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Poly(L-lactide) Nano- and Microfibers by Electrospinning: Influence of Poly(L-lactide) Molecular Weight

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Summary: The electrospinning technique based on single and multi-jet systems was applied for poly(L-lactide) (PLA) nano- and microfibers as well as fibrous mats manufacture; the latter with dimensions suitable for the tensile tests. The PLA's employed were prepared by the controlled ring-opening polymerization of the L,L-lactide (LA) monomer. The resulting fibers thickness was correlated with molecular weights of PLA's and viscosities of spinning solutions. The scanning electron microscopic, thermal, and tensile characteristics of the polymeric materials and fibrous mats were also examined.

Keywords: electrospinning; fibrous mat; nanofibers; poly(L-lactide); tensile properties

Introduction

Nanomaterials show unique properties enabling novel applications in a wide scope of fields, such as filtration, separation, catalysis, electronics, or biomedicine. Polymeric nanofibers belong to the most intensively and systematically studied in this class of materials.[1–3] However, efficient, versatile, and safe technology for manufacture of nanofibers is still a challenge. Currently, it seems that the electrospinning can be such a convenient technology for preparation of polymeric nanofibers, especially from solutions and in the form of nonwovens, coatings, thin layers, and other special forms. On the other hand the control of the electrospinning creates serious problems, particularly when application of longer work time is need. This technique of fibers spinning requires extremely high speed of their formation and simultaneously high speed of solvent evaporation from their surface. Moreover, the electrospinning is very sensitive on the process conditions and, in general, a possibility of obtaining larger amounts of nanofibers with regular and reproducible shapes could be cumbersome. Attempts of keeping the process parameters constant for a longer time (i.e. in order of hours), particularly with multi-jet system application, usually become unsuccessful and result in low quality of manufactured mats or even in stopping the process.[4–6] Thus, most probably, discussed briefly above the electrospinning process features cause that availability of metrological parameters of the well defined electrospun mats is rather limited in the pertinent literature. The present paper aims at presenting preliminary results on using the electrospinning technique based on single and multi-jet systems for poly(L-lactide) micro- and nanofibrous mats manufacture.

Experimental Part

Materials

Poly(L-lactide) (PLA) was prepared by the controlled ring-opening polymerization of the L,L-dilactide (LA) monomer. The polymerizations were carried out in THF as a

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solvent at 80 °C with tin(II) *bis*-octanoate (2-ethylhexanoate) as a coinitiator[7] or with tin(II) *bis*-butoxide as initiator.[8] For the resulting, isolated by precipitation into methanol and dried in vacuum PLA's, the following molecular weights (M_n, SEC, LLS detector) were determined: 22×10^3, 62×10^3, 132×10^3. Additionally, the commercial PLA (supplied by Cargill, USA), containing 4 mol-% of D-lactoyl repeating units randomly distributed, and having $M_n = 98 \times 10^3$ was also used.

Analytical Methods

Microscopy

The electrospun products were observed by a scanning electron microscope (SEM) Quanta 200(W), FEI Co., USA.

Thermal Characterization

The thermal transitions were measured by a differential scanning calorimeter DSC-2 and thermo resistance by Thermo gravimetric analyzer TGS-1, both Perkin-Elmer (with improved electronic registration system), USA.

Viscometry

The viscosity of the spinning solutions were measured by a Brookfield viscometer.

Tensile Tests

The tensile properties were measured by classic (tensile tester, Instron 5544, USA) and special ball piercing (modified Instron apparatus) methods.

Equipment for Electrospinning

All electrospinning experiments were carried out under standard environmental conditions. Temperature of both the surroundings and the spinning liquid ranged within $20 \div 25$ °C, and the relative humidity was about $50 \div 65\%$. Two different, described below, variants of the stand for electrospinning were used.

Variant A

The system was based on the set up stand made of electrically insulating materials immovable during work. The stand was supported on a plastic table and equipped with a vertically movable arm for the attachment of the spinning head. The electrically grounded sheet of aluminum foil, playing a role of the collecting electrode, was placed on the table. The spinning head was connected to a high voltage, which was typically equal to 20 kV. The ES50P-20W voltage supply from Ormond Beach, USA was used. In most cases, a distance between the bottom of the spinning head and the aluminum collecting electrode was 150 mm. The system was equipped with a small peristaltic pump, creating air pressure to drive the spinning liquid from the spinning head. The pressure, not exceeding 40 mm H_2O, was controlled by a u-pipe water manometer.

Variant B

The system was based on a grounded rotating aluminum tube, covered with a sheet of thin aluminum foil as a collecting electrode. The spinning head was clamped to a stand, which could be moved along the track at a fixed distance above the rotating tube. Velocity of rotation was typically equal to 10 rpm, and the spinning head was moved 20 mm/min. longitudinally to the axis of the rotating tube. The other parts of the equipment were of the same construction as described for variant A.

Results and Discussion

Proper conditions for long-term electrospinning were initially established with a variant A spinning device. In agreement with our earlier experience the optimal solvent composition for PLA electrospinning consisted of 90 wt-% of $CHCl_3$ and 10 wt-% of DMSO. The further work was focused on finding suitable concentrations of PLA's having different molecular weights with regard to the resulting viscosities of the spinning solutions (as measured by a Brookfield viscometer). As an example, Figure 1 shows SEM photographs and the corresponding histograms of the electrospun materials obtained with PLA of $M_n = 132 \times 10^3$ and various polymer concentrations.

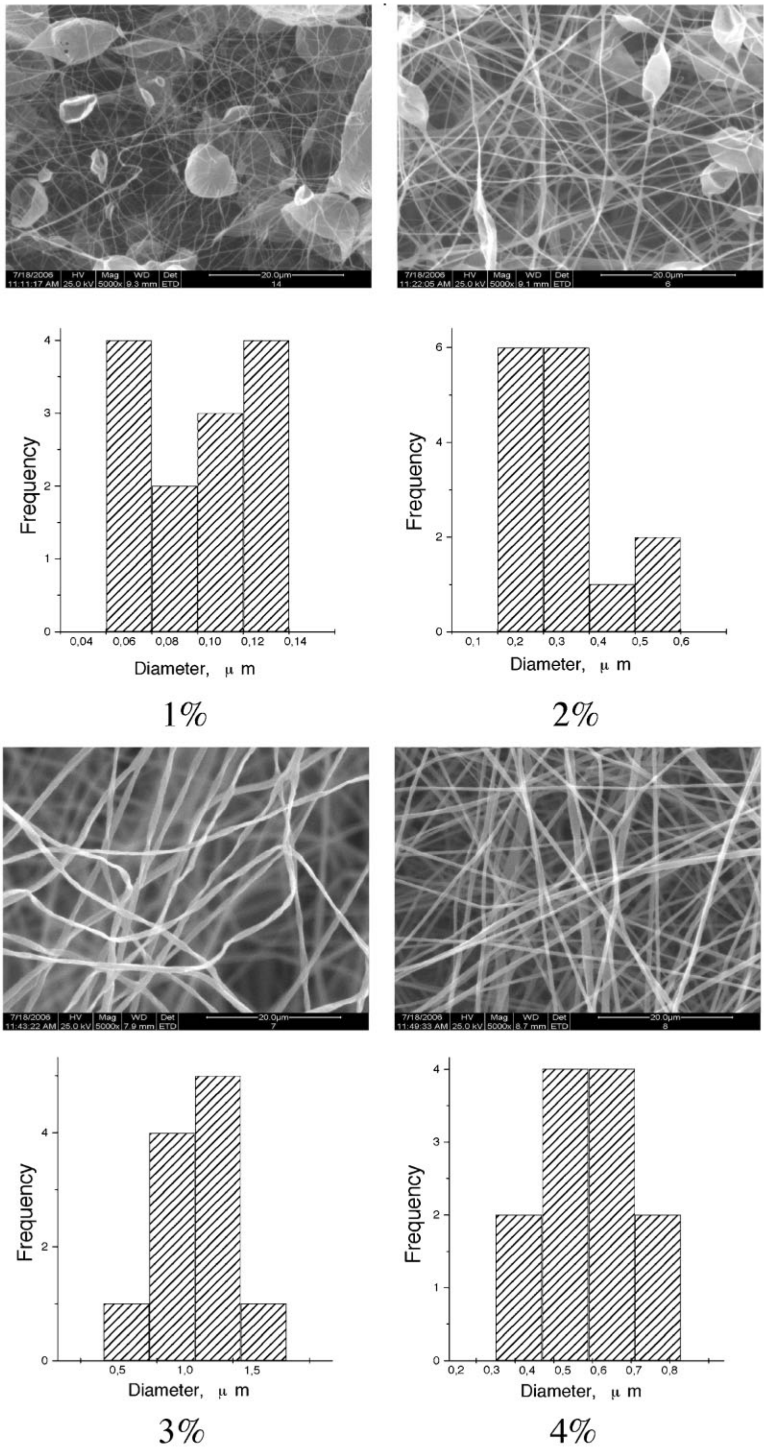

Figure 1.
SEM photographs of electrospun mats surfaces and the corresponding histograms of fiber diameters. Concentrations of PLA ($M_n = 132 \times 10^3$) in spinning solutions are given directly in the figure.

Similar measurements were also carried out for another PLA samples with $M_n = 22 \times 10^3$ and 64×10^3 as well as for the commercial PLA.

Then the long-term experiments were repeated with a variant B spinning device. For almost all samples of PLA formation of mats that reached dimensions of 200 mm × 200 mm was successfully observed. Only PLA sample of $M_n = 22 \times 10^3$ provided non-reproducible results during the long-term electrospinning and thus was not further studied in a more detail.

Some selected parameters of the studied PLA samples, their solutions used for long-term electrospinning experiments as well as characteristics of the resulting nano- and microfibers and fibrous mats are given in Table 1 and 2. Investigations of PLA fibrous mats were carried out after their conditioning during two weeks at room temperature under free contact with atmospheric air. Degree of crystallinity (x_c) was calculated using Equation 1:

$$x_c = 100\% \times (\Delta H_m - \Delta H_{cc})/\Delta H_m^o \qquad (1)$$

where: ΔH_m denotes measured melting enthalpy, ΔH_{cc} – the enthalpy of cold crystallization, and ΔH_m^o – the equilibrium melting enthalpy for PLA equal to $106\ \mathrm{J \cdot g^{-1}}$.[9] Two selected examples of DSC traces recorded for the row electrospun PLA mats are shown in Figure 2.

The spinning solutions used in successful long-term experiments were characterized by viscosities in the range of 162 ÷ 426 cP at PLA concentrations 4 ÷ 7 wt-%, depending on the PLA molecular weight. DSC measurements of all PLA samples revealed glass transition temperatures (T_g) changing slightly in the range of 58 ÷ 61 °C, however, no clear dependence of T_g on M_n was observed. On the other hand, their melting temperatures increased from 171 to 179 °C

Table 1.
Characterization of PLA samples and their solutions.

Sample no.	M_n [a]	x_c [b]	Solution concentration [c]	Viscosity [d]
		wt-%	wt-%	cP
1	132×10^3	41.7	4	426
2	62×10^3	45.8	7	215
3	22×10^3	48.1	14	118
4	98×10^3	41.5	5	162
5	98×10^3	41.5	5	168

[a] Absolute molecular weights – measured by SEC with LLS detector;
[b] Degree of PLA crystallinity determined by DSC (cf. Equation 1); 1st heating run ($20\ \mathrm{K \cdot min^{-1}}$);
[c] $CHCl_3$/DMSO (90/10 wt/wt) mixture as a solvent;
[d] Measured by Brookfield viscometer.

Table 2.
Characterization of fibers and fibrous mats.[a]

	Fibers		Fibrous mats			
Sample no.	Averge diameter	x_c [b]	Thickness	Tenacity	Elongation at break	Ball piercing force
	µm	%	mm	MPa	%	N
1	0.55	17.8	0.09	0.51	87.2	1.22
2	0.79	11.1	0.59	0.35	25.6	5.88
3	1.08	4.2	–[c]	–[c]	–[c]	–[c]
4	1.08	2.2	0.19	0.36	25	1.23
5	0.94	2.3	0.38	0.37	15	2.45

[a] Measured after conditioning during two weeks at room temperature;
[b] Degree of PLA crystallinity determined by DSC (cf. Equation 1); 1st heating run ($20\ \mathrm{K \cdot min^{-1}}$);
[c] Not determined because of not reproducible structure of the resulting mats.

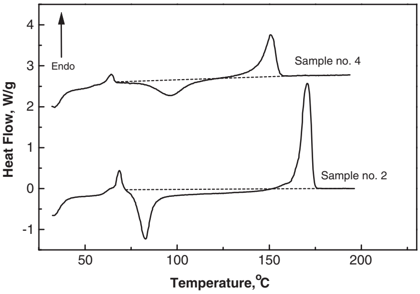

Figure 2.
DSC traces for samples of the row electrospun mats obtained with a heating rate of 20 K · min^{-1}. Areas of cold crystallization and melting are marked with a dotted line.

with M_n increasing from 22×10^3 to 132×10^3, respectively. All PLA's were able to crystallize thermally, but sample of the commercially available PLA exhibited very slow thermal crystallization and after melting and then cooling with 20 K/min rate remained in an amorphous state. The latter can be explained by 4 mol-% D-units admixture in the commercial PLA. Data in Table 1 and 2 show that degree of PLA crystallinity decreases considerably during the electrospinning process. This behavior is typical for the row electrospun PLA fibers. Since data in Table 2 suggest that the higher crystallinity degree results in better tensile properties perhaps further thermal treatment is required to improve mechanical parameters of the PLA based mats. Moreover, preliminary TGA measurements show that a considerable improvement of thermal resistance of the PLA mats, comparing to the native PLA, could be obtained. Studies in this area are in a progress.

Conclusion

The nano- and micro-fibres as well as fibrous mats based on the laboratory scale and commercial PLA's were manufactured by electrospinning technique. PLA M_n's, viscosities of the spinning solutions, and their concentrations were correlated with the fiber thickness and mats quality. DSC measurements and tensile tests of the resulting fibrous mats revealed improvement of the mechanical durability with increased crystallinity degree. In some cases thermal resistance of the PLA mats, comparing to the native PLA, has also been improved.

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