Dry-Jet-Wet Spun Polyurethane Fibers. I. Optimization of the Spinning Parameters

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Received 26 July 2008; accepted 15 August 2009
DOI 10.1002/app.31373
Published online 22 June 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This study examined the spinning of polyurethane-based elastomeric fibers with the dry-jet-wet spinning method. The three important spinning variables that were chosen were the coagulation bath ratio (dimethylformamide/water), the bath temperature, and the stretch ratio. A three-variable factorial design method, proposed by Box and Behnken, was used to optimize these process parameters. The spinning process was further fine-tuned by the variation of the stretch ratio and the dope solid content. The effect of the dry-jet length on the fiber properties was also studied. The tenacity and elastic recovery properties of the fibers were found to be optimum at a bath ratio (dimethylformamide/water) of 60 : 40, a bath temperature of 15°C, and a stretch ratio of 2.5. The density and sonic modulus were measured to determine the effect of varying the process variables on structural parameters such as the density and orientation. The surface morphological features, as revealed by scanning electron microscopy, were correlated to the fiber properties. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2291–2303, 2010

Key words: elastomers; fibers; morphology; polyurethanes; structure-property relations

INTRODUCTION

Polyurethane (PU) elastomeric fibers are generally called elastane or spandex fibers. By definition, these fibers have an elongation to break greater than 200% (usually 400–800%) and, upon the release of deforming stress, return quickly and almost completely to their original length.[1] Textile fabrics containing elastane yarns have widespread applications, especially because of their increased extensibility and elasticity, high degree of recovery, and good dimensional stability. In the apparel industry, these fabrics are used for sportswear and leisure garments, hosiery, underwear, and swimwear and specifically for body-confirming garments, which ensure a stable shape under various loads when they are worn. Elastane fibers may be incorporated into fabrics in the form of yarns, which are typically wrapped with relatively inextensible fibers. Wrapping is done via covering, core spinning, or twisting to produce yarn structures known as wrapped, core-spun, spin-twisted, siro-spun, and air-twisted yarns.[2]

Elastane fibers are made of linear long-chain synthetic polymers composed of segmented PU. The polymer chains in segmented PU consist of two chemically distinct structural units, that is, hard and soft segments, and their glass-transition temperatures are above and below room temperature, respectively. The various physical properties of spandex fibers, such as the strength, modulus, mechanical and thermal stability, elasticity, and elastic recovery, are closely related to their hard segment to soft segment ratio.[3–8] It has been reported that fibers with a 60–70% soft-segment concentration have good elastic recovery properties.[9] Dry and wet spinning methods have been extensively used to spin commercially available PU fibers, but lately, melt spinning has been widely studied to replace solution spinning because of its inherent advantages, including a cleaner and safer environment due to the nonuse of solvents and the simplicity and economy of the process. However, the properties of dry-spun fibers have been reported to be superior to those of melt-spun fibers.[10] To date, there are no reports of PU fibers being produced by a dry-jet-wet spinning process.

Dry-jet-wet spinning is another variant of the solution spinning technique in which there is an air gap (generally called the jet length) between the capillary exit and the coagulation bath. In 1970, Blades[11] discovered that high-strength, high-modulus fibers could be prepared by the dry-jet-wet spinning of anisotropic solutions of aramid polymers. The key feature of this process is that an anisotropic solution is extruded from spinneret holes through an air gap into a coagulation bath. The coagulated filaments are then washed, neutralized, and dried. This process

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Contract grant sponsor: Indian Ministry of Human Resource and Development.

produces fibers with a tenacity and initial modulus 2–4 times greater than those of fibers prepared by the conventional wet spinning process.

When anisotropic solutions are extruded through a spinneret, capillary shear causes liquid-crystalline domains to orient along the direction of the flow. However, at the capillary exit, some disorientation of liquid-crystalline domains occurs because of solution viscoelasticity. This disorientation is quickly overcome by filament attenuation in the following air gap under the spinning tension. The attenuated filaments thus retain a highly oriented molecular structure when they are precipitated, and this produces superior tensile properties.

There have been relatively few investigations of the structure and property correlations of PU-based elastomeric fibers. Yamashiro[12,13] studied the relationship between the chemical structure and the mechanical properties of melt-spun segmented PU and reported that the mechanical properties of these fibers are influenced by the aggregation of hard and soft segments and also the chemical structure of the soft segments. It has been reported[14,15] that the hard-segment orientation affects the mechanical properties of PU fibers and especially the modulus. Abhiraman et al.[16] reported that complete phase separation between the hard and soft segments is essential to obtain good elastic recovery after deformation. Furthermore, the absence of chain folding and loops, besides perfect orientation of hard-segment domains along the fiber axis, also results in good elastic recovery properties. The available literature on the effects of process parameters on the solution spinning of PU fibers is mostly available in patent form.[17,18] The effects of spinning variables on the structure and properties of PU fibers are thus not discussed much in the open literature and are therefore not clearly understood.

The aim of this investigation was to optimize the spinning process for the dry-jet-wet spinning of PU fibers. A Box–Behnken statistical design tool[19] was used to optimize three important spinning variables: the coagulation bath ratio [dimethylformamide (DMF)/water], the bath temperature, and the stretch ratio. The advantage of the Box–Behnken design over other designs is that it is rotatable and requires fewer test runs in comparison with a central composite design. The influence of other factors, such as the dope solid content and jet length, on the structural development and properties of these elastomeric fibers was also studied.

EXPERIMENTAL

Design

To optimize the properties of PU fibers, the three key spinning variables that were considered were the coagulation bath ratio, coagulation bath temperature, and stretch ratio. A three-variable and three-level factorial design technique was used to investigate the effects of all three spinning variables on the elastic recovery and tensile properties of dry-jet-wet spun PU fibers. The spinning trials were conducted with three different coagulation bath ratios and bath temperatures in the range of 11–23°C, with the stretch ratio kept constant to identify the spinnable region. It is clear from Figure 1 that the dope was spinnable under all the conditions except a bath temperature of 11°C and a DMF/water bath composition of 60 : 40; therefore, all further values chosen for the design were within this spinnable region. The actual values of these variables along with the coded levels are given in Table I.

In addition to the experiments related to the Box–Behnken design, two separate investigations of the effects of the dry-jet length and dope solid content on the fiber properties were conducted. Three dry-jet lengths (15, 20, and 25 mm) and three dope solid contents (27, 29, and 31% w/w) were investigated to study their effects on the fiber properties under optimized bath conditions: a bath ratio of 60 : 40, a bath temperature of 15°C, and a stretch ratio of 1.8–2.5.

Materials

Extrusion-grade thermoplastic PU with the trade name Elastane GP85AE (an ester type with a Shore hardness of 85A) was procured from Noveon, Inc. (Belgium). Laboratory-grade DMF from Merck (India) was used as supplied.

Method

Dope preparation

A polymer dope solution with the required solid content (w/w) was prepared through the dissolution

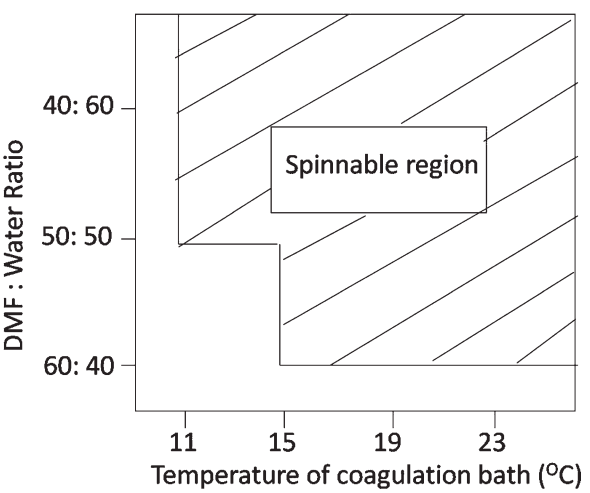

Figure 1 Spinnable region.

TABLE I
Box and Behnken Design for Three Variables

Experimental combination	Coded variables			Actual variables		
	X_1	X_2	X_3	X_1	X_2	X_3
1	−1	−1	0	40 : 60	15	1.5
2	1	−1	0	60 : 40	15	1.5
3	−1	1	0	40 : 60	23	1.5
4	1	1	0	60 : 40	23	1.5
5	−1	0	−1	40 : 60	19	1.2
6	1	0	−1	60 : 40	19	1.2
7	−1	0	1	40 : 60	19	1.8
8	1	0	1	60 : 40	19	1.8
9	0	−1	−1	50 : 50	15	1.2
10	0	1	−1	50 : 50	23	1.2
11	0	−1	1	50 : 50	15	1.8
12	0	1	1	50 : 50	23	1.8
13	0	0	0	50 : 50	19	1.5
14	0	0	0	50 : 50	19	1.5
15	0	0	0	50 : 50	19	1.5

X_1 = bath ratio; X_2 = bath temperature (°C); X_3 = stretch ratio.

of the required amount of polymer (thermoplastic PU) chips in the solvent DMF in a reaction tube with a mercury seal and a mechanical stirrer at room temperature (25°C). The whole mixture was stirred until a clear solution was obtained; subsequently, it was deaerated *in vacuo* at 45°C for 30 min to remove air bubbles.

Spinning

The fiber spinning was carried out on a solution spinning machine supplied by Bradford University Research, Ltd. (UK) (Fig. 2), with a single-hole spinneret that was 0.3 mm in diameter. The ram speed and first take-up roller speed were kept at 0.1 mm/min and 4.2 m/min, respectively.

On the basis of several experiments conducted to optimize the dry-jet-wet spinning process, the spinning conditions were chosen for further experiments, as discussed later. The other standard spinning parameters are given in Table II.

Spinning conditions

The solid content was 27% w/w, the shear viscosity at 40°C (20 rpm) was 17,800 cP, the solvent was DMF, and the dope temperature was 45°C. The air gap length was 20 ± 2 mm, and the jet stretch was 0.85. The jet stretch ratio and stretch ratio were determined as follows:

$$\text{Jet stretch ratio} = V_1/\langle V \rangle$$

$$\text{Stretch ratio} = V_3/V_1$$

where $\langle V \rangle$ is the average velocity of the dope in the spinning hole [i.e., $\langle V \rangle = Q/\pi R^2$, where Q is the flow rate per hole (cc/min) and R is the spinneret hole radius]; V_1 is the surface velocity of the first godet,

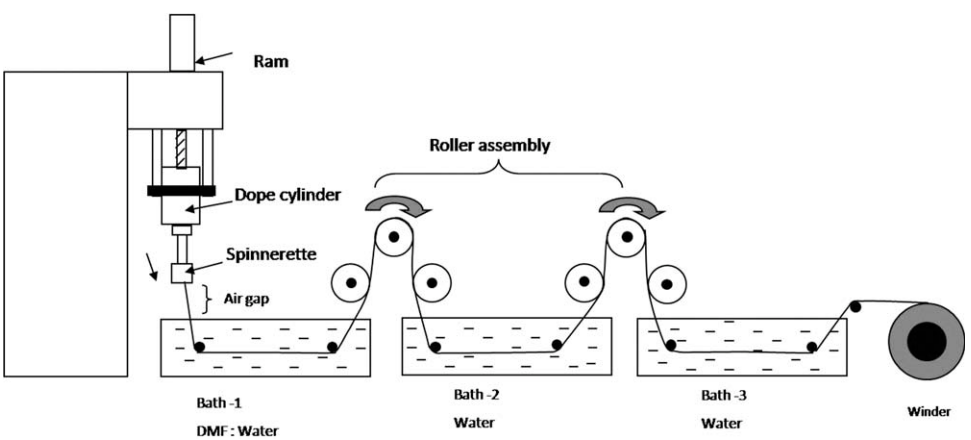

Figure 2 Schematic diagram of the spinning assembly (first roller speed = 4.2 m/min, bath 2 temperature = 48°C, bath 3 temperature = 48°C).

TABLE II
Standard Spinning Parameters

Bath	DMF/water ratio	Bath temperature (°C)
First	Variable	Variable
Second	0 : 100	48 ± 2
Third	0 : 100	48 ± 2

that is, the first roller after the coagulation bath (cm^{-1}); and V_3 is the winding drum speed (cm^{-1}).

Characterization

Linear density

The linear density of the material was tested according to ASTM Standard D 2591. The linear densities of the spun filaments were 185 ± 5.5, 145 ± 5.8, 120 ± 6, 110 ± 4.5, and 90 ± 3 denier for stretch ratios of 1.2, 1.5, 1.8, 2.0, and 2.5, respectively. The unit of linear density was the denier, that is, the weight of 9000 m of fiber in grams.

Tensile tests

Tensile tests were carried out on an Instron model 4301 universal testing machine (UK) with a crosshead speed of 450 mm/min and a gauge length of 25 mm. The regular fiber jaws were modified with neoprene rubber liners to eliminate the problems of filament slippage and compression. The filaments were held at a pretension of 0.05 mN/tex before the jaws were tightened. All the reported results are averages of 10 specimens. The tenacity and modulus values are reported as grams per denier.

Elastic properties

Elastic recovery (ASTM D 2731) tests were carried out on an Instron model 4301 universal testing machine with 10 replicates of each material. Five-centimeter-long filament samples were extended to 300% elongation at a rate of 500 mm/min and allowed to relax. This cycle was repeated five times, and in the fifth cycle, the crosshead was stopped at maximum extension, held for 30 s, and then relaxed. In the sixth cycle, the extension was noted at a tension of 0.05 mN/tex. The permanent deformation (set) was calculated with the following relation:

$$S = (E \times 100)/L$$

where S is the permanent set (%), E is the extension on the sixth cycle at a tension of 0.05 mN/tex (mm), and L is the gauge length (mm). The elastic recovery (%) was determined with the following relation:

$$\text{Elastic recovery} = 100 - S$$

Density

The density of the PU filaments was measured with a density gradient column supplied by Davenport, Ltd. (London, United Kingdom). *n*-Heptane and carbon tetrachloride were used for the preparation of the density gradient column. The column was calibrated with glass beads of accurately known densities. The measurements were made on a single 1-cm-long filament at 25°C. The results are averages of 10 readings.

Sonic modulus

The sonic velocity of the samples [C (km/s)] was measured on a PPM-5R dynamic modulus tester (H. M. Morgan Co., USA). The sonic modulus (E) was calculated with the following expression:

$$E(\text{g/denier}) = 11.3 \times C^2$$

This relationship is independent of the density of the samples.

Software

Surface contour diagrams were generated with Systat 10. Eigenvalues were calculated with Matlab 7.

Scanning electron microscopy (SEM)

Fiber samples for SEM cross-section studies were first drawn through a soft wooden cork, and then very thin slices were sectioned with a sharp blade and sputtered with silver. A Zeiss Evo 50 (Germany) scanning electron microscope operated at an accelerating voltage of 20 kV and a current of 100 μA was used for fiber cross-section and morphology studies.

RESULTS AND DISCUSSION

Theoretical aspects of solution spinning

In the case of solution spinning, process variables such as the bath conditions and stretch ratio determine structural variables of fibers such as the orientation and density, which further determine the physical properties. Mathematically, the interrelationships between the process, structural, and physical property variables can be described as follows:

1. Process variables (x): bath ratio (x_1), bath temperature (x_2), and stretch ratio (x_3).
2. Structural variables (y): density (y_1) and orientation (y_2).
3. Physical properties (z): elastic recovery (z_1), tenacity (z_2), and elongation (z_3).

Then, we can obtain the following functional relations:

$$y_1 = f_1(x), \quad y_2 = f_2(x) \tag{1}$$

$$z_1 = g_1(y), \quad z_2 = g_2(y), \quad z_3 = g_3(y) \tag{2}$$

$$z_1 = g_1\{f_1(x), f_2(x)\}, \quad z_2 = g_2\{f_1(x), f_2(x)\}, \quad z_3 = g_3\{f_1(x), f_2(x)\} \tag{3}$$

where the function f_1 relates density parameter y_1, with process variables bath ratio (x_1), bath temperature (x_2) and stretch ratio (x_3). It is defined as $f_1(.) : R^3 \rightarrow R$, where R is the real axis. Similarly, the function f_2 relates orientation parameter y_2 with bath ratio (x_1), bath temperature (x_2) and stretch ratio (x_3). It is defined as $f_2(.) : R^3 \rightarrow R$. The function g_1 relates elastic recovery parameter, z_1 with structural variables, density y_1 and orientation y_2. The function g_1 is defined as $g_1(.) : R^2 \rightarrow R$. Similarly, g_2, g_3 relates tenacity, elongation respectively with structural variables, density y_1, and orientation y_2. The function g_2, g_3 are defined as $g_2(.)$, $g_3(.) : R^2 \rightarrow R$.

Stretching is done both in the fluid state and after coagulation. The stretching process causes orientation and dense packing of the molecular chains, enabling more crystalline domains to become oriented along the fiber axis. The density depends on the coagulation process, bath temperature, and stretching. Therefore, parameter y_1 depends on x_1, x_2, and x_3:

$$y_1 = f_1(x_1, x_2, x_3) \tag{4}$$

To prove this, we can factorize eq. (4) to

$$y_1 = f_1(x_1, x_2, x_3) = \Phi_1(x_1, x_2)\, \Phi_2(x_3)$$

and measure the density at fixed values of several levels of x_3 as follows:

$$\begin{aligned} y_1^{(1)} &= \Phi_1(x_1, x_2)\Phi_2(x_3^{(1)}) \\ y_1^{(2)} &= \Phi_1(x_1, x_2)\Phi_2(x_3^{(2)}) \\ y_1^{(n)} &= \Phi_1(x_1, x_2)\Phi_2(x_3^{(n)}) \end{aligned} \tag{5}$$

where the functions $\Phi 1(x_1, x_2)$ and $\Phi_2(x_3)$ are the factors of the function $f_1(x_1, x_2, x_3)$. The function Φ_1 can be defined as $\phi_1(.) : R_2 \rightarrow R$ and Φ_1 can be defined as $\Phi_1(.) : R_2 \rightarrow R$.

Orientation is determined during the stretching step. If the coagulation step does not involve a significant deformation (elongation) process, then we can conclude that the coagulation step maintains the orientation achieved during the stretching step. Because the thermal motion of polymer chains destroys the orientation achieved during the stretching step, solidification by coagulation reduces the thermal motion to preserve the orientation, and this gives rise to the factorization of $f_2(x)$ as follows:

$$y_2 = f_2(x_1, x_2, x_3) = \Phi_1(x_1, x_2)\Phi_2(x_3) \tag{6}$$

To prove eq. (6), we can measure the orientation at fixed values of several levels of x_3:

$$\begin{aligned} y_2^{(1)} &= \Phi_1(x_1, x_2)\Phi_2(x_3^{(1)}) \\ y_2^{(2)} &= \Phi_1(x_1, x_2)\Phi_2(x_3^{(2)}) \\ y_2^{(n)} &= \Phi_1(x_1, x_2)\Phi_2(x_3^{(n)}) \end{aligned} \tag{7}$$

From eq. (7), we can determine the following:

$$\frac{y_2^{(2)}}{y_2^{(1)}} = \frac{\Phi_2(x_3^{(2)})}{\Phi_2(x_3^{(1)})}, \ldots \frac{y_2^{(n)}}{y_2^{(1)}} = \frac{\Phi_2(x_3^{(n)})}{\Phi_2(x_3^{(1)})} \tag{8}$$

If the experimental data satisfy eq. (8) for any set of $\{x_1, x_2\}$, then the factorization is valid. The validity of eqs. (6) and (7) gives the functional structure of $\Phi_2(x_3)$. Knowledge of $\Phi_2(x_3)$ makes response surface analysis easy because the relationship $y_2 = \Phi_2(x_3)$ depends on two independent variables, such as x_1 and x_2. Thus, we can exploit the merit of the two-dimensional contour map. Equations (1)–(3) provide two new independent variables, y_1 and y_2, which allow us to use two-dimensional contour maps. Measurements of the structural variables can thus give us a better understanding of the effects of process variables on properties.

TABLE III
Response Surface Equations of the PU Filaments

Property	Response surface equation	R^2
Elastic recovery	$54.667 + 1.5X_1 - 0.375X_2 + 2.375X_3 + 0.292X_1^2 + 0.542X_2^2 + 0.542X_3^2 - 0.25X_2 \times X_3 - 0.5X_3 \times X_1$	0.945
Tenacity	$0.517 + 0.054X_1 - 0.015X_2 + 0.041X_3 + 0.004X_1^2 + 0.007X_2^2 - 0.001X_3^2 - 0.038X_1 \times X_2 - 0.007X_2 \times X_3 + 0.025X_3 \times X_1$	0.912
Elongation	$541 + 52.25X_1 + 21.75X_2 - 79X_3 + 82X_1^2 + 21X_2^2 - 30.5X_3^2 - 11.5X_1 \times X_2 + 23X_2 \times X_3 - 45X_3 \times X_1$	0.991

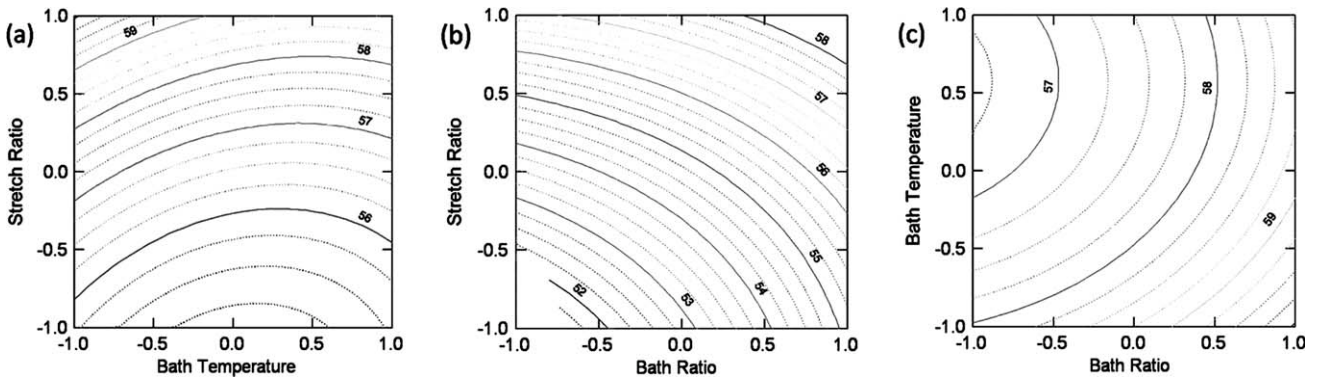

Figure 3 Selected surface contours indicating the effects of (a) the bath ratio, (b) the bath temperature, and (c) the stretch ratio on the elastic recovery.

Optimization of the spinning variables with the Box–Behnken design

Table III shows the response surface equations of PU filaments obtained with the Box–Behnken design. It is clear from these response surface equations that the key fiber properties—the elastic recovery, elongation, and tenacity—are significantly dependent on all three chosen spinning variables, that is, the coagulation bath composition, bath temperature, and stretch ratio. The coefficient of determination (R^2) values greater than 0.9 also suggest a good correlation between the variables and fiber properties. The select contour plots for the three variables are shown in Figures 3–5.

To arrive at the optimum conditions from the equations shown in Table III, a full-search method over the grid (surface contour plots) of $x^{(i)}{}_k = -1 + 2i/50$ (for $k = 1$, 2, or 3 and $i = 0$–50; where the variable $x(^{\mathrm{i}})\mathrm{k} = -1 + 2i/50$ is the i^{th} location on the grid of the k^{th} process parameter) was employed. The calculated maximum and minimum values are given in Table IV. Table IV shows that the optimum conditions are outside the experimental conditions chosen, such that $-1 \leq x_k \leq 1$. Therefore, it is necessary to calculate the extreme points for the three physical properties. We can denote the functions of the physical properties as follows:

$$z_k = g_k(x_1, x_2, x_3,) = \alpha^k_{000} + \alpha^k_{100}x_1 + \alpha^k_{010}x_2 + \alpha^k_{001}x_3 + \alpha^k_{110}x_1x_2 + \alpha^k_{011}x_2x_3 + \alpha^k_{101}x_3x_1 + \alpha^k_{200}x_1^2 + \alpha^k_{020}x_2^2 + \alpha^k_{002}x_3^2$$

where z_{k} is the k^{th} physical property, α^{K}, k = 0,1,2 $\ldots k$, are regression coefficents, g_{k} is a function which relates k^{th} physical parameters z_{k}, k = 1,2,3 with process variables x_1, x_2, x_3.

Then, the extreme point must satisfy

$$\left.\begin{array}{l}\frac{\partial z_k}{\partial x_1} = 0\\ \frac{\partial z_k}{\partial x_2} = 0\\ \frac{\partial z_k}{\partial x_3} = 0\end{array}\right\} \Rightarrow \begin{bmatrix} 2\alpha^k_{200} & \alpha^k_{110} & \alpha^k_{101} \\ \alpha^k_{110} & 2\alpha^k_{020} & \alpha^k_{011} \\ \alpha^k_{101} & \alpha^k_{011} & 2\alpha^k_{002} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} \alpha^k_{100} \\ \alpha^k_{010} \\ \alpha^k_{001} \end{bmatrix}$$

To check the convexity, it is necessary to calculate the Hessian matrix ($\mathbf{H}_k$):

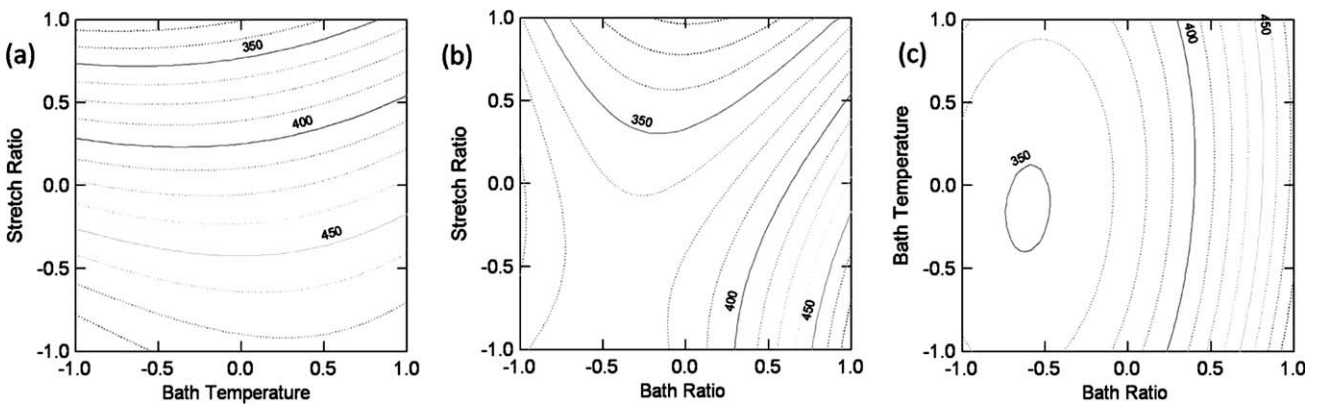

Figure 4 Selected surface contours indicating the effects of (a) the bath ratio, (b) the bath temperature, and (c) the stretch ratio on the elongation at break.

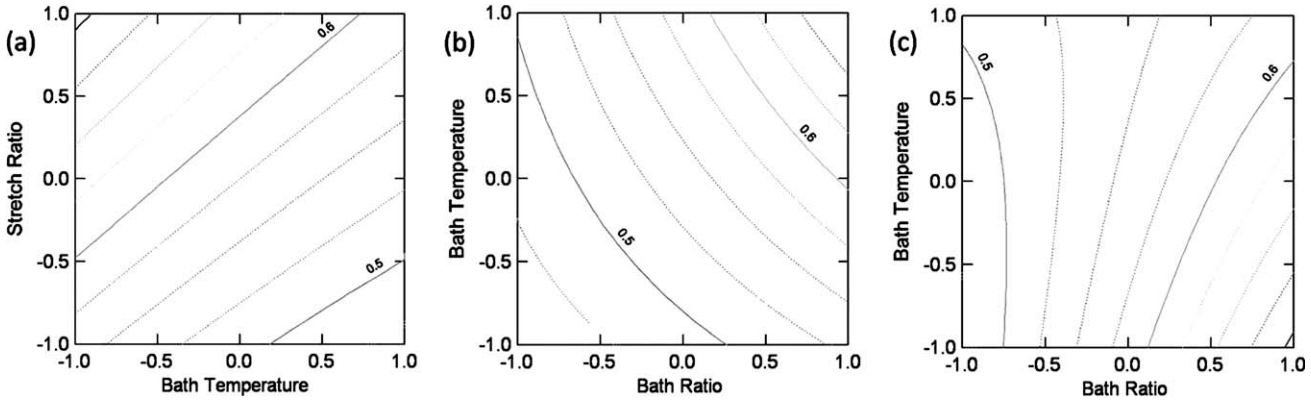

Figure 5 Selected surface contours indicating the effects of (a) the bath ratio, (b) the bath temperature, and (c) the stretch ratio on the tenacity.

$$[\mathbf{H}_k] = \begin{bmatrix} 2\alpha^k_{200} & \alpha^k_{110} & \alpha^k_{101} \\ \alpha^k_{110} & 2\alpha^k_{020} & \alpha^k_{011} \\ \alpha^k_{101} & \alpha^k_{011} & 2\alpha^k_{002} \end{bmatrix}$$

The sum of the diagonal component matrix (A_k) is determined as follows:

$$A_k \equiv 2(\alpha^k_{200} + \alpha^k_{020} + \alpha^k_{002})$$

The determinant of $\mathbf{H}_k$ (D_k) is determined as follows:

$$D_k \equiv \det \mathbf{H}_k$$

Whenever a_{ii} is greater than 0 for all values of i, $a_{ii} + a_{jj}$ is greater than $2R[a_{jj}]$ for $i \neq j$, and det $\mathbf{H}_k$ is greater than 0 or all eigenvalues are positive, $\mathbf{H}_k$ is said to be positive-definite,[20] and so the extreme point of the function is the local minimum. If all the eigenvalues of $\mathbf{H}_k$ are negative, the matrix is said to be negative-definite, and the extreme point is the local maximum. If the eigenvalues have both positive and negative values, then the stationary point is the saddle point.[21] To obtain the optimum conditions, all the process variables with positive effects should be maximized, and those with negative effects are to be minimized.

The eigenvalues for the physical properties are given in Table V. All the eigenvalues for elastic recovery are positive, and this indicates that the stationary point is a point of minimum response; however, the elongation and tenacity have negative and positive eigenvalues, and this suggests that their stationary points are saddle points. Thus, it can be concluded that all the properties have no local maxima, as is readily evident from Table IV. The results of the Box–Behnken design analysis can be summarized as follows:

1. Maximization of the bath ratio (DMF/water) is good for all three properties, that is, the elastic recovery, elongation, and tenacity.
2. Minimization of the bath temperature is good for all three physical properties.
3. Maximization of the stretch ratio is good for elastic recovery and tenacity but degrades the elongation values.

Experimental validation of the design results

The properties for elastomeric filaments in the order of their importance are the elastic recovery, elongation, and tenacity. Any attempt to improve one physical property affects the other properties as well. In the current case, in which multiple responses are observed, it would therefore be

TABLE IV
Process Parameter Conditions for the Maximum and Minimum Values of the Physical Properties

	Maximum value			Minimum value		
Variable	Elastic recovery (%)	Tenacity (g/denier)	Elongation (%)	Elastic recovery (%)	Tenacity (g/denier)	Elongation (%)
Bath ratio	60 : 40	60 : 40	60 : 40	40 : 60	40 : 60	40 : 60
Bath temperature	15	15	15	19	15	15
Stretch ratio	1.8	1.8	1.2	1.2	1.2	1.8
Value	60	0.71	734	51.1	0.43	426

TABLE V
Eigenvalues for the Elastic Recovery, Elongation, and Tenacity

Physical property	Eigenvalues
Elastic recovery	0.39, 0.74, 1.6
Elongation	−45.47, 27.3, 108.92
Tenacity	0.097, −0.079, 0.006

The eigenvalues were calculated with Matlab 7.

appropriate for the property with the highest importance (elastic recovery) to be optimized first and for the other properties (the elongation and tenacity) to be ascertained to also be in the acceptable range.

The design analysis suggests that the true optimum region for elastic recovery is far from the experimental region, and there is thus room for further enhancement of the elastic recovery property by maximization of the bath ratio and stretch ratio and minimization of the temperature. To validate this, a set of spinning trials was carried out with an increased DMF/water bath ratio of 65 : 35 at the bath temperature of 15°C, but the spinning was not feasible. Spinning was also not possible with a bath concentration of 60 : 40 at a lower bath temperature of 13°C. Therefore, it has been concluded that a DMF/water bath ratio of 60 : 40 and a bath temperature of 15°C are the optimum conditions under this experimental setup. To study the influence of higher stretch ratios, fibers were spun with increasing stretch ratios (up to 2.5) with a bath ratio of 60 : 40 at 15°C. A significant improvement in the elastic recovery property (Fig. 6) with an increase in the stretch ratio (>1.8) further validated the results of the Box–Behnken design. A stretch ratio higher than 2.5 could not be employed because of the practical difficulty of handling low-modulus, very fine denier monofilaments obtained at higher stretch ratios (>2.5) on the existing machine. Therefore, the stretch ratio of 2.5 was taken to be optimum. Although higher stretch ratios were expected to cause a decrease in the elongation, as predicted by the design, nevertheless, both the elongation and tenacity remained in the acceptable range, as shown in Table VI.

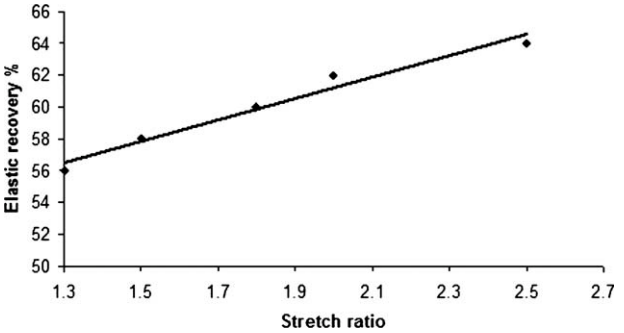

Figure 6 Influence of the stretch ratio on the elastic recovery.

Influence of the spinning conditions on the fiber properties

Bath concentration and temperature

The influence of the bath concentration (DMF/water) and bath temperature on the elastic recovery, elongation, and tenacity is shown in the contour diagrams of Figures 3, 4, and 5, respectively. As the DMF (solvent) concentration in the coagulation bath increases, the enhancement of all three physical properties can be observed. However, decreasing the bath temperature causes an enhancement of the tenacity and elastic recovery, whereas the elongation suffers slightly. SEM photographs (at both low and high magnifications) of PU fibers spun with three different bath concentrations are shown in Figure 7. The pore density in the cross section increases as the

TABLE VI
Mechanical Properties of the Fibers Spun with Various Dope Solid Contents

Dope solid content (%)	Property	Stretch ratio 1.8	2.0	2.5
27	Elastic recovery (%)	59	62	64
	Elongation (%)	822	743	611
	Tenacity (g/denier)	0.58	0.60	0.63
29	Elastic recovery (%)	60	61	62
	Elongation (%)	839	781	658
	Tenacity (g/denier)	0.62	0.60	0.58
31	Elastic recovery (%)	58	60	61
	Elongation (%)	956	871	761
	Tenacity (g/denier)	0.57	0.56	0.44

The spinning conditions were as follows: a DMF/water ratio of 60 : 40 and a bath temperature of 15°C. Coefficient of variation (CV) was ≤1.5% for elastic recovery, ≤ 4% for elongation, and ≤ 7% for tenacity.

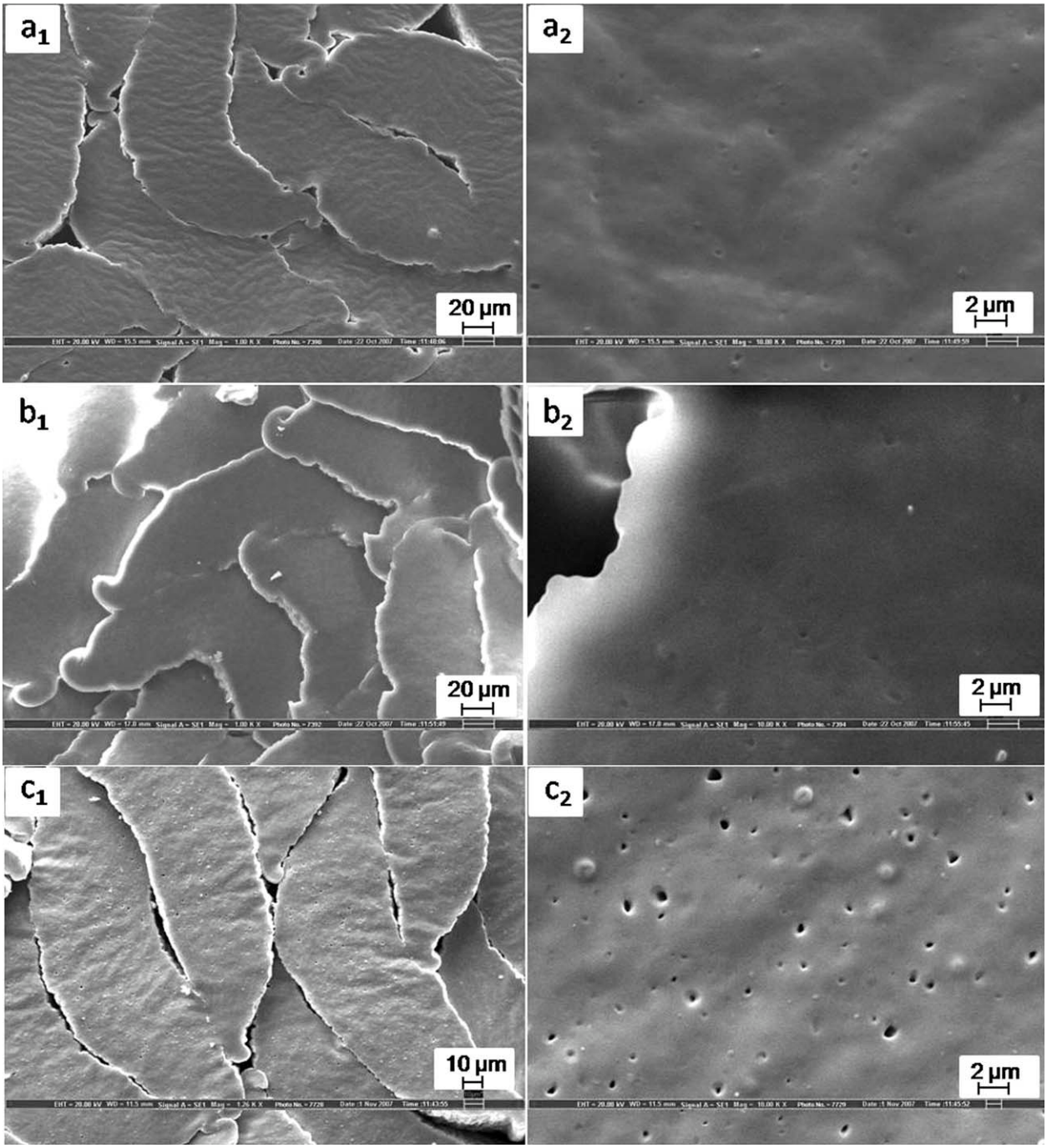

Figure 7 Effect of the coagulation bath concentration (DMF/water) on the cross-sectional shape (1000×) and pore density (10,000×) of the PU fibers: (a) 60 : 40, (b) 50 : 50, and (c) 40 : 60 (spinning conditions: bath temperature = 15°C, stretch ratio = 1.8, dope solid concentration ~ 27%).

nonsolvent content in the bath increases. A large value of the heat of solution with a high nonsolvent content in the coagulation bath is responsible for the large void content, as reported by Hancock et al.[22] At a constant bath ratio, the pore density increases with an increase in the temperature. A high concentration of the solvent (DMF) in the bath and a reduced bath temperature lead to lower coagulation rates and thus result in improved fiber properties. At low temperatures, coagulation is retarded, and thus more time is available for the internal adjustment of osmotic stresses; this results in a denser and more homogeneous fiber.[23] In addition, slower coagulation results in less skin formation, and this, in turn, probably leads to reduced voids. The increased coagulation rates at higher temperatures may result in highly coiled soft segments to maximize the elongation at break. These results confirm the established

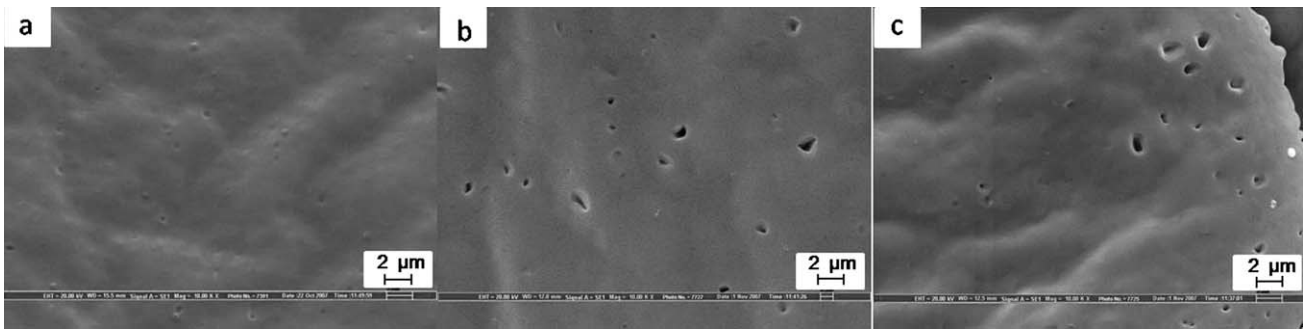

Figure 8 Effect of the coagulation bath temperature on the pore density (10,000×) of the PU fibers: (a) 15, (b) 19, and (c) 23°C (bath ratio = 60 : 40, stretch ratio = 1.8, dope solid concentration ~ 27%).

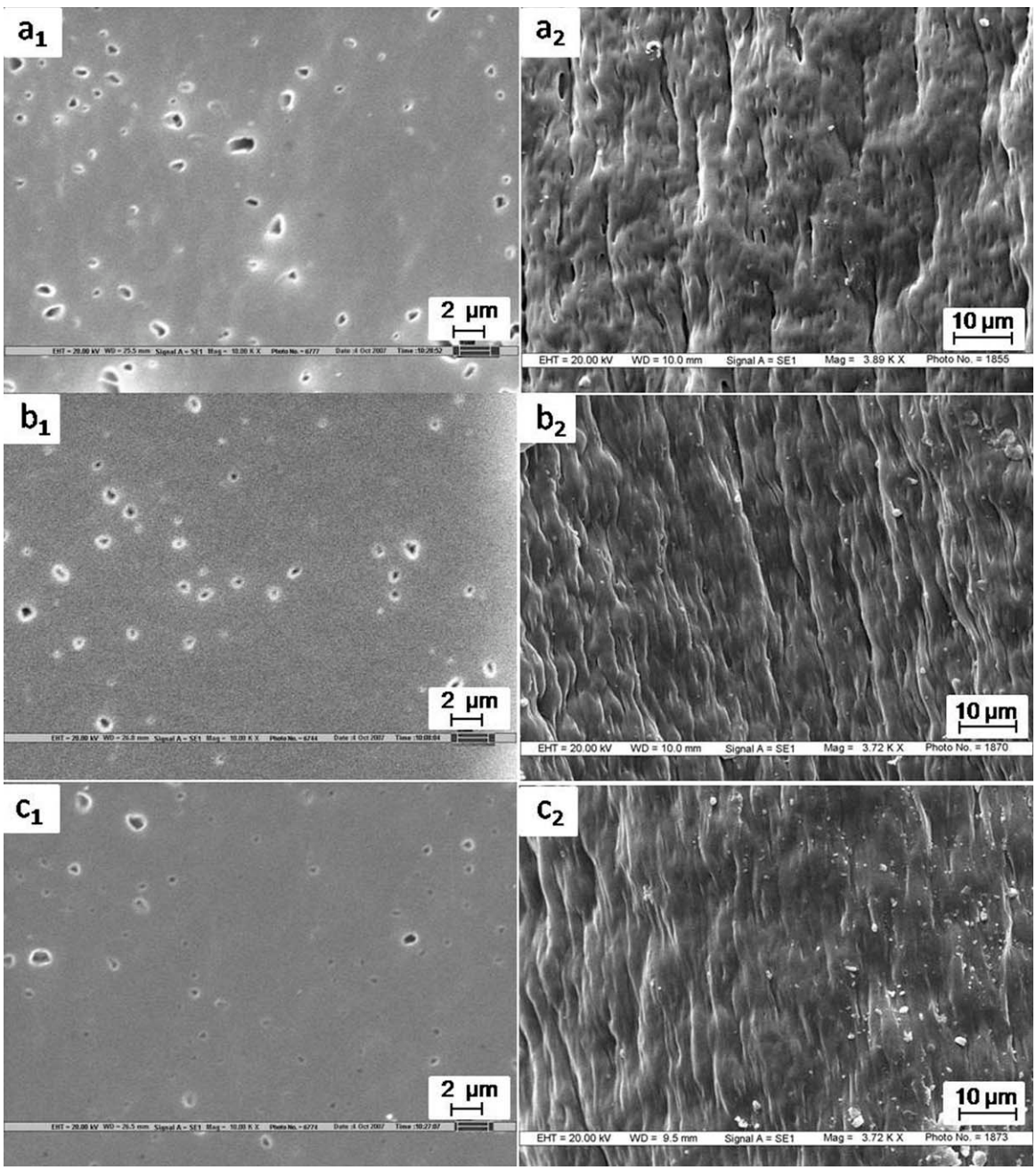

Figure 9 Influence of the stretch ratio on the pore density in the cross section (10,000×) and surface morphology (3890×) of the PU fibers: (a) 1.5, (b) 2.0, and (c) 2.5 (bath ratio = 60 : 40, bath temperature = 15°C, dope solid concentration ~ 27%).

TABLE VII
Fiber Density for the Dry-Jet-Wet Spun PU Fibers

	Fiber density (g/cc)				
Dope solid content (%)	Stretch ratio = 1.2	Stretch ratio = 1.5	Stretch ratio = 1.8	Stretch ratio = 2.0	Stretch ratio = 2.5
27	1.265	1.267	1.269	1.27	1.273
29	–	–	1.269	–	1.271
31	–	–	1.268	–	1.271

The results were averages of 10 readings (CV $\leq$ 0.6%). The other spinning conditions were as follows: a bath ratio of 60 : 40 and a bath temperature of 15°C.

trend that slow coagulation leads to superior properties. The bean-shaped cross section of the fiber may be attributed to the higher outflux of the solvent from the filament into the bath in comparison with the influx of the nonsolvent from the bath into the filament.[24] The effect of increasing the bath temperature with a constant concentration of the solvent in the bath (Fig. 8) is the same as that of decreasing the concentration of the solvent in the coagulation bath.

Stretch ratio

The influence of the stretch ratio on the elastic recovery, elongation, and tenacity is shown in the contour diagrams of Figures 3, 4, and 5, respectively. It is clear from the contour diagrams that the elastic recovery and tenacity increase with an increase in the stretch ratio, whereas the elongation decreases. The increase in the tenacity and elastic recovery at higher stretch ratios is generally attributed to (1) the superior orientation of hard segments along the fiber direction, which eliminates the resistance to recovery from deformation that would result from the nonaxially oriented crystalline domains; (2) the high degree of bridging of hard-segment domains along the fiber direction through coiled soft segments; and (3) the elimination of chain folding, regular or irregular, which prevents loops that would not contribute to elasticity.[16] Increasing the stretch ratio contributes to all these possibilities.

The SEM photographs shown in Figure 9 illustrate the surface morphology of PU fibers. The fibers appear to have a rough surface structure with irregular stripes. These are formed by the depression of voids in the fibers, which are common in fibers made in low-concentration regions, and the fibers are elongated while in the coagulation bath.[25] The photographs also suggest that the surface smoothness of the fibers improves as the stretch ratio is enhanced. The surface morphology of the fibers, shown in Figure 9(a_2), indicates that the elongated pores which are conspicuous at lower stretch ratios (1.2–1.8) are stretched at higher stretch ratios (2.5), as shown in Figure 9(c_2), because of the healing effect. Thus, the pore size and number of pores are reduced with the stretch ratio [Fig. 9(b_1,c_1)]. The increase in the elastic recovery of the fibers at a high stretch ratio of 2.5 may be due to the orientation of hard-segment domains.

Influence of the spinning parameters on the structural variables

In wet spinning, structural variables such as the orientation and density of the fiber depend on the process variables, which govern the phase equilibria and the kinetics of phase separation (the coagulation rate). The densities of fibers spun under various process conditions are presented in Table VII. The data suggest that the density of the fibers increases with the stretch ratio, and this validates eqs. (4) and (5). The sonic modulus, which is a measure of the molecular orientation, was measured for the fibers spun with a DMF/water bath ratio of 60 : 40 and a bath temperature of 15°C for different stretch ratios and is presented in Figure 10. The increase in the sonic modulus of the filaments with the stretch ratio indicates an enhancement of the degree of molecular orientation for the fibers, which validates eqs. (6) and (7). The increase in the density and orientation at higher stretch ratios can be attributed to (1) the elimination of chain folding, which prevents loops; (2) the superior orientation of hard segments along

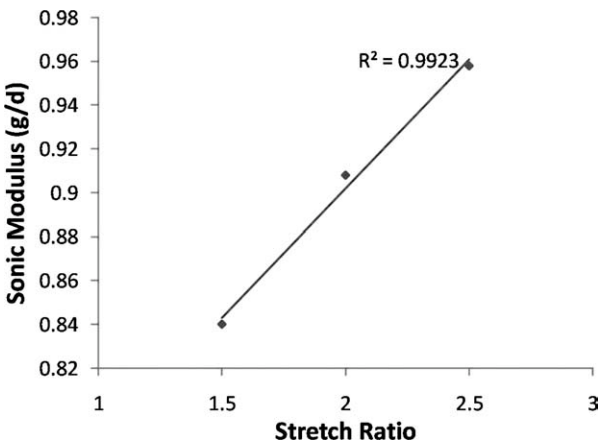

Figure 10 Sonic modulus of the fibers with various stretch ratios (bath ratio = 60 : 40, bath temperature = 15°C).

TABLE VIII
Mechanical Properties of the Fibers Spun with Various Jet Lengths

Property	Jet length (mm)		
	15	20	25
Elastic recovery (%)	63	64	64
Elongation (%)	600	611	626
Tenacity (g/denier)	0.63	0.63	0.63

The optimum spinning conditions were as follows: a bath ratio of 60 : 40, a bath temperature of 15°C, and a stretch ratio of 2.5.

the fiber axis; and (3) the facilitation of a high degree of bridging by hydrogen bonding and better packing of the long-chain molecules.

Effect of the dope solid content on the elastic recovery

Generally, a higher dope solid content increases the productivity of a spinning operation in addition to the chain entanglement density, and hence superior fibers are expected. To explore the influence of the dope solid content on the fiber properties, a set of spinning trials was carried out with dope solid contents of 25, 29, and 31% and with optimized parameters obtained by the Box–Behnken design, that is, a bath ratio of 60 : 40, a bath temperature of 15°C, and stretch ratios of 1.8, 2.0, and 2.5. Fibers spun with a solid content of 25% were weak, and frequent breaks were encountered in the stretching bath; hence, dope solid contents of 27, 29, and 31% were considered for comparison. Table VI summarizes the mechanical properties of fibers spun with dope solid contents of 27, 29, and 31%. The fibers spun with a dope solid content of 27% exhibit better elastic recovery than those spun with dope solid contents of 29 and 31%. The pore size and pore density also increase with the dope solid content, as shown in the inset of Figure 11. This increase in the pores/voids may be responsible for the decrease in the fiber properties as well as fiber density (Table VII). In solution spinning, the mechanism of fiber formation is controlled by phase separation during coagulation: the dope solution is segregated into a polymer-rich phase and a polymer-lean phase. When the concentration of the spinning dope is below the critical point, the polymer-lean phase is continuous, and the polymer-rich phase is discontinuous; eventually, fewer voids are formed, and the converse is true for concentrations above the critical point. This accounts for the possible deterioration in the properties with dope solid contents greater than 27%.

Effect of the dry-jet length on the fiber properties

To study the influence of the dry-jet length (i.e., the air gap length) on the fiber properties, a set of fiber spinning trials was carried out through the variation of the jet length from 0 to >30 mm. Wet spinning (when the dry-jet length is zero) was not feasible with this machine setup. Dry-jet-wet spinning below the dry-jet length of 10 mm and above 30 mm was also not possible because of frequent breaks. However, trouble-free spinning was observed in the jet length range of 15–25 mm. The reason may be that at a jet length below 10 mm, the natural spin draw in the air gap is quite low, and this results in a coarse-diameter fluid jet at the point of coagulation. The coagulation causes a skin formation that may inhibit or delay the coagulation of the fluid core. The

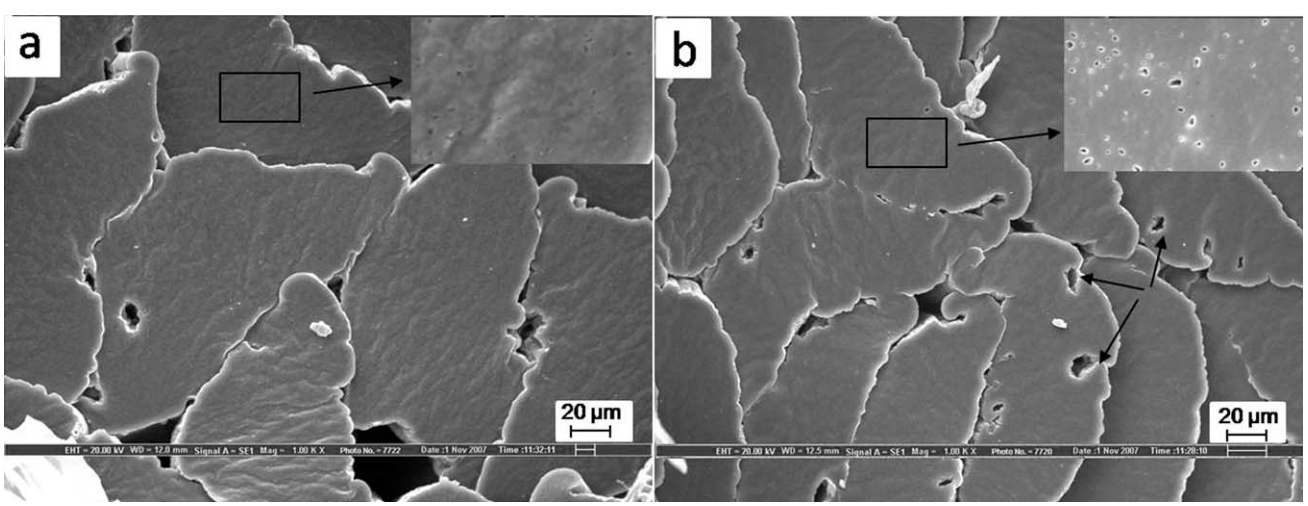

Figure 11 Effect of the dope solid content on the cross-sectional shape (×1000) and pore density (in the inset; 10,000×) of the spun PU fibers: (a) 29 and (b) 31% (bath ratio = 60 : 40, bath temperature = 15°C, stretch ratio = 1.8).

take-up forces from the godet roller may cause slippage between the solid skin and the fluid core, resulting in breakage. On the other hand, at jet lengths of about 30 mm and greater, the spin draw in the air gap is too high, presenting a much finer jet at the point of coagulation. The rheological forces that develop in the coagulated fine-denier filament cannot sustain the stresses of the take-up rollers and thus break. Hence, fiber spinning was observed to be difficult at jet lengths of less than 10 and more than 30 mm. For a comparison of the effect of the jet length, fibers were therefore spun with three dry-jet lengths (15, 20, and 25 mm) and tested for the elastic recovery and tensile properties. No statistically significant differences were observed at the 95% confidence level in the elastic recovery and tensile properties among the fibers obtained with various jet lengths, as shown in Table VIII.

CONCLUSIONS

Elastomeric PU fibers have been successfully spun with the dry-jet-wet spinning technique and are reported for the first time in the open literature. The spinning variables, that is, the coagulation bath concentration, bath temperature, and stretch ratio, have been optimized with the Box–Behnken design. The minimization of the bath temperature and coagulation bath ratio (DMF/water) is good for all three physical properties, whereas maximization of the stretch ratio is good for the elastic recovery and tenacity but reduces the elongation. The optimum fiber properties have been obtained at a DMF/water bath ratio of 60 : 40, a bath temperature of 15°C, and a stretch ratio of 2.5.

Increasing the bath temperature has an effect similar to that of increasing the nonsolvent (water) content in the coagulation bath. Higher stretch ratios cause the healing of pores on the surface, resulting in improved smoothness and elastic recovery of the fibers; however, there is a slight decrease in the elongation. The structural parameters, that is, the density and molecular orientation, also increase with the stretch ratio. A dry-jet length in the range of 20 mm and a dope solid content of 27% produce reasonably good fibers. The effects of the Shore hardness of PU on the spinnability and fiber properties will be discussed in our next article.

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