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Polymer 44 (2003) 6857–6862

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Mechanical behavior of electrospun polyurethane

Angelo Pedicini*, Richard J. Farris[1]

Silvio O. Conte National Center for Polymer Research, 120 Governors Drive Amherst, MA 01003, USA

Received 23 June 2003; received in revised form 28 August 2003; accepted 28 August 2003

Abstract

Electrospinning is a method to produce polymer fibers from solution (or melt) with diameters ranging from 100 to 500 nm. A thermoplastic polyurethane was electrospun from solution to produce an isotropic fiber mat. The mechanical behavior of the mat was characterized by uniaxial tensile tests. The electrospun polyurethane produces a stress–strain response characteristically different to that of the material from which the mat is spun. Scanning electron microscopy and infrared spectroscopy were also used to characterize the electrospun material and determine the source of the differing mechanical responses.

Keywords: Polyurethane; Electrospinning; Infrared dichroism

1. Introduction

The concept of using static electricity to move fluids is over 500 years old [1]. Patents from the early 20th century describe electrospinning in more practical terms [2–4], and most recently electrospinning has experienced a renewal in interest from academic research as well as practical applications. Electrospun materials have proven to be useful in the medical field, for vascular grafts and prosthetic blood vessels, as well as for filtration applications [5–9]. The current body of work in the scientific literature is concentrated primarily on the phenomenon and physics of electrospinning [10–14]. Many polymers have been electrospun and characterized by various methods—electron and light microscopy, atomic force microscopy and X-ray diffraction are among some of them.

Electrospinning is a robust process, capable of producing fibers from a variety of polymer/solvent systems with diameters typically one to two orders of magnitude smaller than conventional solution or melt-spun fibers. In addition, the ability to produce highly porous membranes with structural integrity is also an attractive feature of electrospinning. These fundamental characteristics alone make electrospinning a novel and interesting process.

Thermoplastic polyurethanes (TPU) present a class of polymers that possess a range of very desirable properties: they are elastomeric, resistant to microorganisms and abrasion, and have excellent hydrolytic stability. Many commercially available TPU's can be used to make good electrospinning solutions. The future use of electrospun materials in practical applications will require a thorough understanding of their mechanical behavior. Currently, there is a limited amount work on the mechanical properties of electrospun polymers [15–17]. This study compares the mechanical behavior of an electrospun polyurethane to the behavior of the bulk material, and attempts to describe the observed differences by combining macro, micro, and molecular scale characterization.

2. Experimental

2.1. Materials

All reagents were used without further purification. *N*,*N*-Dimethyl formamide was purchased from the Aldrich Chemical Co. Pellethane® 2103-80AE is a polyether-based thermoplastic polyurethane, received from Dow Chemical Co. Electrospinning solutions were prepared by

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* Corresponding author. Address: Department of Polymer Science and Engineering, University of Massachusetts Amherst, 120 Governors Drive, Amherst, MA 01003, USA. Tel.: +1-413-577-2366; fax: +1-413-545-0082.

E-mail addresses: jello@mail.pse.umass.edu (A. Pedicini), rjfarris@polysci.umass.edu (R.J. Farris).

[1] Tel.: +1-413-577-1312; fax: +1-413-545-0082.

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doi:10.1016/j.polymer.2003.08.040

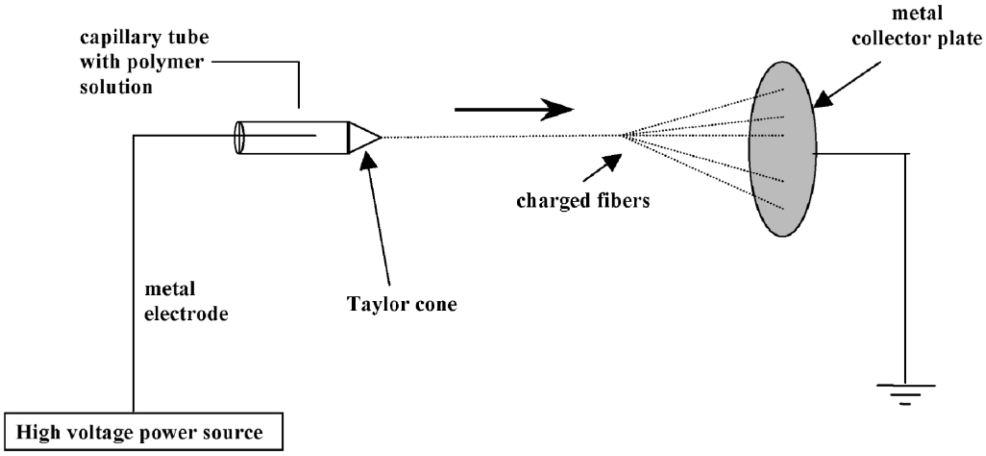

Fig. 1. Diagram of the electrospinning process.

dissolving the polymer in DMF at room temperature at a concentration of 7% polymer by weight. Bulk samples were prepared by thermally processing plaques from polymer pellets.

2.2. Electrospinning process

Isotropic fiber mats for tensile tests and infrared spectroscopy experiments were prepared by electrospinning the PU solution from a 1 ml glass pipette with a capillary tip of approximately 1 mm inner diameter. A stainless steel electrode was placed in the polymer solution and the solution was spun onto a grounded aluminum foil target. Oriented electrospun samples for IR dichroism studies were prepared by spinning the PU solution from a 10 ml syringe with metal capillary tip of 1 mm inner diameter and a backpressure applied with a syringe pump set at a volume flow rate of 0.040 ml/min. An alligator style clip was used to charge the syringe tip, and solution was electrospun onto a rotating stainless steel drum. The electric field for electrospinning was produced by a high voltage power supply (Gamma High Voltage Research) capable of generating voltages of 20 kV. A schematic diagram of the electrospinning process is shown in Fig. 1.

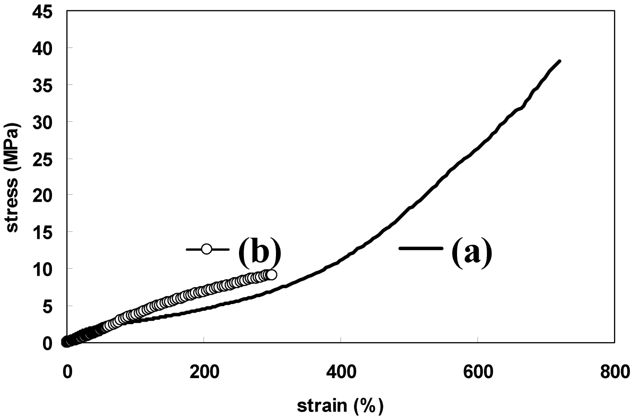

Fig. 2. Engineering stress–strain curves for Pellethane® 2103-80AE tested in uniaxial tension; (a) bulk and (b) electrospun.

2.3. Mechanical behavior

The tensile behavior of the electrospun and bulk PU was tested on an Instron 5500R with a cross-head speed of 5 mm/min at room temperature. Dumbbell-shaped tensile specimens were prepared as per ASTM 1708D from isotropic electrospun PU mats and compression molded plaques.

2.4. Morphology

The morphology of the electrospun fiber mats was studied by high resolution scanning electron microscopy (FE-SEM, JEOL 6320 Field Emission Scanning Electron Microscope) operating at an accelerating voltage of 5 kV. All specimens were sputter-coated with gold prior to SEM.

2.5. Infrared dichroism

Infrared dichroism studies were conducted using a BIO-RAD FT-IR spectrometer at a rate of 300 scans per specimen. Dichroic ratios were computed using peak values obtained from IR spectra of oriented electrospun samples with linearly polarized light parallel and perpendicular to the principle direction of fiber orientation.

3. Results and discussion

3.1. Stress–strain behavior of electrospun PU

The data from uniaxial tensile tests show the behavior of the electrospun Pellethane® 2103-80AE to be distinctly different from the bulk. Fig. 2 is a plot comparing the engineering stress–strain curves from electrospun and bulk Pellethane® 2103-80AE. The bulk material gives a characteristic response for elastomeric materials—sigmoidal in shape, with strain hardening resulting from molecular orientation at high degrees of strain. Qualitatively, the electrospun mat is also elastomeric in nature, but the shape of the stress–strain curve for the electrospun material is not sigmoidal. The curve is monotonic and does not experience an inflection in its slope and undergo an upturn in stress at high strain.

When a strain is applied to the electrospun mat, fibers oriented in the direction of cross-head displacement are stretched uniaxially, while fibers oriented at some angle relative the principal strain direction experience a rotation. In addition, the electrospun PU has a density of approximately one-third that of the bulk. These two factors explain the relatively low stress in the electrospun material at less than 50% strain. As the strain in the electrospun mat increases and more fibers become oriented in the direction of strain, the relative number of fibers stretched to fibers rotated increases, and the stress in the electrospun mat increases. In fact, from approximately 60–300% strain, the stress in the electrospun PU increases more rapidly than stress in the bulk. This discrepancy lies in a higher degree of molecular orientation within the electrospun fibers than in the bulk. The strain-induced orientation of the electrospun mat is illustrated in Fig. 4. At equal amounts of strain, the electrospun material maintains a higher stress until failure at approximately 300% strain. This seemingly premature failure is another difference between the two stress–strain curves, as the bulk PU has an ultimate strain to failure of over 700% strain. The fundamental differences observed in the stress–strain behavior of the two forms of the PU may be deciphered by comparing morphology and molecular orientation in each.

3.2. Morphological characterization

Macroscopically, the electrospun PU mat appears to be a film. Field emission SEM reveals that, in fact, the electrospun material is fibrous and highly porous, held together by bonding sites among many fibers. Fig. 3 shows a series of SEM micrographs illustrating the morphology of the electrospun material and the adhesion/cohesion among fibers at various bonding sites, which leads to the film-like character and structural integrity of the electrospun fiber mats.

The random orientation of electrospun fibers in the PU mat illustrates a similarity between the electrospun and bulk material—they are both mechanically isotropic in the plane of the material. This similarity will be confirmed later with IR dichroism.

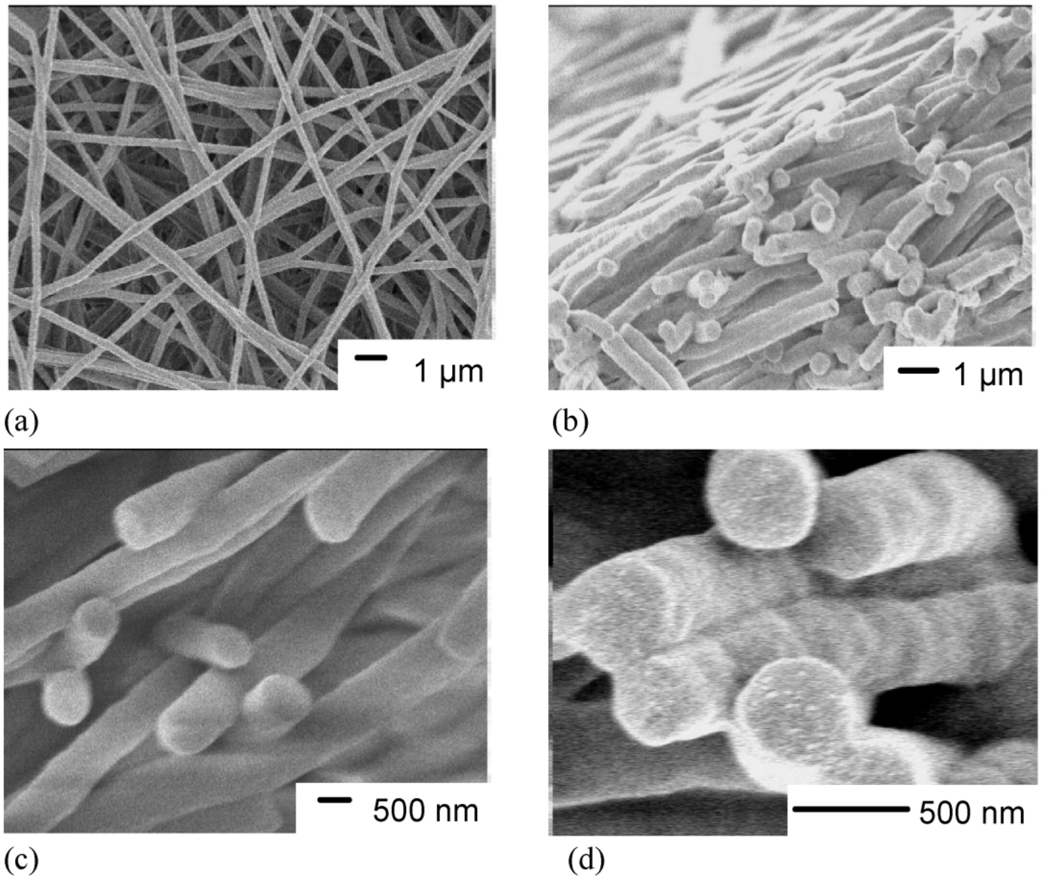

Fig. 3. SEM micrographs of electrospun Pellethane® 2103-80AE; spun from 7 wt% solution in DMF. (a) View orthogonal to the plane of the electrospun mat; (b)–(d) are cross-sectional views taken from a cryo-fractured electrospun mat.

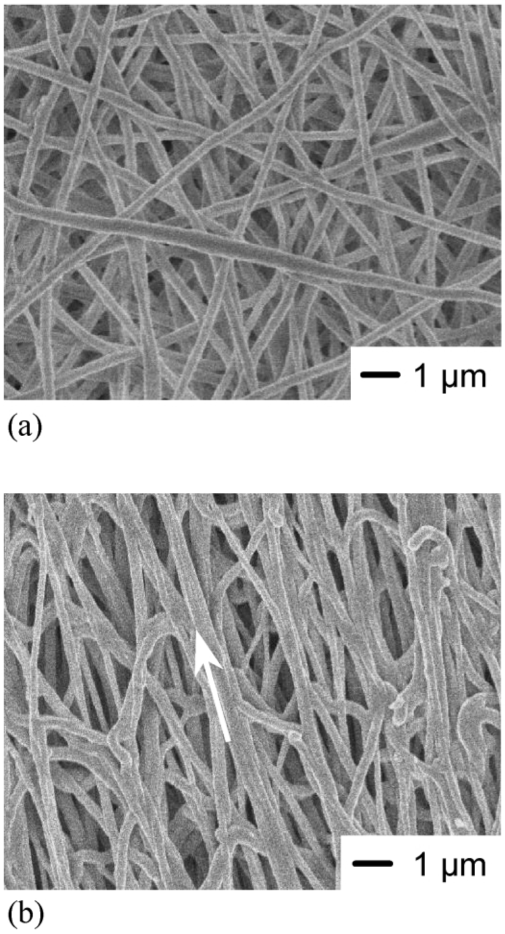

Fig. 4. Electrospun Pellethane® 2103-80AE; spun from 7 wt% in DMF. (a) 0% Strain, (b) ≈100% strain (arrow indicates the direction of applied strain).

3.3. Infrared dichroism

The strain applied to the electrospun mat serves to orient both the fibers and the molecules within the fibers. Molecular orientation also occurs in the bulk material when a strain is applied. Strain-induced orientation is illustrated in the stress–strain curve of the bulk material at high degrees of strain, as described previously. While the electrospun mat is globally isotropic, the individual fibers comprising the mat have a certain degree of molecular orientation prior to stretching. The electrospun material experiences higher stress than the bulk at strains between 60 and 300% because of this preexisting molecular orientation. Molecular orientation in the electrospun fibers can be shown with polarized infrared spectroscopy. In order to isolate the effect of molecular orientation in the electrospun fibers, a unidirectionally oriented mat of fibers was prepared. This was achieved by electrospinning the PU/DMF solution onto a rotating mandrel. An image taken from SEM of oriented electrospun Pellethane® 2103-80AE fibers is shown in Fig. 5. Although the orientation of electrospun fibers is not perfect, it is sufficient to study the molecular orientation in the fibers. Because of this imperfect orientation, the orientation function ultimately computed for the electrospun mats will be a conservative value.

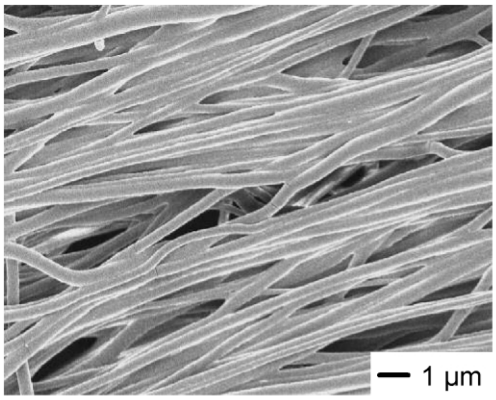

Fig. 5. Oriented electrospun Pellethane® 2103-80AE fibers.

An orientation function is calculated by analyzing the N–H stretching peak at 3320 cm^{-1} as described by Cooper et al. [18]. This stretching vibration is located in the urethane linkage, and characterizes the orientation of the hard domains in the polyurethane. Assuming that molecular orientation in the electrospun fibers is not perfect, the molecules will have an average angle with the fiber direction, θ. The average angle, θ, and the fraction of perfectly oriented molecules are related by the following equation

$$f = [3\langle\cos^2\theta\rangle - 1]/2 \tag{1}$$

called Herman's orientation function [19]. Theoretically, the value of f can range from 1, for perfectly oriented molecules, to zero for an isotropic material. If molecular orientation is perfectly orthogonal ($\theta = 90°$) to the fiber direction, f is equal to $-\frac{1}{2}$. An orientation function can also be calculated using the dichroic ratios from IR absorption. The dichroic ratio for a particular absorption band is defined by

$$D = A_{\parallel}/A_{\perp} \tag{2}$$

where $A_{\parallel}$ and $A_{\perp}$ represent the peak absorbance of infrared radiation polarized parallel and perpendicular to the fiber direction, respectively. An orientation function can then be defined by

$$f = [(D_0 + 2)/(D_0 - 1)][(D - 1)/(D + 2)] \tag{3}$$

in which D_0 is the dichroic ratio for perfect alignment. It is related to the transition moment direction (of a particular vibration) α by the expression

$$D_0 = 2\cot^2\alpha \tag{4}$$

According to Fraser [20], the N–H vibration lies essentially in the NH bond direction, which is 90° relative to the main chain direction (fiber direction), and $\alpha = 90°$ is a reasonable value. If molecular orientation exists in the fibers, greater absorbance is expected when light is polarized perpendicular

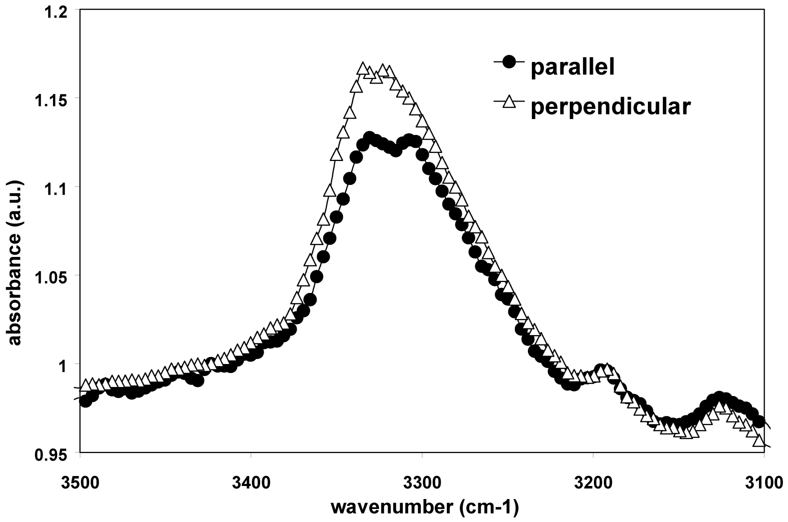

Fig. 6. IR absorption scans for oriented electrospun PU.

to the principle fiber direction than for parallel-polarized light. The absolute value of the orientation function is not of primary concern. More important is the relative value of f for the oriented electrospun fibers compared to the bulk PU. Simply, if the electrospun fibers possess some degree of molecular orientation, this orientation will partially account for the higher stress in the electrospun PU relative to the bulk, between 60 and 300% strain.

Table 1
IR absorbance and orientation function values for electrospun PU (oriented and isotropic) and bulk PU

	IR absorbance at 3320 cm^{-1} (arbitrary units)		Orientation function (f)
	Parallel	Perpendicular	
PU film	0.404	0.405	0.002
Isotropic espun PU	0.249	0.249	0.000
Oriented espun PU	1.122	1.164	0.025

Figs. 6–8 show IR absorption scans for oriented electrospun PU fibers, isotropic electrospun fibers, and a PU film, respectively. The spectrum for oriented PU fibers shows higher peak absorbance at 3320 cm^{-1} for perpendicular polarized than for parallel polarized light. For the unoriented electrospun fibers and the PU film, there is no difference in peak absorbance at 3320 cm^{-1}. Dichroic ratio and orientation function (f) values for each sample are presented in Table 1. The orientation function for isotropic electrospun fibers and bulk PU are both essentially zero. The orientation function for oriented electrospun PU fibers is small, but not zero, and an order of magnitude larger than f for the PU film. These results indicate that molecular orientation is, in fact, induced by the process of electrospinning, and must be a contributing factor to the 'stiffer'

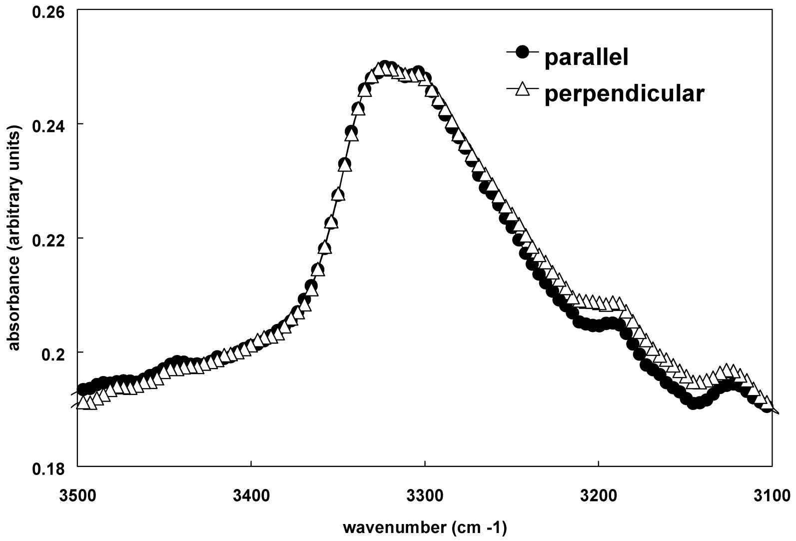

Fig. 7. IR absorption scans for isotropic electrospun PU.

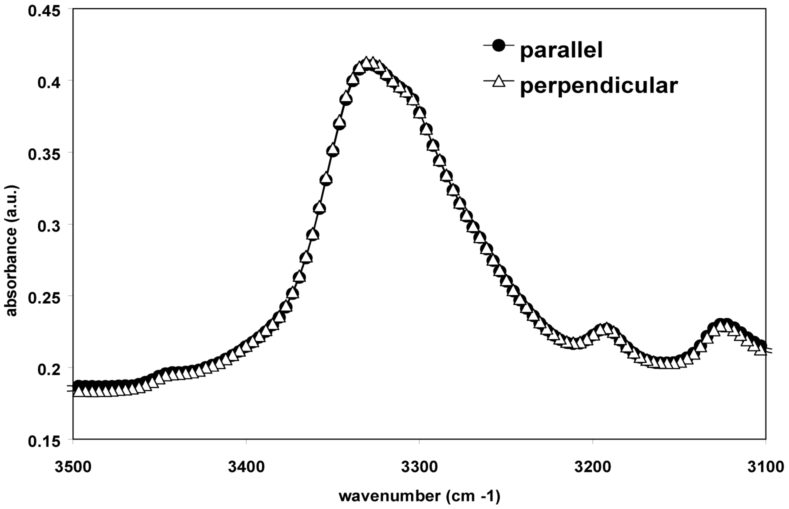

Fig. 8. IR absorption scans for bulk PU.

stress–strain response, and premature failure, of the electrospun PU when tested in uniaxial tension.

4. Summary

The stress–strain behavior of an electrospun thermoplastic polyurethane has been observed and compared to the bulk material from which it is spun. The two forms of the PU have characteristically different stress–strain responses resulting from two phenomena—molecular orientation within the fibers as a result of electrospinning, and a strain-induced orientation of the electrospun fiber mat. Electron microscopy and vibrational spectroscopy were used to illustrate this morphological change upon stretching and molecular orientation in the electrospun fibers, respectively. The apparent molecular orientation in the electrospun fibers also leads to the pronounced reduction in elongation to failure of the electrospun mat, relative to the bulk.

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