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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.

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

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* 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

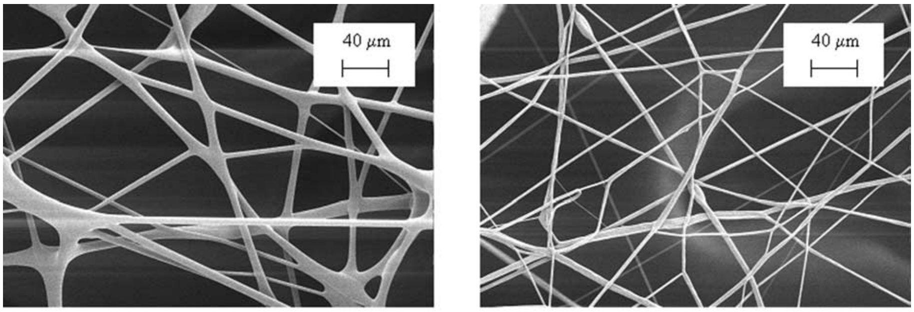
[a] SEC solvent: tetrahydrofuran for linear polymer and hexafluoroisopropanol for highly branched polymer.
[b] Electrospinning conditions: 20 kV, 10 ml/h, 20 cm distance from syringe to collector.

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 10×10 cm^2) were collected for the linear and highly



a) Linear poly(urethane urea) **b) Highly branched poly(urethane urea)**

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.

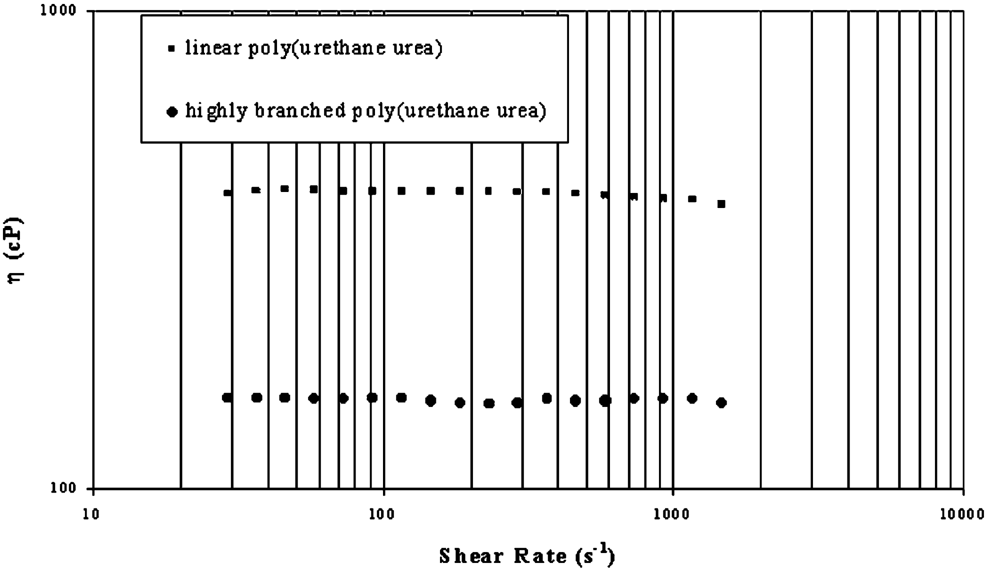


Fig. 2. Shear rate dependence of viscosity for linear and highly branched poly(urethane urea) segmented copolymers. Both copolymers showed Newtonian behavior over the range of shear rates investigated.

branched polymers with average fiber diameters of 5.5 ± 1.8 and 4.0 ± 1.5 μm, respectively. Field emission scanning electron microscopy (FESEM) images of the fibers are shown in Fig. 1. Both linear and highly branched segmented copolymers formed uniform electrospun fibers without bead defects, suggesting the polymer concentrations shown in Table 1 are above $2C_e$, where C_e is a function of chain length, molecular topology, and intermolecular interactions [21]. The solutions of linear and highly branched poly (urethane urea)s displayed significantly different zero shear rate viscosities (η_0), where the η_0 for the linear solution was 420 cP and the η_0 of the highly branched solution was 160 cP. Fig. 2 shows that over the shear rate range studied, the segmented copolymers displayed Newtonian behavior. Despite having a higher absolute M_w, the highly branched polymer displayed a lower η_0 compared to the linear chain due to its reduced hydrodynamic volume.

Stress–strain experiments were performed using dog bone samples cut from a die as specified in ASTM D3368, and the tensile testing was performed on a 5500R Instron® universal testing machine at a crosshead displacement rate of 15 mm/min. Reported tensile values were obtained from an average of five dog bone samples cut from each electrospun mat to ensure there was no heterogeneity in thickness within the nonwoven mat. Fig. 3 compares the stress–strain behavior of linear and highly branched

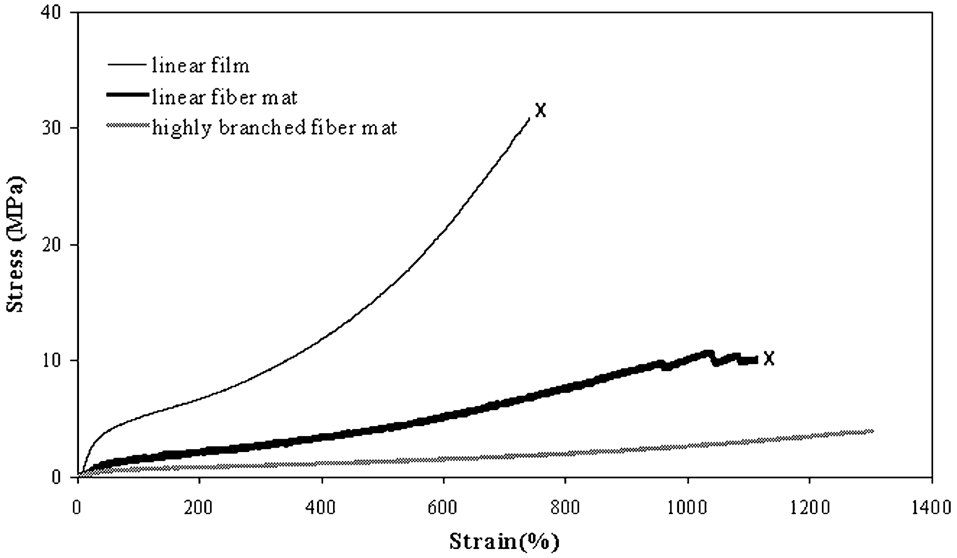


Fig. 3. Stress–strain results for linear and highly branched segmented poly(urethane urea)s. Comparison of the tensile performance of electrospun fiber membranes to a poly(urethane urea) film. Failure at break is denoted by the X, and the highly branched fibrous mat did not break at 1300% elongation.

Table 2
Stress–strain summary for the poly(urethane urea) electrospun fiber mats and film

Material	Young's modulus (MPa)	Strain at break (%)	Stress at break (MPa)	Permanent set (%)
Linear film	17±1	830±61	38±9	Failed
Linear fiber mat	3.7±0.4	970±100	10±1	Failed
Highly branched fiber mat	1.3±0.3	>1300%	N/A	21±7

N/A, sample did not break, stress at 1300% elongation (4.5±0.5 MPa).

poly(urethane urea) electrospun fiber mats to a film prepared from the linear poly(urethane urea). Since, the nonwoven fiber mats were not continuous and contained a high degree of sub-micron porosity [29], the apparent stress was evaluated by employing the equivalent thickness (t_{eq}) of the electrospun mat. The t_{eq} is defined as,

$$t_{\mathrm{eq}} = \frac{m}{\rho A} \tag{1}$$

where m, ρ, and A corresponds to the dog bone specimen mass, density, and the area of the die, respectively. Fig. 3 shows that both the linear and highly branched electrospun fiber mats exhibited higher elongation before break than the corresponding linear poly(urethane urea) film. The linear film failed at 830% elongation, while the linear electrospun fibers failed at 970% elongation, although these values are nearly within the standard deviation of the measurement. However, the highly branched fibrous mat did not fail at 1300% elongation. The higher elongation at break for the highly branched compared to the linear membrane may be a result of different electrospinning solvents. Khil et al. reported a higher concentration of point-bonded contacts between fibers with increasing solvent volatility [30]. Since the highly branched poly(urethane urea) was electrospun from a THF rich solvent compared to the linear, the significantly larger elongation at break may be attributed to a higher concentration of point-bonded contacts between individual fibers.

The improved elongation behavior of the electrospun fibers compared to the poly(urethane urea) film is attributed to increased tear resistance of the fiber mats compared to the neat poly(urethane urea) film at high elongation [31]. Unlike, the poly(urethane urea) film, which exhibited relatively poor resistance to tear, the interconnected, network structure of the electrospun fibers hindered tear propagation, which resulted in higher elongations prior to break. In fact, the oscillations in the stress–strain curve for the linear fibrous mat, which occurred at approximately 1000% strain, were a result of the interconnected fibers preventing tear propagation. Table 2 shows a summary of the stress–strain results for the segmented copolymer fiber mats and film. The Young's modulus for the linear and highly branched fiber mat was 1 to 4 MPa, which was significantly lower than the bulk film (17 MPa) due to the discontinuous, microporous nature of the nonwoven fibers. As mentioned previously, the linear and highly branched fibrous mats displayed enhanced elongation behavior compared to the film. After 1300% elongation, the highly branched fiber mat exhibited only minor permanent set (21%), indicating the nonwoven fibers formed a highly elastic interconnected network structure.

In conclusion, electrospun membranes were formed from linear and highly branched poly(urethane urea)s. Although much work has focused on using branched polymers for conventional spinning processes [32,33], this is the first example of the formation of elastic *electrospun* fibers from a highly branched polymer architecture. Stress–strain experiments revealed a lower modulus and higher elongation for the electrospun fibrous mats compared to the corresponding film. Moreover, the highly branched fibers did not fail at 1300% elongation, which enables potential applications where enhanced tear strength resistance is required.

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References

[1] Stevens MP. Polymer chemistry an introduction. New York: Oxford University Press; 1999.
[2] Oertel G. Polyurethane handbook. 2nd ed. New York: Hanser Publishers; 1994, p. 629.
[3] Szycher MS. Szycher's handbook of polyurethanes. New York: CRC Press; 1999.
[4] O'Sickey MJ, Lawrey BD, Wilkes GL. Polymer 2002;43:7399.
[5] Aneja A, Wilkes GL. J Appl Polym Sci 2002;85:2956.
[6] Aneja A, Wilkes GL. Polymer 2004;45:927.
[7] Sheth JP, Yilgor I, Yilgor E, Wilkes GL. Polym Prepr (Am Chem Soc, Div Polym Chem) 2004;45:563.
[8] Tyagi D, Yilgor I, McGrath JE, Wilkes GL. Polymer 1984;25:1807.
[9] Yilgor E, Yilgor I. Polymer 2001;42:7953.
[10] Yilgor E, Atilla GE, Ekin A, Kurt P, Yilgor Y. Polymer 2003;44:7787.
[11] Yilgor I, Mather B, Unal S, Yilgor E, Long TE. Polymer 2004;45:5979.
[12] Pedicini A, Farris RJ. Polymer 2003;44:6857.
[13] Demir MM, Yilgor I, Yilgor E, Erman B. Polymer 2002;43:3303.
[14] Lee KH, Kim HY, Ryu YJ, Kim KW, Choi SW. J Polym Sci, Part B: Polym Phys 2003;41:1256.
[15] Reneker DH, Chun I. Nanotechnology 1996;7:216.

[16] Shin YM, Hohman MM, Brenner MP, Rutledge GC. Polymer 2001;42:9955.

[17] Grafe T, Graham K. Nonwoven Technol Rev 2003;51.

[18] Kenawy ER, Layman JM, Watkins JR, Bowlin GL, Matthews JA, Simpson DG, et al. Biomaterials 2003;24:907.

[19] Matthews JA, Wnek GW, Simpson DG, Bowlin GL. Biomacromolecules 2002;3:232.

[20] Gupta P, Wilkes GL. Polymer 2003;44:6353.

[21] McKee MG, Wilkes GL, Colby RH, Long TE. Macromolecules 2004;37:1760.

[22] Yamauchi K, Lizotte JR, Long TE. Macromolecules 2003;36:1083.

[23] McKee MG, Elkins CL, Long TE. Polymer 2004;45:8705.

[24] Lin Q, Long TE. Macromolecules 2003;36:9809.

[25] Lin Q, Unal S, Fornof AR, Wei Y, Li H, Armentrout SR, Long TE. Macromol Symp 2003;199:163.

[26] Lin Q, Pasatta J, Long TE. J Polym Sci, Part A: Polym Chem 2003;41:2512.

[27] Kang HL, Lin Q, Armentrout SR, Long TE. Macromolecules 2002;35:8738.

[28] Unal S, Yilgor I, Yilgor E, Sheth JP, Wilkes GL, Long TE. Macromolecules 2004;37:7081.

[29] Gibson P, Schreuder-Gibson H, Rivin D. Colloids Surf A: Physiochem Eng Aspects 2001;187–188:469.

[30] Khil MS, Kim HY, Kim MS, Park SY, Lee D-R. Polymer 2004;45:295.

[31] Freakley PK, Payne AR. Theory and practice of engineering with rubber. London: Applied Science Publishers Ltd; 1978, pp. 642–643.

[32] Hess C, Hirt P, Opperman W. J Appl Polym Sci 1999;74:728.

[33] Baker AME, Windle AH. Polymer 2001;42:651.