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Solvent-free preparation of poly(lactic acid) fibers by melt electrospinning using an umbrella-like spray head and alleviation of the problematic thermal degradation

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Abstract: Melt electrospinning is an even simpler and safer method compared to solution electrospinning in the production of ultra-fine fibers. Poly(lactic acid) (PLA) is a biodegradable and resorbable aliphatic ester that has received significant attention in recent years. PLA is easily degradable at high temperatures during the process of melt electrospinning. Highly efficient fibers were made using a self-designed umbrella-like spray head spinning facility in. Differential scanning calorimeter and X-ray diffraction analysis were used to determine how to alleviate the problematic degradation, as well as which factors could be relevant to the degradation, temperature and relative molecular mass, by comparing the results obtained before and after spinning. The results showed that fibers spun at 245 °C were facile, shorter and fractured while the relative molecular mass of PLA fibers had decreased markedly as compared with those spun at 210 °C. In attempts to hinder the degradation, several experiments were implemented with the addition of antioxidants, raising the spinning voltage, lowering the temperature and reducing the residence time. After such modifications, it was observed that the relative molecular mass of the PLA fibers was higher than that of those without the modifications. The addition of the antioxidant 1010 was found to be the most promising method for the alleviation of the problematic thermal degradation of PLA.

Keywords: PLA fibers; melt electrospinning; X-ray diffraction; antioxidants.

INTRODUCTION

Since the 1990s, with the quick development of nanomaterials and nanotechnology, increasing interest and attention have been focused and paid on electro-

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spinning, primarily due to its simplicity, validity, and directness in producing nanofibers.¹⁻³ Electrospinning can be conducted by two methods: solution electrospinning and melt electrospinning^{4,5}. Most researchers utilize solution electrospinning because of its simple instrumentation and ease of operation. Melt electrospinning, on the other hand, is commonly ignored because of its complexity in instrumentation and thickness of the resulting fibers.

However, solution electrospinning has some disadvantages: 1) some solvents are expensive and extremely hazardous to the environment, and thus, must be recovered through highly complicated retrieval processes;⁶ 2) in the spinning process, the capillary are often blocked, hence seriously affecting the continuity of spinning;⁷ 3) it is difficult to find suitable solvents for some polymer, such as poly(propylene) and polyethylene, when spun at ambient temperatures although it is not relevant to this current study; 4) the evaporation of the solvent in the spinning process can leave defects on the fiber, leading to relatively low mechanical strength⁸ and 5) the concentration of the solution is low, and its corresponding evaporation greatly reduces the yield and production efficiency.

In view of these intrinsic problems with solution electrospinning, melt electrospinning has gradually gained increasing attention since melt electrospinning produces fibers directly from polymer melts in absence of solvent. Therefore, it is considered as a safer, economic and environmentally friendly method compared with solution electrospinning.^{9,10}

The raw material, lactic acid, is derived from natural resources and is easily prepared in high yield by fermentation of molasses of potato starch or dextrose from corn.^{11,12} Then lactic acid is polymerized into poly(lactic acid) (PLA) which can be spun further into PLA fibers.¹³ PLA is one of the most promising biodegradable polymers owing to the profile of its mechanical properties, thermoplastic processibility and biological properties. L-Lactic acid provides a polymer with higher mechanical strength than the DL-form,¹² particularly in terms of tensile strength¹⁴ as the pure L-form has a high degree of crystallinity, and thus sufficient mechanical strength only in its fully isotactic form.¹⁵ In some chitosan-based composites, the addition of PLA leads to an improvement in the modulus.¹⁶ Moreover, the degradation products of polylactides are non-toxic which enhances practical applications in biomedicine and other fields.^{11,17} PLA is well-known as biodegradable polymer in daily applications, such as disposable cutlery, plates, cups, lids, packaging bags, films, and containers for liquid foods.¹⁸ In most applications of biodegradable polymers and composites, PLA is one of the important candidates for high value side and specific applications, such as tissue engineering, prosthetic devices, implants, catheters, sutures and anticancer drug delivery.¹⁷ In addition to biomedical usages, the employment of the biodegradability of PLA in packaging¹⁹ and agricultural materials is worth highlighting because PLA and its fibers can eventually be decomposed into carbon

dioxide and water through the actions of microorganism actions and finally these degraded species become recyclable materials.^{15,20,21} Due to the biodegradability and recyclability of PLA in nature, PLA has been referred to as the environmental cycle material of the 21st century.²² Many investigations have recently been conducted on PLA fibers.^{23–26}

It was reported that PLA fibers can be obtained easily through solution electrospinning, but that it is relatively difficult to accomplish under melt electrospinning.²⁷ Recently, PLA fibers were obtained through a series of melt electrospinning experiments using a uniquely designed umbrella-like spray head, when it was found that the molecular mass of PLA fiber was significantly influenced by the melt electrospinning.²⁸ In order to alleviate the problematic degradation of PLA in melt electrospinning, several attempts were undertaken to hinder the degradation of the polymer, *i.e.*, through the addition of additives, refining the processing conditions and examination of aspects of the equipment.

EXPERIMENTAL

Materials

L-PLA (melting point: 210 °C) was purchased from Nature Works LLC of America (trademark: 2002D). The PLA sample was baked at 70 °C for about 4 h before spinning. Antioxidants 1010 and 168 were purchased from Beijing Additive Institute.

Equipment

A diagram of the melt electrospinning equipment,^{28,29} specifically self-designed for this study, is shown in Fig. 1. The cylinder, piston, and spray head were made of steel. The heating system included electrical heating rings, thermal sensors, and a temperature control subsystem. The spray head was a cone-type instead of the traditional capillary tube. The melts

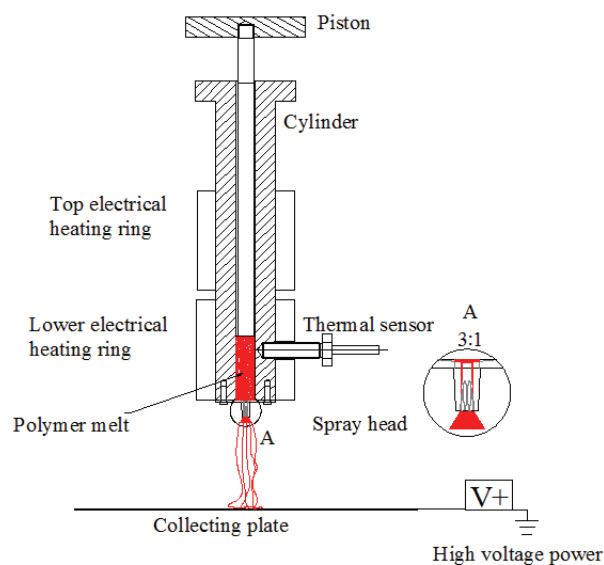


Fig. 1. Scheme of the melt electrospinning apparatus.

flowed onto the surface of an umbrella-like spray head and then formed Taylor's cones automatically at the bottom edge of the head in the high voltage electrostatic field.²⁹

Preparation of PLA fibers

The cylinder was heated to the required temperature (200–250 °C). Then, the granular or powdery material was put into the cylinder at the pre-set temperature for approximately 10 min (*i.e.*, until the melts were spread uniformly on the spray head), the high voltage supply device was switched on and adjusted to an appropriate value (30–100 KV). Thus, the melts were formed several cones along the bottom edge of the spray head, and several stripes of the PLA melt flew to the collecting mesh, as shown in Fig. 2. The distance between collecting mesh and spray head was set at around 10–23 cm.



Fig. 2. Melt electrospinning with an umbrella-like spray head.

Characterization

The morphologies of the electrospun fibers were observed by scanning electron microscopy (SEM, Hitachi S4700). Fiber samples were coated with a 10 nm layer of platinum before observation. Scanning voltage was 20 KV. The relative molecular mass of the PLA fibers was measured by a gel permeation chromatograph (Shimadzu LC-6A). X-Ray diffraction (XRD) patterns of the fibers were recorded using a Rigaku D/Max-III C (CuK_α radiation). The thermal transition curves of the PLA samples was recorded using a differential scanning calorimetry (DSC, Perkin Elmer Pyris1) to demonstrate the crystalline state of the PLA before and after electrospinning.

RESULTS AND DISCUSSION

Effect of temperature on the spun fiber morphology

It is well-known that temperature has significant effects on melt electrospinning.^{4,5,29} Overheating at high temperatures leads to a sharp decrease in the melt viscosity, indicating a molecular weight decrease; consequently, the polymer melts flow faster and the residence time in the spinning device is shorter. The SEM micrograph of the PLA fibers obtained from melt electrospinning with the

cylinder temperature set at 210 °C and at a voltage of 60 KV is shown in Fig. 3. The average diameter of the resultant fibers was 7.65 μm with a fiber diameter variance of 0.21 μm and the spinning efficiency of electrospinning was 4 g h^{-1} when using the abovementioned conditions. It was noticed that in Fig. 3 that the surface of the PLA fiber was quite smooth, suggesting the fibers had higher tensile strength compared with those with defects on the surface; such defects results in the typical poor mechanical properties from solution electrospinning.

However, if the temperature is higher than some limit, the polymer will start to degrade, especially for an easy-degradable polymer. From a DSC scan, it was evidenced that PLA starts to degrade significantly at 250 °C.¹⁵ An SEM image of PLA fibers fabricated at a spinning temperature of 245 °C is shown in Fig 4. Apparently, many of the PLA fibers were broken into short fibers and the fiber diameter distribution was broader. However, during spinning, fibers were seen on the collection mesh with continuity and unbroken. It could be reasoned that the short fibers might be due to the pressing force from the tweezers when the electron microscopy samples were prepared. Although such an augmentation might

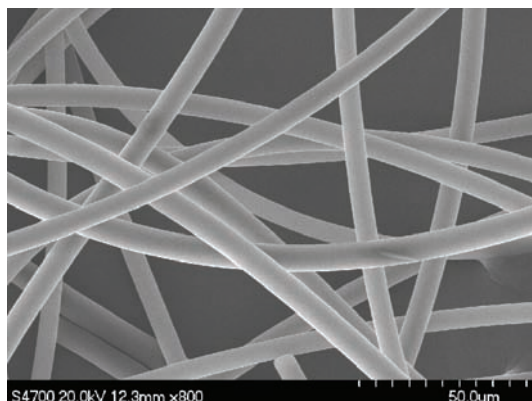


Fig. 3. SEM Micrograph of PLA fibers spun at 210 °C. The distance between the spray head and collection mesh was 11 cm.

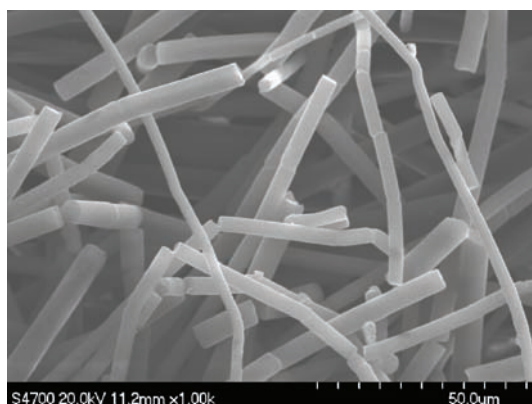


Fig. 4. SEM Micrograph of PLA fibers spun at 245 °C. The distance between the spray head and collection mesh was 11 cm.

be reasonable, it must be born in mind bear in mind that the pressing force was also applied to the fibers resulting from lower temperature spinning (*e.g.*, 210 °C). However, under the same action and pressing force from the tweezers, only the PLA fibers that had undergone chain scission and a decrease in molecular mass with the resulting compromised mechanical properties would be brittle with shorter fibers and hence easily powderized. Thus, temperature is a key parameter necessary to take into consideration and to be well controlled during PLA melt spinning.

Effect of temperature on the relative molecular mass of spun PLA fibers

As heating is a necessary condition to realize melt electrospinning, it is important to know the extent of degradation of spun fibers. To determine the intrinsic relationship between thermal spinning at a certain temperature and the extent of degradation, the relative molecular mass (M_p , as a function of molecular mass vs. eluent volume) of PLA before and after melt electrospinning at 245 °C was measured. A comparison of the M_p of the PLA before and after melt electrospinning at 245 °C is shown in Fig. 5 and given in Table I. The M_p of the PLA had clearly decreased (by 56.2 %) after melt electrospinning. The possible reason for this is that high spinning temperatures (*e.g.*, above 230 °C) causes thermal degradation of the PLA molecules. It was reported from some available experimental data at temperatures above 200 °C that PLA may experience a minimum of four

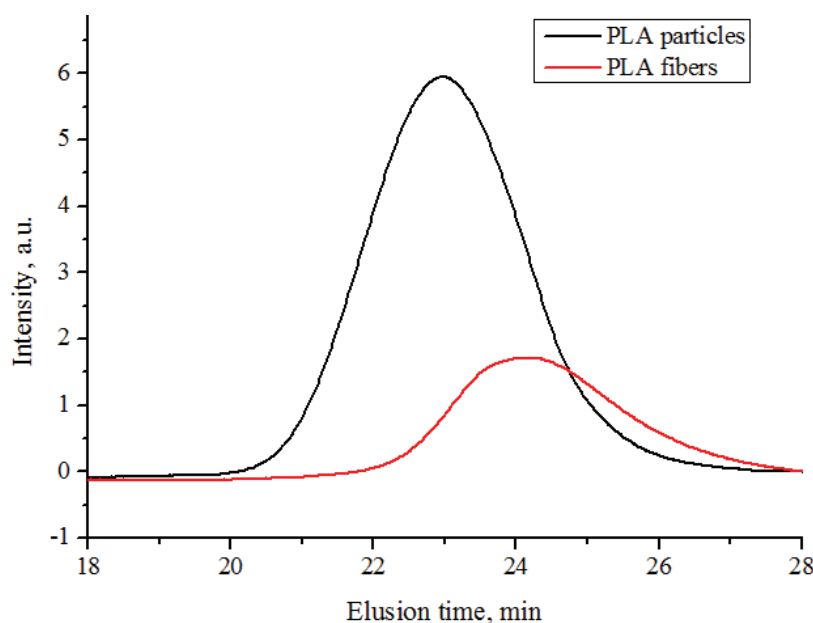


Fig. 5. Comparison of relative molecular mass of PLA before (Particles) and after (Fibers) melt electrospinning at 245 °C.

reaction pathways during thermal decomposition:¹⁵

1) intra- and intermolecular ester exchange to produce lactide and cyclic oligomers;

2) *cis*-elimination to generate acrylic acid and acyclic oligomers;

3) radical and concerted non-radical reactions to produce CH₃CHO and CO;

4) radical reactions to generate CH₃CH=C=O, CH₃CHO and CO₂.

Among these possible pathways, Kopinke³⁰ believed that there are two principal pyrolysis mechanisms for polyesters: *cis*-elimination and *trans*-esterification, but that at temperatures above 300 °C, non-selective radical reactions may also occur. Therefore, the outcome in Fig. 5 and Table I for PLA breaking down into short-chain molecules can be readily understood. It can be concluded that melt electrospinning for pure PLA material will naturally lead to a certain extent of degradation of PLA at above 200 °C because heating is necessary for PLA melting and then for the spinning process.

TABLE I. Relative molecular mass of PLA before and after melt electrospinning

PLA	M_p	M_n	M_w/M_n
Particles	131277	92736	1.8
Fibers	57497	34733	2.0

XRD and DSC investigations before and after spinning

Degradation leads to a decrease in tensile strength because PLA is either a crystalline or a partially crystalline polymer and tensile strength is relevant to its isotactic form.¹⁵ The tensile strength of individual fibers is difficult to measure because the fibers are very fine and thin. The degree of Crystallinity can reflect the strength in an aspect. Hence, the XRD and DSC patterns of PLA were recorded, as shown in Figs. 6 and 7. From Fig. 6, it can be seen that the PLA particles had a clear crystalline peak before electrospinning. After spinning, however, the sharp crystalline peak had disappeared and a smooth and broad amorphous band peaked at round $2\theta = 17^\circ$. The raw PLA from the polymerization reaction of L-lactic acid can form a high degree or partial isotactic structure of polymer and the isotactic structure constructs a lattice during polymerization. Consequently, a sharp crystalline peak existed in the XRD scan of the raw PLA. Comparatively, after electrospinning, the relative molecular mass of PLA became lower due to the thermal decomposition of the molecular chains. Although the chains underwent strong orientation, they could not crystallize as well because the chains were short and the decomposition impurities generated amorphous domains and caused high defects in the existing lattices. The DSC thermograms of PLA before and after spinning (Fig. 7) demonstrates this well. It can be seen that the PLA particles have two sharp melting peaks at 140 and 146 °C. However, after spinning, the sharp melting peak had disappeared. The small and smooth

melting peak indicates an incomplete crystalline state. Although crystallization occurred, the amount of crystallinity was too small to be registered in the XRD patterns.

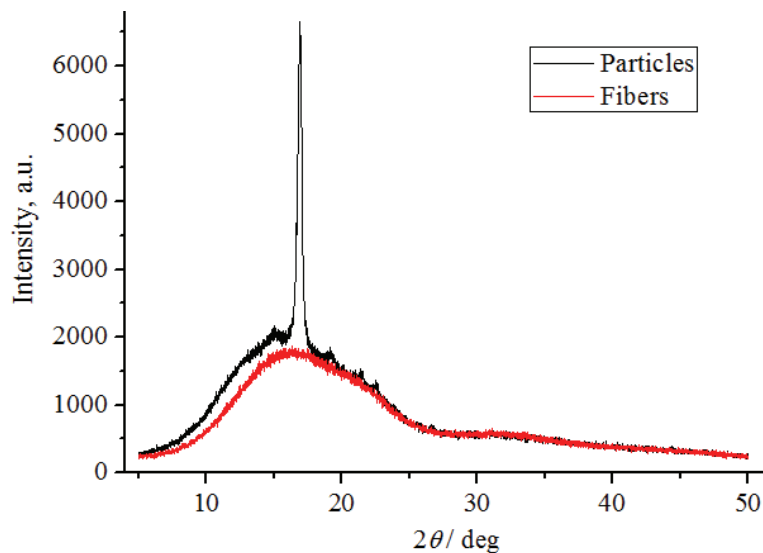


Fig. 6. XRD Patterns of PLA particles and fibers.

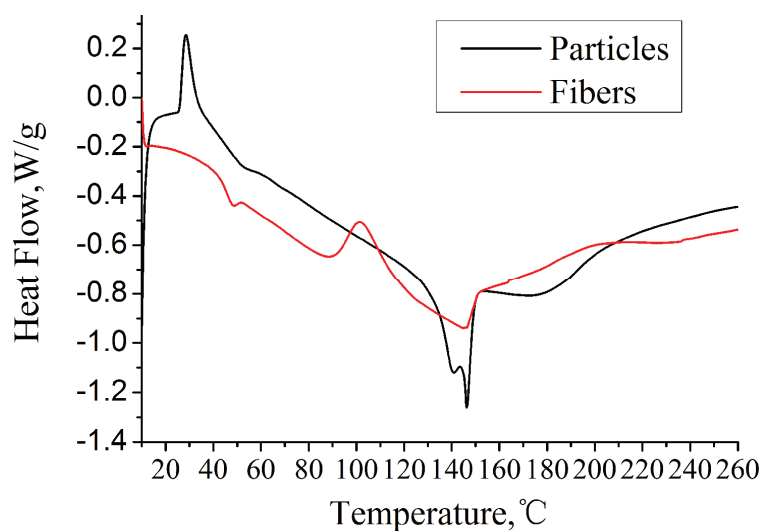


Fig. 7. DSC Thermograms of PLA particles and fibers.

Methods in alleviating the problematic degradation of PLA spun fibers

In order to minimize the side effects of thermal decomposition or to alleviate the thermal degradation for PLA in the melt electrospinning process, the initial electrospinning process was modified in terms of addition of antioxidants, the equipment and the processing conditions.

For the additives, antioxidant 1010 and antioxidant 168 were added to reduce the chain scission reaction. The antioxidant 1010 is a hindered phenolic antioxidant, the molecule of which loses a hydrogen atom to form a stable aryl radical. This radical captures chain-free radicals generated from thermo-oxidative degradation of PLA, thus partially terminating reactions at the chain break. Antioxidant 168 is a phosphite ester antioxidant. It is able to trap peroxy radicals³¹ and effectively decompose hydroperoxides produced during the processing of polymeric materials and hence inhibits the PLA from undergoing thermal degradation.

In terms of equipment, a low- and a high-temperature electrical heating ring, rather than two high-temperature heating rings, were installed and used to reduce the high temperature shock/input for avoiding unwanted longer residence times of PLA feed in the cylinder. The gap between the spinning head and the cylinder was increased to ensure that the viscous melt could flow down continuously and constantly along the conical surface of the spray head, thereby decreasing the residence time of the PLA in the hot cylinder.

As for the processing conditions of electrospinning, the spinning temperature was reduced from the usual 230 down to 210 °C. A new high voltage supply device with a maximum output of 100 kV replaced the initial one that had a maximum output 60 kV. The spinning voltage could then be increased from lower to higher, that is, from the initial 60 up to 100 kV.

Effect of additives on degradation of PLA

Antioxidants as additives can alleviate the problematic degradation of PLA fibers. After adjusting the heating temperature and adopting a new electrospinning device, a considerably higher efficiency (about 6 g h⁻¹) of fiber formation, as opposed to 4 g h⁻¹ obtained using the initial device settings, was obtained. The detailed effects of temperature and voltage on PLA fiber properties was reported previously.²⁹ In the present study, the impact of antioxidants on PLA degradation was examined in detail (shown in Fig. 8 and Table II). The mass ratio of the antioxidant and PLA in the feed was 3:1000. In case of a mixture of antioxidants, the mass ratio of antioxidant 168 to antioxidant 1010 was 1:1. The spinning voltage was set at 100 kV with a spinning distance of 12 cm. On comparing curves a and b in Fig. 8, it could be seen that the antioxidant 168 had little effect in moderating the degradation of PLA fibers. A comparison of curves a and c indicates that the 1:1 mixture of antioxidant 168 and antioxidant 1010 had enhanced effects in alle-

viating degradation. In the case of the mixed antioxidants, the relative molecular mass (curve c) was 18.05 % higher than that of the antioxidant-free counterpart (curve a). The antioxidant 1010 showed the most distinct effect in hindering the degradation of PLA fibers among the cases shown by curves b, c and d. The M_p of the PLA fibers processed in the presence of antioxidant 1010 (curve d) was 35.5 % higher than that of the fibers fabricated in the absence of antioxidant (curve a).

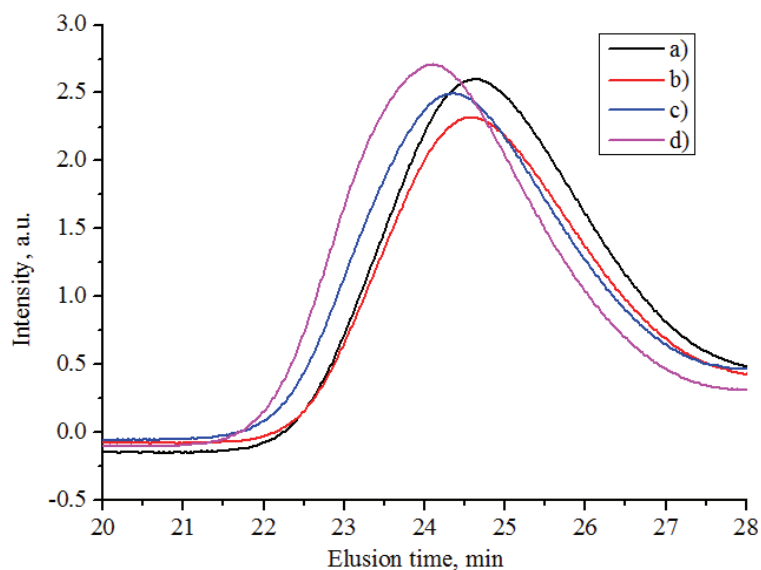


Fig. 8. Comparison of the relative molecular mass of PLA fibers spun under the same temperature and processing parameters: a) PLA fibers; b) PLA fibers + antioxidant 168; c) PLA fibers + antioxidant 168 + antioxidant 1010; d) PLA fibers + antioxidant 1010.

Finally, a comparison of Figs. 5 and 8a shows that the PLA fibers produced in this study in the absence of antioxidant had a relatively lower molecular mass than those obtained in a previous study performed several months earlier. It is possible that the PLA used in the present study, which had been stored under natural conditions, had been degraded by the oxygen in the air in presence of moisture.

TABLE II. Relative molecular mass of PLA fibers electrospun under the same temperature and processing parameters

PLA	M_p	M_n	M_w/M_n
PLA fibers	35367	7970	4.2
PLA fibers + antioxidant 168	36919	7403	6.0
PLA fibers + antioxidants 168 and 1010	41751	6437	4.5
PLA fibers + antioxidant 1010	48482	9664	4.9

CONCLUSIONS

The problematic degradation of facile degradable PLA in melt electrospinning was studied and alleviated by means of hindering thermal degradation of the spun PLA fibers by the addition of antioxidants, and modification of the equipment and processing parameters, particularly, temperature. Lowering the temperature and addition of antioxidant were found effective in alleviating the degradation of PLA in melt electrospinning. The effects of two antioxidants, individually and as a mixture, were compared and it was found that antioxidant 1010 had a remarkable capability to hinder the thermal degradation of PLA during melt electrospinning.

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ИЗВОД

ИЗРАДА ВЛАКАНА ПОЛИ(МЛЕЧНЕ КИСЕЛИНЕ) ПОСТУПКОМ ЕЛЕКТРОСПИНИНГА ИЗ РАСТОПА ПРИМЕНОМ ГЛАВЕ У ОБЛИКУ КИШОБРАНА И СМАЊЕЊЕ ПРОЦЕСА ТЕРМИЧКЕ ДЕГРАДАЦИЈЕ

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Израда ултра-финих влакана поступком електроспининга из растопа је једноставнији и сигурнији поступак у односу на електроспининг из раствора. Поли(млечна киселина) (PLA) је алифатски полиестар који у последње време привлачи све већу пажњу због својих биодеграбилних и ресорбујућих својстава. PLA лако деградира на високим температурама у процесу израде влакана електроспинингом из растопа. У овом раду је приказана израда високо-квалитетних влакана коришћењем специјално дизајниране главе у облику кишобрана. У намери да се елиминише термичка деградација растопа полимера, анализиран је утицај температуре на моларну масу, термичка својства и степен кристаличности полимера, поређењем DSC термограма и WAXS дифрактограма полимерних узорака пре и после обликовања. Резултати су показали да се добијају краћа и оштећена влакна уколико се обликовање изводи на температури 245 °C, док је моларна маса ПЛА значајно опала у односу на влакна добијена на температури 210 °C. Да би се смањила термичка деградација полимера примењене су различите експерименталне технике: повећање напона при извлачењу влакана, снижење температуре и времена задржавања растопа полимера као и додаток антиоксиданаса. Побољшање експерименталних услова извођења електроспининга довело је до повећања моларне масе PLA влакана. Примена антиоксиданса 1010 дала је најбоље резултате у погледу смањења термичке деградације PLA.

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