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Electrospinning of linear and highly branched segmented poly(urethane urea)s

Matthew G. McKee, Taigyoo Park, Serkan Unal, Iskender Yilgor[1], Timothy E. Long*

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

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Abstract

Electrospun fibrous mats were formed from linear and highly branched poly(urethane urea)s. The highly branched poly(urethane urea)s were synthesized using an A_2+B_3 methodology, where the A_2 species is an oligomeric soft segment. Since the molecular weight of the A_2 oligomer is above the entanglement molecular weight, the highly branched polymers formed electrospun fibers unlike typical hyperbranched polymers that do not entangle. Stress–strain experiments revealed superior elongation for the electrospun fibrous mats. In particular, the highly branched fiber mats did not fail at 1300% elongation, making the electrospun mats promising for potential applications where enhanced tear strength resistance is required.
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Keywords: Electrospinning; Hyperbranched; Poly(urethane urea)

1. Introduction

Polyurethanes are used in a large number of commercial applications, including fiber production, coatings and adhesives [1]. The synthesis of segmented polyurethanes with alternating hard and soft segments, typically result in a microphase separated morphology, which displays highly elastomeric behavior that is suitable for elastomeric fiber applications [2]. In general, the hard segments form crystalline regions due to strong hydrogen bond associations between the urea or urethane groups, while the soft segments form the continuous phase and remain amorphous [3]. Recently, significant research attention has illustrated the importance of hydrogen bonding and percolation through the hard phase on the performance of polyurethanes in foam and elastomer applications [4–7]. For example, structure–property relationships of well-defined polydimethylsiloxane (PDMS) based segmented copolymers displayed the influence of hydrogen bonding in the hard segment on the thermal and mechanical properties of the copolymers [8,9]. In particular, a linear relationship between the hard segment content and tensile strength was developed for the segmented copolymers. Silicone–urea copolymers with a very high urea hard segment content (42 wt%), are achievable using isopropyl alcohol (IPA) as the polymerization solvent, and tensile strengths greater than 20 MPa were observed [10]. The synthesis of segmented poly(ether urea)s in IPA was recently investigated using in situ FTIR spectroscopy in our laboratories [11]. Since segmented linear poly(urethane urea) copolymers display high tensile strength and elastomeric behavior, many researchers have utilized electrospinning as a means to form sub-micron fibers of linear segmented poly(urethane urea)s [12–14].

Electrospinning occurs when a charged polymer solution or melt that possesses chain entanglements emits a fluid jet in the presence of an electric field [15]. The jet undergoes a fluid instability, which causes a whip-like motion of the jet, thereby greatly increasing the path-length and degree of stretching that the filament undergoes before collection on a target [16]. The resulting electrospun nonwoven fiber mats possesses a high specific surface area, high porosity, and small pore size, which lend themselves to a wide range of

* Corresponding author. Tel.: +1 540 231 2480; fax: +1 540 231 8517.
E-mail address: telong@vt.edu (T.E. Long).
[1] Permanent address: Department of Chemistry, Koc University, Sariyer 34450, Istanbul, Turkey

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Table 1
Description of linear and highly branched poly(urethane urea)s

Polymer architecture	Hard segment composition (wt%)	Soft segment M_n (g/mol)	M_w (g/mol)[a]	M_w/M_n[a]	Solution concentration (wt%)[b]	Electrospinning solvent (wt:wt)[b]
Linear	35	2000	42,000	1.56	10.0	1:4 THF:IPA
Highly branched	30	2000	91,900	5.78	10.8	1:2 THF:IPA

[a] SEC solvent: tetrahydrofuran for linear polymer and hexafluoroisopropanol for highly branched polymer.
[b] Electrospinning conditions: 20 kV, 10 ml/h, 20 cm distance from syringe to collector.

applications including filtration devices, membranes, vascular grafts, protective clothing, reactive templates, and tissue scaffolds [17–19]. Previous tensile analyses of electrospun polyurethane fibers showed distinctly different mechanical properties compared to a film [12]. In particular, the fibers showed a lower elongation and a higher stress at equivalent elongation compared to the polyurethane film. Recently, simultaneous electrospinning of poly(vinyl chloride) and segmented polyurethane solutions in a side-by-side set-up, yielded bicomponent submicron fibers that possessed properties of each of the polymer components [20].

Previously, our laboratories have electrospun both linear and randomly branched polyesters, and developed relationships between fiber morphology and the entanglement concentration (C_e) [21]. Fibers formed from a branched polymer exhibit advantages over fibers formed from linear analogs. Branching allows (1) control of chain end concentration for tailored functionalization, (2) controlled degradation for specific drug delivery profiles, and (3) reduced viscosity for potential melt processing of nanofibers. To date, a comparison of the mechanical behavior of linear and branched poly(urethane urea) electrospun fibers has not received attention. Earlier, the synthesis of novel poly(alkyl methacrylates) with pendant quadruple hydrogen bonding groups that associated in nonpolar environments was investigated in our laboratories, and the influence of strong hydrogen bonding on electrospun fiber formation was elucidated [22,23]. Herein, the electrospinning performance and mechanical properties of linear and well-defined highly branched segmented poly(urethane urea)s are discussed. The synthesis of branched and functional polymers that were synthesized via step-growth methodologies has received much attention in our laboratories [24–27].

2. Results and discussion

The highly branched poly(urethane urea)s were synthesized using an A_2+B_3 methodology, where the A_2 species is an oligomeric soft segment, described elsewhere [28]. If the molecular weight of the A_2 oligomer is above the entanglement molecular weight (M_e), these highly branched polymers form electrospun fibers unlike typical hyperbranched polymers that do not entangle. Table 1 summarizes the hard segment composition, soft segment molecular weight, the weight average molecular weights, and the electrospinning conditions for the linear and highly branched poly(urethane urea)s. The soft segments of both copolymers consisted of 2000 g/mol poly(tetramethylene oxide) (PTMO), while the hard segment composition was 30 and 35 wt% for the highly branched and linear copolymer, respectively. Absolute molecular weight determination was performed with a triple detector size exclusion chromatography (SEC) column. Due to differences in their solubilities, the linear ($M_w=42{,}000$ g/mol, $M_w/M_n=1.56$) and branched ($M_w=91{,}900$ g/mol, $M_w/M_n=5.78$) poly(urethane urea)s were, respectively, dissolved in tetrahydrofuran and hexafluoroisopropanol for the SEC measurements. Electrospinning conditions were constant at 20 kV, 10 ml/h volumetric flow rate, and 20 cm from the syringe needle to the collecting target. Nonwoven fiber mats (approximately $10\times10\ cm^2$) were collected for the linear and highly

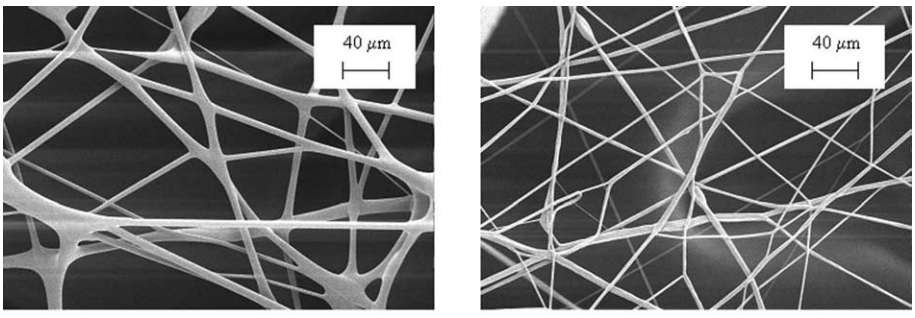

Fig. 1. FESEM images of electrospun poly(urethane urea) fibers. The electrospinning conditions were 20 kV, 10 ml/h, and 20 cm distance from the syringe tip to the collector.

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