU/THF, 30 w/v % BDO-extended PU/THF, and 30 w/v % Dow BPU). The dimension of each sample used was 5.0 × 100.0 × 0.5 mm and the effective length of the sample was 50 mm. The dynamic storage modulus (E'), loss modulus (E''), and mechanical loss tangent (tan $\delta = E''/E'$) were recorded.

Mechanical Measurement. Mechanical properties of the silk-inspired PU film samples was tested on an Instron 5566 Universal Testing Machine (Instron, MA), at a gauge length of 50 mm and strain rate of 20 mm min^{-1}. The dimension of each sample used was 5.0 × 100.0 × 0.5 mm. All samples were preconditioned at 20°C and 65% (RH) for 24 h before tensile testing. All tensile data were measured with ten specimens for each sample. Tensile strength was determined in accordance with the Chinese Textile Industrial Standards FZ/T 50006-94 (idt. BISFA-Test methods for bare elastane yarns).

RESULTS AND DISCUSSION

Morphological Features

As a facile processing technique, electrospinning is governed by a number of parameters that greatly affect fiber formation and structure. Among these parameters are polymer molecular-weight, polymer solution properties (solvent, viscosity, conductivity, and surface tension), especially concentration [C, % (w/v)], applied electrical potential (V, kV), volumetric flow rate (υ, mL/h) of polymer solution, distance between spinneret and collector (working distance, h, cm), static or rotatory nature of the grounded target, and ambient parameters (temperature, humidity, and air velocity). To produce desired fibers, the above mentioned parameters have to be precisely controlled. In this work, the solution properties (concentration and solvent) and processing parameters (applied electric field, solution flow rate, and needle to collector distance) have been chosen as the result optimized by Caracciolo et al. with some requisite modifications.[24] The effect of polymer concentration on the morphology of electrospun membranes has been examined while keeping the other parameters such as V, υ, h, syringe, and needle configuration constant. Elastomeric fibrous membranes have been obtained by electrospinning the silk-inspired PU solution of varying concentrations in THF at predetermined processing conditions (Table I). The concentrations have been varied to study their role on the membrane morphologies and properties. All electrospun membranes fabricated using the silk-inspired PU/THF solution is white in appearance. Selected SEM images of electrospun/electrosprayed depositions are presented in Figure 3.

Only beads could be obtained for 10 w/v % and lower concentrations. Figure 3(a) shows the nearly spherical microbeads formed with $C = 10$ w/v %. Electrospraying instead of electrospinning in the case of dilute solutions of the silk-inspired PU occurred. This can be attributed to the lack of sufficient polymer-chain entanglements when the solution is too dilute. The beads are produced when the jet at the end of the Taylor cone splits into many mini-jets and each mini-jet disintegrates into small droplets, phenomena also referred to as electrospraying.[25] As the concentration increases to 20 w/v %, the solution becomes viscoelastic and takes a longer time to break up into drops. As a result, "bead-on-string" morphology is formed as shown in Figure 3(b). Shah et al. have developed an L-tyrosine PU (PCL-L-DTH) for potential biomedical applications.[26] At a lower concentration of 15 w/v % PCL-L-DTH in 1,1,1,3,3,3 hexafluoro-2-propanol, fibers with beads on a string morphology are also observed. This may be attributed to the lower molecular weight of our silk-inspired PU than that of PCL-L-

Table I. Processing Parameters of the Silk-Inspired PU Solutions

Concentration (w/v %) in THF	Volumetric flow rate (mL/min)	Electric potential (kV/cm)	Morphology
10	0.8	1	droplets
20	0.8	1	beads on strings
30	0.8	1	fibers

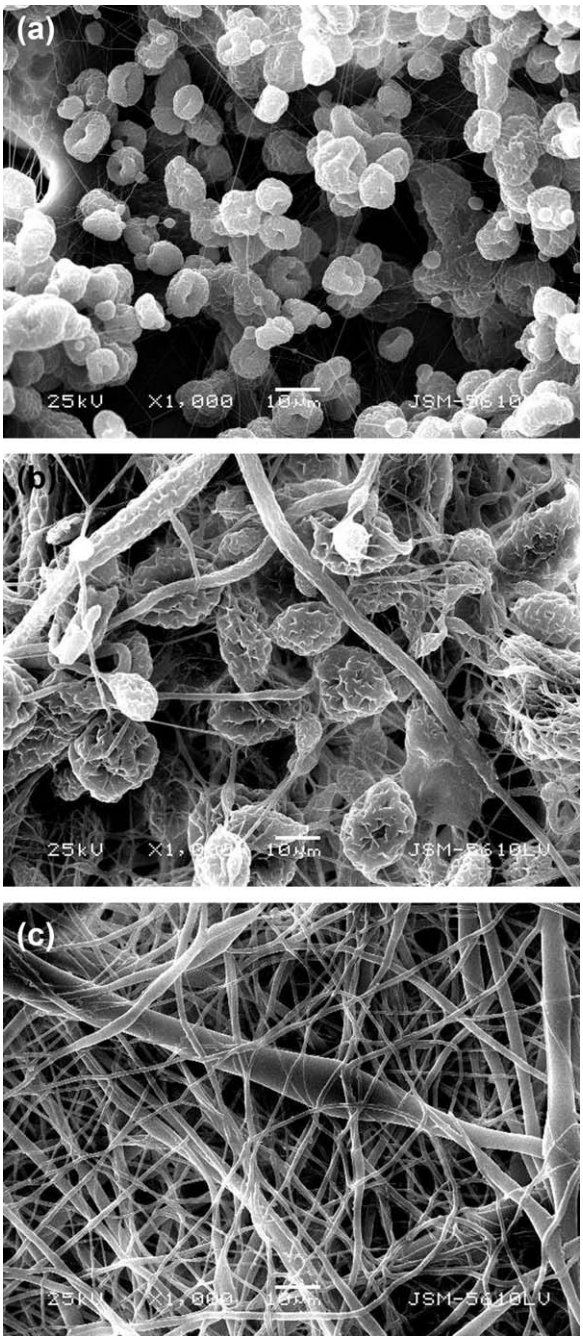

Figure 3. SEM micrographs of electrosprayed or electrospun silk-inspired PU/THF solutions, $\upsilon = 1$ mL/h, $V = 15$ kV, $h = 15$ cm at: (a) $C = 10$ w/v %; (b) $C = 20$ w/v %; (c) $C = 30$ w/v %. The scale bar is 10 μm.

DTH. When the concentration of silk-inspired PU in THF is above the critical concentration, polymer solution may form a network of entanglements, making the solution more elastic and electrospinnable into fibers. For silk-inspired PU/THF solution, the critical concentration is 30 w/v % to form randomly oriented non-woven fibers as shown in Figure 3(c). More concentrated solutions of 40 w/v % or higher could not be processed by electrospinning or even electrospraying due to the high viscosity achieved. A similar observation was reported for PU solutions.[24]

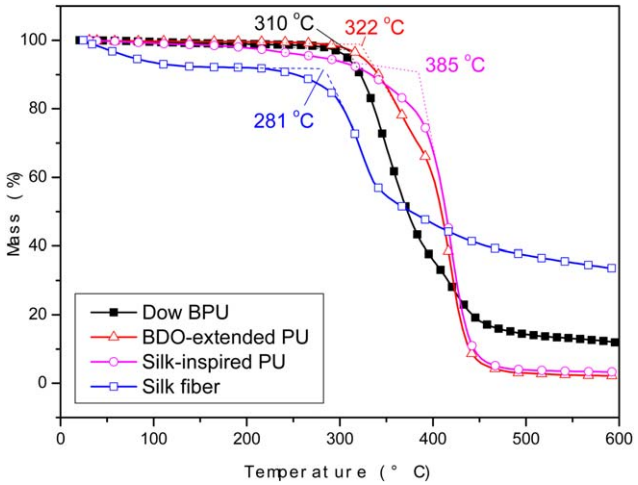

Figure 4. TGA traces for 3 PUs and silk fiber under nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal Properties

The TGA traces of as-obtained Dow BPU, as-synthesized BDO-extended PU, as-synthesized silk-inspired PU, and as-obtained natural silk fiber are shown in Figure 4. TGA data for each of the four materials are also collected in Table II. Only natural silk fiber presents two main regions of mass loss. The first region in the 25–120°C range ($\triangle m = 10\%$) is related to the evaporation of water molecules, as the conventional moisture regain of natural silk fiber is 11%.[28] PU thermal decomposition is characterized by a mass loss of <5% in the range 25–200°C, due to the evaporation of residual solvent. The main feature of the decomposition pattern of the PUs is a greater mass loss than the silk fiber in the 25– 350°C range. Degradation of the PUs begins at about 200°C and is essentially completed at 550°C as similar to the related literature reported.[29] The decomposition temperature for 5% weight loss, as a valuable criterion for thermal stability was in the range of 281–326°C. Maximum decomposition temperature (according to first derivative of TGA versus temperature) was in the range of 310–385°C. As shown in Figure 4 and Table II, the silk-inspired PU was the most thermally stable between 350 and 400°C. This may be due to the polar peptide linkages, as which tend to produce more intermolecular force at this range of temperature. When the temperature is higher, the polar peptide linkages are also destroyed.

DMA curves (tanδ-T) for cast films of 30 w/v % silk-inspired PU/THF film, 30 w/v % BDO-extended PU/THF film, and 30

Table II. Thermal Stability and Thermal Behavior Data of Samples

Code	$T_{5\%}$ (°C)	T_{max} (°C)
Dow BPU	307	310
BDO-extended PU	326	322
Silk-inspired PU	281	385

$T_{5\%}$: temperature of 5% weight loss obtained from TGA; T_{max}: maximum decomposition temperature obtained from TGA.

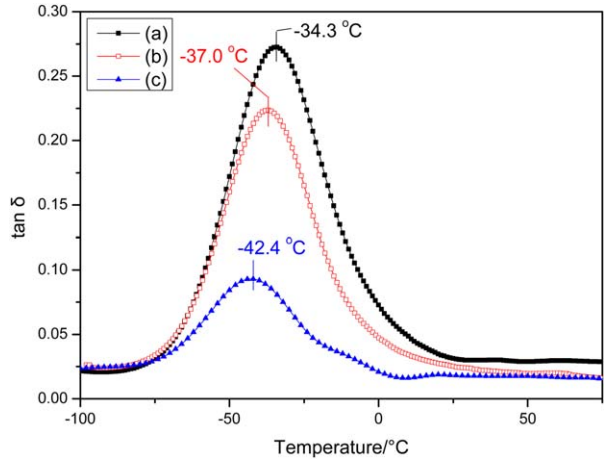

Figure 5. DMA curves (tanδ-T) for PUs: (a) 30 w/v % silk-inspired PU/THF film; (b) 30 w/v % BDO-extended PU/THF film; (c) 30 w/v % Dow BPU/THF film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

w/v % Dow BPU/THF film are presented in Figure 5. The tanδ peaks corresponding to glass transition temperatures for them were detected at −34.3, −37.0, and −42.4°C, respectively. This is attributed to the chain extender length of silk-inspired PU, resulting the elastomeric properties of silk-inspired PU is inferior to those of commercially available Dow BPU.

About the glass transition temperature (T_g) of silk fibroin, some are reported more than 170–180°C,[30–32] others are reported −20–−30°C,[33] and the T_g depends on the absorbed moisture. For silk fibroin films prepared at ambient humidity (~35%) the T_g is ~100°C while for water saturated films the T_g is room temperature.[34,35] Generally, the T_g of soft segment of linear PU is well below room temperature, while that of hard segment is normally above room temperature.[36] To mimic the properties of whether native or regenerated silk fibroin, it is necessary to improve the T_g of PU. In the idealism situation with enough

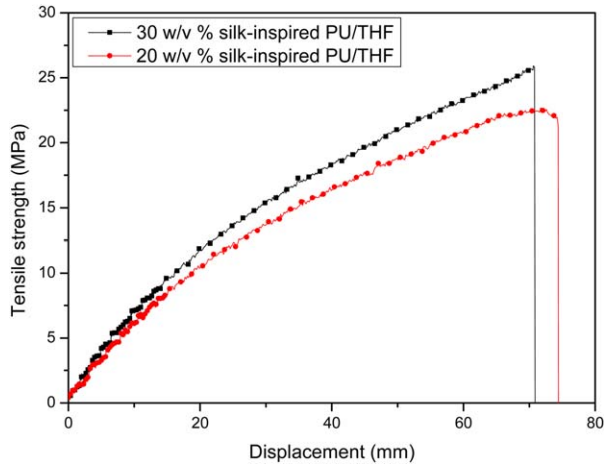

Figure 6. Selected displacement-tensile strength curves for fibrous films electrospun from 30 w/v % and 20 w/v % silk-inspired PU/THF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Tensile Strength of Silk Fiber and the Silk-Inspired PU

	Raw natural silk fiber[37]	Electrospun regenerated silk fiber[38,39]	Silk-inspired PU
Tensile strength (MPa)	500	19	22–27

GlyAlaGlyAla tetrapeptide links, the silk-inspired PU of this study would increase the T_g of PU and decrease its ultimate elongation to those of silk fibroin.

Mechanical Study

Mechanical properties of PU are important with respect to practical applications. Selected displacement-force curves for fibrous films electrospun from 30 to 20 w/v % silk-inspired PU/THF are presented in Figure 6. Though other PU with a concentration of 10 w/v % in solutions can be wetspun or electrospun to form fibers or films,[19,26] the fibrous films electrospun from 10 w/v % silk-inspired PU/THF are too thin and weak (due to the low molecular weight) to be taken from the aluminum foil collector, and much more concentrated solutions of 40 w/v % or higher could not be processed by electrospinning or even electrospraying due to the high viscosity achieved. It can be seen that the PUs have elongation at break of about 140–150% (displacement of about 70–75 mm at a gauge length of 50 mm). The breaking tensile strength ranges from 22 to 27 MPa (close to that of natural rubber), which is consistent with the data of the PUs containing L-alanine residue.[22] As summarized in Table III,[37–39] although the tensile strength of is the silk-inspired PU far below that of natural silk fiber, it is comparable to that of electrospun regenerated silk fiber. Moreover, it is seen that the breaking tensile strength of fibrous films electrospun from the silk-inspired PU/THF increases with increasing the concentration, while the elongation at break has the opposite trend. Correlating with the microscopic studies as shown in Figures 3 and 6, breaking tensile strength of fibrous films electrospun from 30 w/v % silk-inspired PU/THF with randomly oriented nonwoven fibers morphology, is superior to that of fibrous films electrospun from 20 w/v % silk-inspired PU/THF with "bead-on-string" morphology. This is due to the fibrous entanglements.

CONCLUSIONS

This article presents experimental results of morphological, thermal, and mechanical features of the silk-inspired PU containing GlyAlaGlyAla tetrapeptide in the form of non-woven fabric produced by electrospraying and electrospinning. The synthesized silk-inspired PU can be easily dissolved in THF. The cast PU film morphologies of droplets, beads on strings, and fibers formed depending on varying solution concentrations. The thermograms confirm high thermostability of the silk-inspired PU between 350 and 400°C due to the polar peptide linkages. The tanδ peak of DMA curve corresponding to its glass transition temperatures is detected at −34.3°C. Its elongation at break is about 140–150%, and the breaking tensile strength ranges from 22 to 27 MPa, which is consistent with the

data of other PUs containing *L*-alanine residue. Information provided by this study can be used to better understand the correlation between the natural and man-made silk polymers.

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