Simple Methods Influencing on Properties of Electrospun Fibrous Mats

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ABSTRACT: In many cases, potentially good electrospun materials are not satisfactory to the intended uses, but the use of the additional processing allows for an achievement of more suitable properties. Sometimes certain modifications of the spinning solutions are needed to improve its spinning ability and to properly carry out the electrospinning. For example an introducing of ionic and nonionic surfactants as Tebac or Triton X-100 significantly improved spinning ability of PLA or chitosan solutions. In turn the annealing or the annealing under pressure has enhanced crystallinity, mechanical strength, and an apparent density of raw electrospun fibrous mats from various PLAs, making them more useful.
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Key words: nanofiber; electrospinning; surfactant; chitosan; PLA

INTRODUCTION

An electrospinning turned out as very useful technique for fabrication of micro and nanofibrous nonwovens during the last about 20 years of practice. These materials with different structures are made from various synthetic as well as natural polymers, have potentially a broad range of applications in the fields such as filtration, medicine, drug delivery, tissue engineering, wound dressing, functional textiles, radioprotection, and many others. Some good reviews on the topic of electrospinning are listed e.g., in Refs. 1–3. The beneficial features of these materials are mainly based on high ratio of surface area to mass, which is a primary characteristic of nanofibers due to their dimensions. Many other ways are employed to achieve functionality of fibrous mats as oriented fiber alignment, multilayer electrospinning and mixing electrospinning, fabrication of porosity, two-phase electrospinning, and fabrication of core-shelled nanofibers.[4] For laboratory-scale production of the nanofibers the electrospinning is a very useful and simple method. The electrospinning setup mainly consists of three major components: a high voltage power supply, a spinneret (usually a metal capillary), and a grounded collector (a metal screen, plate, or rotating pipe).[5] When a charged polymer solution is fed through the spinneret under an external electric field, a suspended conical droplet is formed. When the applied electric field is strong enough to overcome the surface tension, a tiny jet is ejected from the droplet and drawn toward the collecting plate. During journey of the jet the solvent is evaporated and nanofibers or microfibers are created. The thickness and morphology of fibers can be controlled by many parameters, such as solution properties, viscosity, elasticity, conductivity and surface tension, electric field strength, distance between the spinneret and the collector, temperature, and humidity. The resulting product is mostly a fibrous porous mat. Quite often the properties of products obtained by this technique are not consistent with expectations. This article presents several methods that changed the properties of the electrospun fibrous mats, through processing them or modifications of spinning solutions, in the positive sense for our applications for filtration and medical materials.

MATERIALS AND METHODS

Materials

Poly (lactic acid), PLA25, was synthesized by solution method in diphenyl ether with tin catalyst. It is characterized by molecular weight of 160×10^3 g mol^{-1} and melting temperature of 163°C. Resomer L207S is a commercial poly (L-lactide) characterized

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TABLE I
Effect of Adding Tebac and Triton X-100, Respectively, on the Increase in Electrical Conductivity of the Mixture of Chloroform/DMSO and Lowering the Surface Tension of the Spinning Solution of Chitosan/PEO

Mixture of chloroform/DMSO 90/10		Spinning solution of chitosan/PEO 80/20		
Concentration of Tebac in wt %	Electric conductivity in pS cm^{-1}	Concentration of Triton X-100 in wt %	Surface tension in mN m^{-1}	Viscosity in cP
0	1.72	0	85	390
1	142.0	1	46	376
5	417.0	2	43	368
10	709.0	3	41	361

by inherent viscosity of 1.5–2.0 dL g^{-1} (0.1% in chloroform, 25°C). It was supplied by Boehringer Ingelheim. Chitosan FG-90 was supplied by Primex. Chloroform and DMSO (dimethyl sulfoxide), used as the solvents for the PLA spinning solution in the form of mixture of 90 wt % chloroform and 10 wt % DMSO were supplied by Sigma–Aldrich.

PEO [poly(ethylene oxide)], 4×10^6 g mol^{-1} from Sigma–Aldrich was also used in this study. Tebac (benzyl tri ethyl ammonium chloride) an ionic surfactant was used as agent to increase the conductivity of the PLA spinning solution. It was supplied by Sigma–Aldrich. Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$) from Sigma–Aldrich is a high-purity, water-soluble, liquid, nonionic surfactant. It was used as agent for the lowering of the surface tension of the chitosan spinning solution.

Spinning solutions

The spinning solutions were prepared no more than a day before electrospinning. The PLAs were dissolved in chloroform and then, DMSO in the amount of 10 wt % was added. The final concentrations of the polymers were in the range from 5 to 7 wt %. The spinning solution was modified by addition of Tebac in the amount of 5 wt % for the enhancement of electric conductivity of the solution, Table I.

The chitosan in the amount of 2 wt % was dissolved in the aqueous solution of acetic acid at concentration of 1 wt %. Then, it was mixed by stirring with suitable amount of aqueous solution of PEO at concentration of 1 wt %. Finally, the weight ratio of chitosan to PEO in the spinning solution was 80/20. To lower surface tension of the spinning solution Triton X-100 was added to the solution in the amount of 1–3 wt %, Table I.

Electrospinning process

A scheme of the electrospinning setup used in this study to fabricate nanofibers is shown in Figure 1. The setup consists of the grounded rotating collector and the multijet spinneret. The collector is made in the form of aluminum tube, which was covered with a sheet of thin aluminum foil.[6] The collector rotated with velocity of about 10 rpm and simultaneously was moving forward and backward with typical velocity of 2 cm min^{-1}. The multijet spinneret was attached usually in distance of 15 cm above the collector. The spinneret was connected to high voltage supply ES50P-20W (Ormond Beach, USA). The system is equipped with a small peristaltic pump, which compresses the air above the spinning solution in the nozzle and pushing it through the needle to the outside. The air pressure was controlled by the U-tube manometer with water and it does not exceed 10 cm H_2O. Spinning efficiency achieved at these conditions was about 30 mg of fibers within an hour of one capillary. The electrospinning process was carried out for 4–6 h at high voltage of about 20 kV at room temperature. The temperature of the

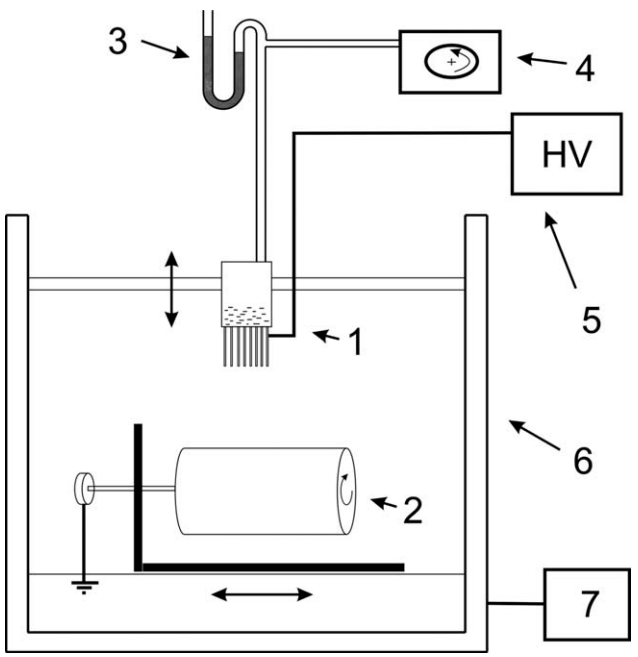

Figure 1 Scheme of the electrospinning setup: 1—spinneret, 2—collector, 3—U-pipe manometer, 4—peristaltic pump, 5—high voltage supply, 6—frame of the setup, 7—electronic controller for the collector drive.

TABLE II
Mechanical and Physical Properties of Raw and Treated Electrospun Mats

Type of polymer and treatment method	Average diameter of fibers (μm)	Thickness (mm)	Mass per unit area (g m^{-2})	Apparent density (g cm^{-3})	Elongation at break (%)	Tenacity (MPa)	Ball piercing force (N)
PLA 25 raw	1.23	0.122	29.3	0.24	27.5	1.47	4.90
PLA 25 annealed	1.23	0.121	30.3	0.25	23.3	3.19	8.58
L207S raw	2.40	0.70	9.23	0.013	143.0	0.126	1.15
L207S ironed	1.38	0.113	9.22	0.081	41.0	0.270	1.84
L207S + Tebac	0.70	0.50	12.3	0.025	69.0	0.104	2.75

spinning solution was in the range of 20–25°C. The relative humidity was about 65%.

Annealing and annealing under pressure (ironing)

The obtained electrospun fibers were modified. The annealing of the raw electrospun PLA 25 microfibrous mat was carried out by positioning the mats between two hot plates at temperature of 90°C, without any pressure, for 20 min. The electrospun Resomer L207S microfibrous mat was annealed under pressure. The mat positioned between two hot plates at temperature of 80°C was compressed with the pressure of about 20–30 G cm^{-2} during 10 min.

Characterization of the electrospun mats and the spinning solutions

The electrospun mats were characterized with respect to their structure, thermal, and mechanical properties. The microstructure of the mats directly sputter-coated with gold was observed using a scanning electron microscope (SEM, Quanta 200(W), FEI, USA). The thermal transitions of the mat materials were characterized by differential scanning calorimeter (Diamond, Perkin-Elmer, USA). The degree of crystallinity X_c of PLA in form of the electrospun nonwoven was determined by DSC method according to the Formula 1:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^o} \times 100\% \quad (1)$$

where ΔH_m is the enthalpy of the melting in J g^{-1}; ΔH_{cc} is the enthalpy of the cold crystallization in J g^{-1}; and ΔH_m^0 is the equilibrium melting enthalpy of PLA equals 106 J g^{-1} in accordance to Ref. 7.

The tensile properties were measured by two methods, longitudinal and multidirection (ball piercing method) using modified Instron apparatus, all in accordance with industry standards.

Apparent density of the electrospun mat before and after ironing was calculated, based on recalculated original meteorological data (Table II) to suitable units, by the Formula 2:

$$\text{Apparent density} = \text{mass per unit area}/\text{thickness} \quad (2)$$

The spinning solution viscosity was analyzed using viscometer (Brookfield, USA) and its surface tension was investigated by stalagmometric method. The electrical conductivity of solvents, both before and after modification of the ionic additive, was measured using Teraohmmeter (Knick, Germany).

RESULTS AND DISCUSSION

Quality of the electrospun fibers and fibrous mat structure are very important with respect to their applications. The changes of properties of the raw electrospun mats were possible through the use of additional treatments on them or some modifications of the spinning solutions. Below we present four such examples from our practice.

Example 1

The raw electrospun mat from PLA 25 had a very low degree of crystallinity. Its DSC heating curve shown in Figure 2 includes visible exothermic peak of a cold crystallization near 90°C. This revealed the low crystallinity of the material and suggested possibility of its crystallization by annealing at similar temperature. The exothermic peak was not present after annealing of the mat, Figure 2. However, the

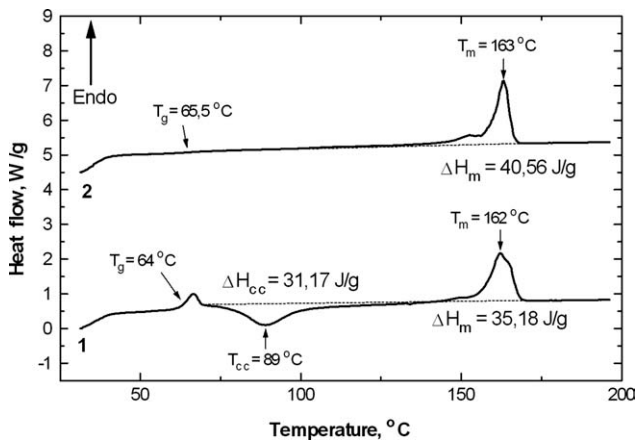

Figure 2 DSC curves at heating rate 20°C min^{-1} for PLA25 mat: 1—raw, 2—annealed. Marked temperatures: glass—T_g, cold crystallization—T_{cc}, and melting—T_m.

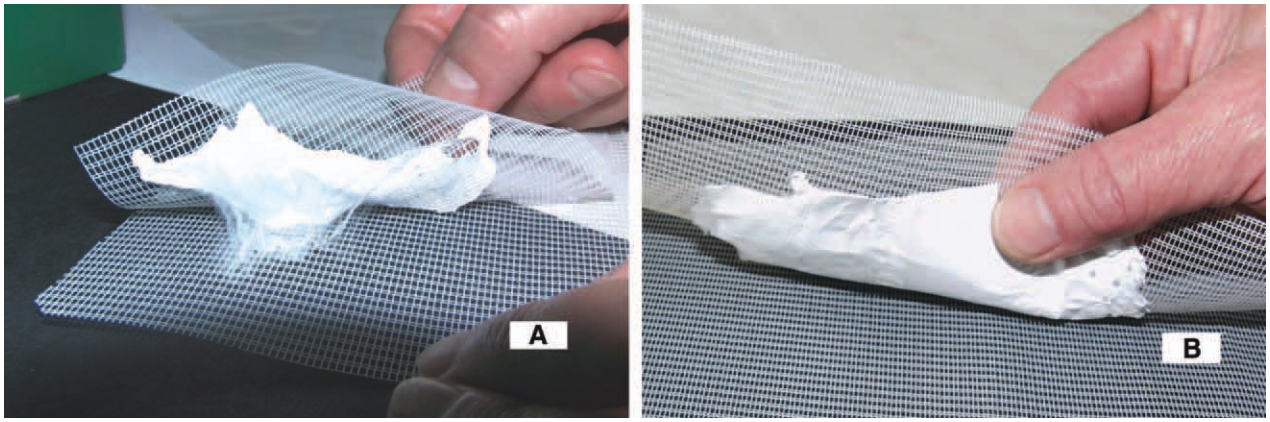

Figure 3 The electrospun mats from L207S. A—a raw mat vulnerable on fingers touching, B—an ironed mat useful for farther manual operation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

strong melting peak appeared this time. This proves that the material after annealing treatment is much more crystalline than in the previous form. Indeed, using eq. (1) we can evaluate the degree of crystallinity as 3.8% for the starting material and 38.3% for the material after heat treatment. Most importantly, this procedure allowed to obtain significantly, because two times, higher mechanical strength for

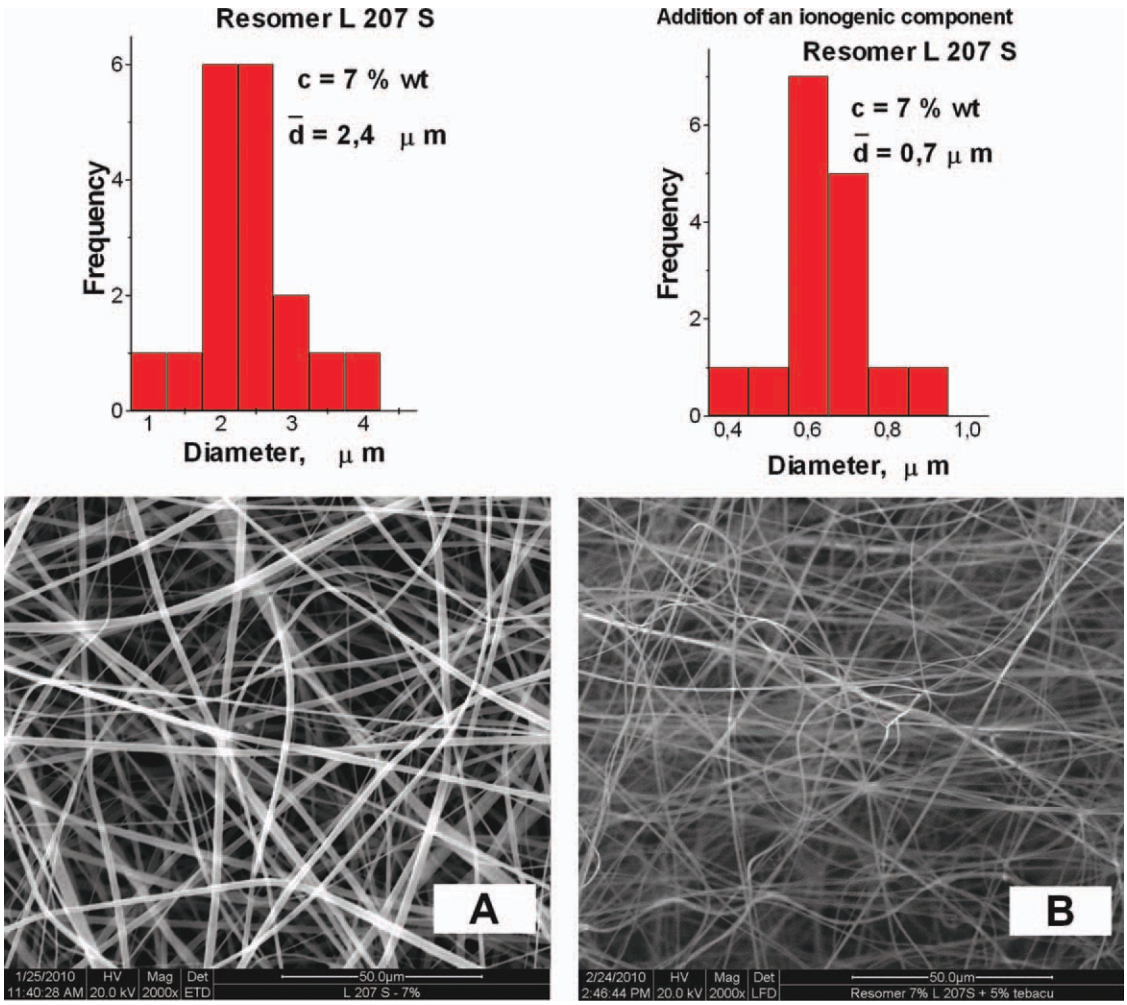

Figure 4 SEM images and distributions of fiber diameters of electrospun mats made of L207S. A—without modification, B—electrospun from solution modified by addition of Tebac. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

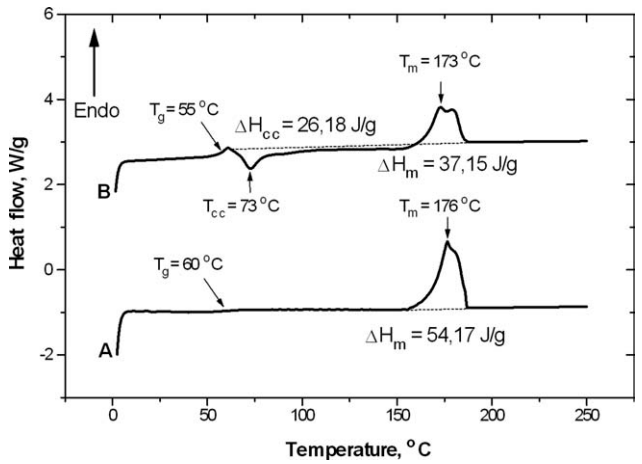

Figure 5 DSC curves at heating rate 20°C min^{-1} for L207S mat: A—raw, B—electrospun from solution modified by addition of Tebac.

the annealed mats (Table II). Obtained in this way, more durable and crystalline microfibers are more suitable for use in the construction of filters for air.

Example 2

The electrospun mat from Resomer L207S had very loose structure with an apparent density of only 0.013 g cm^{-3}, Table II. It was easy to damage when touching the fingers and prevents further use of, Figure 3(A). To improve mechanical properties of this mat the described method of annealing under pressure (ironing) was used. The treated fibrous mat has achieved much more compact structure which characterized six times higher an apparent density of 0.081 g cm^{-3} and more than three times shorter an elongation at break. Additionally both kinds of the mechanical strengths of the treated mat also increased, Table II. After this treatment, the mat is suitable for manual handling and can be used for further investigation in direction of wound dressing, Figure 3(B).

Example 3

An ionic modification of spinning solution of the PLA (Resomer L207S) by addition of Tebac also resulted in change of the mat properties. The elongational force on the electrospinning jet caused by more mobile smaller ions could yield fibers with smaller diameter. This type of ionic surfactant, used to increase conductivity of the solution, Table I, may at the same time reduce the surface tension,[8] but currently this feature was not investigated. The fibers electrospun from such solution have an average diameter about four times lower. In this example, it is the most important. The distributions of fiber thickness, before and after the solution modification, are shown together with the SEM images of the fibers in Figure 4(A,B). The solution modification also led to an increase in multidirection strength of the mat at only slightly lower tenacity, Table II. It should also be noted that the mat electrospun from modified solution is more mechanically cohesive. The DSC investigations of the modified material revealed significantly lower crystallinity compared to the material obtained from an unmodified solution, respectively 10.3 and 51.1%. The small peak of cold crystallization, during heating modified material, was observed in DSC curve, Figure 5. This effect may be due to a much more rapid evaporation of the solvent in the formation of a couple of times

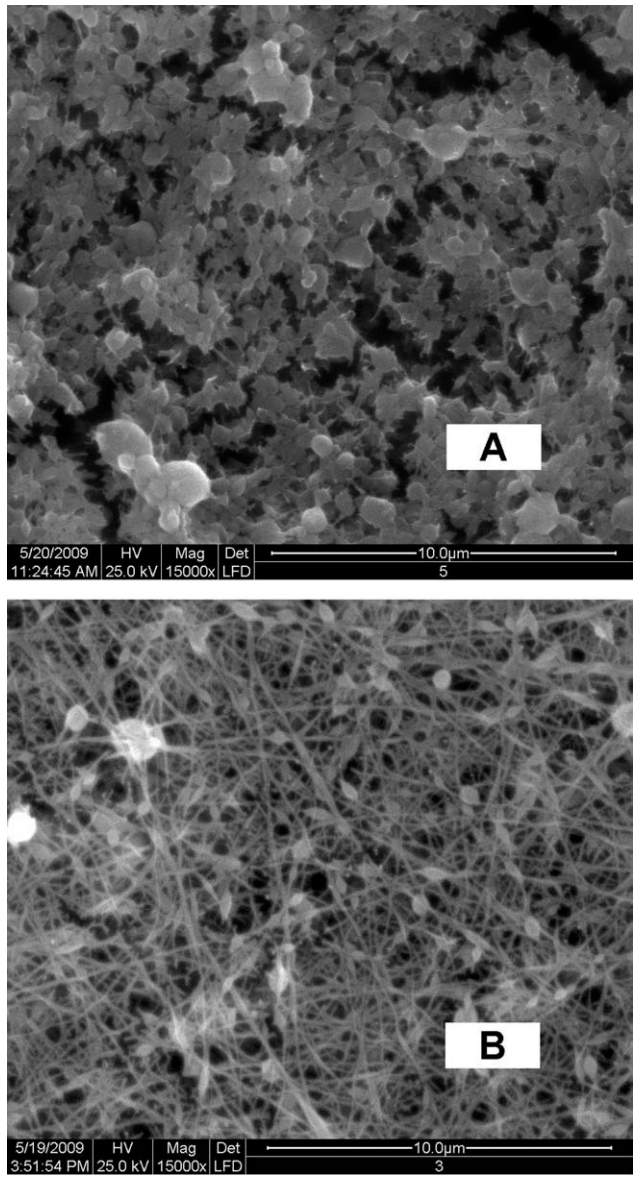

Figure 6 SEM images of electrospun products from chitosan/PEO ratio of 80/20 solutions. A—from original solution, B—from solution modified by addition of Triton X-100.

thinner fibers. If needed, the lower crystallinity of the material can easily be raised by annealing as described above in Example 1. Obtained in this example are thinner microfibers (even nanofibers) already suitable for use in the construction of microfiltration materials.

Example 4

The product, electrospun from an original solution of chitosan and PEO in dilute acetic acid, contains only few short fibers and plenty beads [Fig. 6(A)]. Typically such a bad result of electrospinning corresponds inappropriate relation between surface tension and viscosity in the spinning solution. If the viscosity of the solution is satisfactory, then the cause may be too large surface tension. Lowering the surface tension can easily be obtained by adding a surfactant. Because of the nature of the medical applications of the electrospun chitosan materials only certain surfactants can now be used. We decided to base the modification of chitosan spinning solutions on nonionic surfactant such as Triton X-100. The influence of this additive on the surface tension and viscosity of solutions are given in Table I. In practice, modification of the spinning solution with Triton X-100 was already in an amount of 1 wt % allowed to obtain a satisfactory result of electrospinning, Figure 6(B). This modification reduced the surface tension of the spinning solution from 85 to 46 mN m^{-1} but further increasing the concentration of modifying agent did not lead to a significant reduction in the surface tension or improve the quality of electrospun fibers. This procedure modified spinning solution has enabled us to ultimately produce mats of nanofibers which, after further chemical treatment was used in the construction of scaffolds in regenerative medicine.

CONCLUSIONS

The article describes some simple methods of modified spinning solutions or the properties of electrospun fibrous mats, which ultimately improved the materials within the meaning of their better suitability to the intended uses. An introduction of ionic surfactant such as Tebac into PLA spinning solution has allowed for obtaining four times thinner fibers. The use of nonionic detergent as Triton X-100 significantly improved spinning ability of chitosan solution and electrospinning of the fibers. The annealing at higher temperature or the annealing at higher temperature under pressure leads to enhance crystallinity, mechanical strength, and apparent density of the electrospun mats from various PLAs.

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