

Orthogonal Design Study on Factors Affecting the Degradation of Polylactic Acid Fibers of Melt Electrospinning

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ABSTRACT: Melt electrospinning is a much simpler and safer method in the production of ultra-fine fibers compared with solution electrospinning. However, high-spinning temperature usually leads to serious degradation of polymer materials. In determining factors that affect the relative molecular mass of polylactic acid (PLA) fibers during melt electrospinning, an orthogonal design method was used to examine the influence of melting temperature, spinning distance, and species and content of antioxidants. Results showed that antioxidant content at the present three

levels (i.e., 0.1%, 0.3%, and 0.5%) has the most considerable effect on the relative molecular mass of PLA fibers. Error analysis showed that changes in temperature, distance, and antioxidant content influence the experiment's results significantly. All interaction effects were larger than those of the single factor in the experimental results. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2652–2658, 2012

Key words: antioxidant; degradation; fibers; melt electrospinning; relative molecular mass

INTRODUCTION

Polylactic acid (PLA) is a completely biodegradable polymer.^{1,2} It is environmentally benign because the degraded products include water and carbon dioxide only. Thus, there has been an increasing interest in the said material. Because of its biodegradability, biocompatibility, and absorbability, PLA is widely used in biomedicine, such as for wound closure sutures, tissue engineering scaffolds,^{3,4} drug delivery carriers,⁵ among many others. Nonwoven PLA fibers, particularly nanofibers with very large surface area-to-volume ratio,⁶ can also be used to clean the air because they can collect dust particles efficiently. However, the application of PLA fiber is limited with respect to thermal degradation and thermal oxidative degradation under high temperatures. High temperature can affect the relative molecular mass of PLA and is believed to cause direct damage to the mechanical properties of nanofibers.⁷

Melt electrospinning is an easy and efficient way of producing PLA nanofibers.^{8–11} Unlike in solution electrospinning, solvent volatilization is not used in melt electrospinning.^{12–17} Thus, melt electrospinning does not cause harm to the environment, and the surface of the

resulting fibers does not have cavities, which will lead to a decrease in mechanical properties.¹⁸ However, the primary difficulty involved in melt electrospinning relates with temperatures that exceed melting points of 20–30°C. Mechanical properties, such as tensile strength, are dependent on the relative molecular mass of PLA, which is lowered for PLA fiber degradation at high temperatures. Changes in relative molecular mass during melt electrospinning are important in obtaining optimum spinning conditions to elevate the properties of fiber.

Numerous factors, like spinning temperature, spinning distance (i.e., the distance between spray head and collecting plate), and species of the antioxidant, among others, could affect fiber degradation. On account of multitudinous parameters, the researchers had to prepare many samples. Based on a limited supply of PLA and to shorten the experiment period, a simplified method (i.e., orthogonal design) was used to study factors affecting the degradation of PLA fibers of melt electrospinning.

MATERIALS AND METHODS

Materials

PLA was purchased from the Ningbo Materials Science and Engineering Company, China, whereas tris(2,4-di-*tert*-butylphenyl)phosphate (antioxidant 168) and Tetrakis[methylene(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)]methane (antioxidant 1010) were bought from the Beijing Additive Institute, China.

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TABLE I
Contents of Orthogonal Factors and Their Levels

	A	B	C	D
Factor Level	Temperature (°C)	Distance (cm)	Species of antioxidant	Content of antioxidant (wt %)
1	200	12	X	0.1
2	210	14	Y	0.3
3	220	16	X : Y = 1 : 1	0.5

Note: X is antioxidant 1010. Y is antioxidant 168.

Pretreatment

PLA particles were first broken down into fine powder in a mill. PLA powder and corresponding antioxidant content, as shown in Table I, were put into the mill. Then, the two materials were mixed uniformly under high-speed deals. In this way, nine samples were prepared according to the species and content of the antioxidants in Table I. The mass of each sample was 3 g. An additional blank PLA powder sample did not include additives. The 10 PLA samples were baked at 70°C for 4 h to drive out any water, which could initiate serious degradation.

Electrospinning

Figure 1 shows the diagram of the patented equipment^{19,20} used in this study. The collector consists of a round, flat aluminum plate with a 20 cm diameter. The high-voltage supply device purchased from Tianjin High Voltage Power Supply Plant (China) provided a maximum output of +100 kV and a maximum current output of 2 mA. The electric heating ring was custom built, with a power of 300 W.

The temperature for the top electrical heating ring was set to 170°C, and the lower was set to the

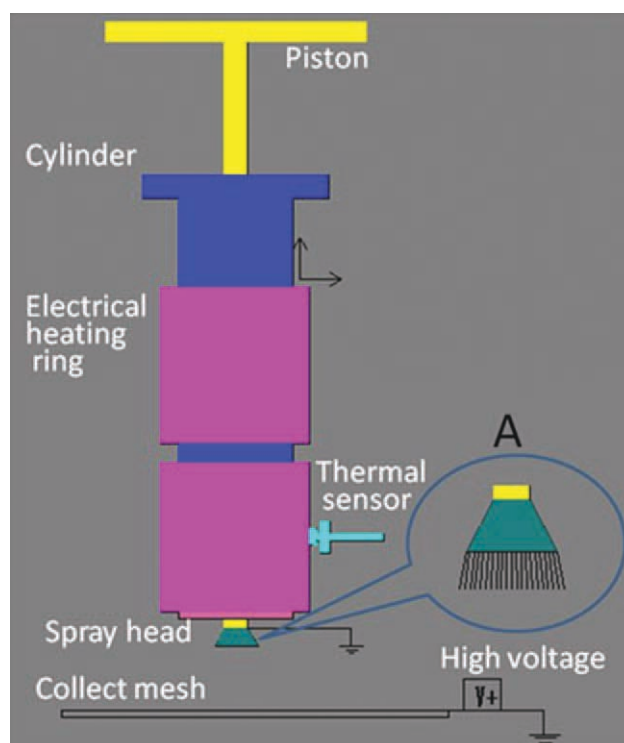


Figure 1 Schematic illustration of the experimental apparatus.^{19,20} "A" is the mimic diagram of electrospinning. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

required temperature based on Table I. The distance between the spray head and the collecting plate was adjusted according to their required values. Each experiment was conducted after temperatures reached steady states. Then, the piston was pulled out, and the cylinder was loaded with 3 g PLA powders. After the PLA melts covering spray head uniformly, forming several cones (Taylor cones) along the bottom edge of the spray head, the high-voltage supply device was switched on and adjusted to 55.6 kV. The time within

TABLE II
Effects of the Four Factors on Relative Molecular Mass of Melt Electrospinning Fibers

	A	B	C	D	
Experiment	Temperature (°C)	Distance (cm)	Species of antioxidant	Content of antioxidant (wt %)	Relative molecular mass (M_n)
1	1	1	1	1	26,349
2	1	2	2	2	7922
3	1	3	3	3	8856
4	2	1	2	3	20,815
5	2	2	3	1	21,769
6	2	3	1	2	7498
7	3	1	3	2	6597
8	3	2	1	3	6446
9	3	3	2	1	7403
M_{1j}	14,376	17,920	13,431	18,507	
M_{2j}	16,694	12,046	12,047	7339	
M_{3j}	6815	7919	12,407	12,039	
R_j	9879	10,001	1384	11,168	

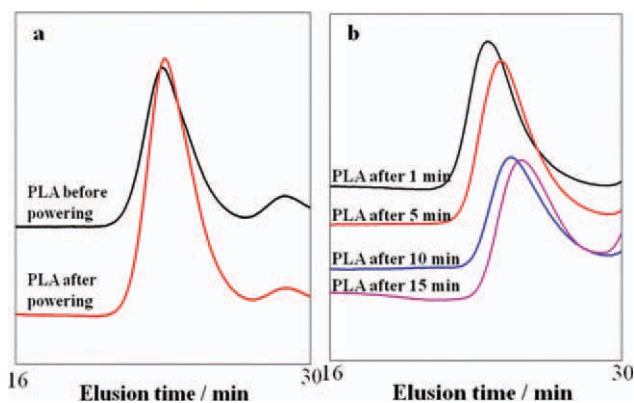


Figure 2 GPC elution profiles of (a) PLA before and after powdering and (b) PLA fibers after 1, 5, 10, and 15 min electrospun. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which the PLA flowed out of the cylinder was about 1–1.5 min, which varied under different conditions. After electrospinning for 15 min, the resulting fibers were collected to characterize the relative molecular mass. Different contents were selected based on Table I. The blank sample was electrospun at the condition shown in Sample 5 in Table II. The resulting pure PLA fibers after electrospinning for 1, 5, 10, and 15 min were collected as the contrastive sample.

Characterization

The relative molecular mass of electrospun fibers was measured by gel permeation chromatography (GPC, Shimadzu LC-6A). The solvent used was tetrahydrofuran. The column temperature was 30°C. Figure 2(a) and Table III show changes in the relative molecular mass of PLA before and after being powdered. In the process of powdering, a small amount of heat emerges, leading to a tiny degradation of PLA particles.

The thermal transition of PLA powder was studied using differential scanning calorimetry (DSC, Netzsch DSC-204F1) in the air. The heating rate was 5°C/min. Figure 3 is the thermal analysis curve of PLA powder. From the curve, glass-transition temperature (T_g), which equals 60°C, is obtained. There are two types of crystal forms: α -crystal and β -crystal. The melting point of β -crystal is lower, which equals 130°C. The melting point of α -crystal is higher, which equals 150°C. When the processing

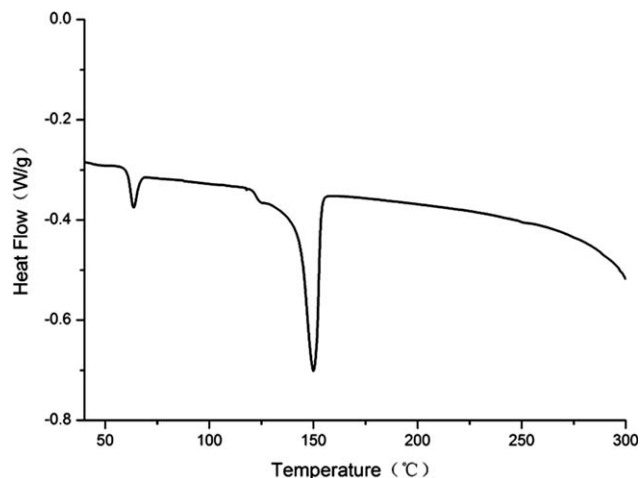


Figure 3 Thermal analysis curve of PLA powder.

temperature surpasses the melting point of α -crystal, the degradation of PLA is severe. The relative molecular mass of PLA decreases quickly.²¹

RESULTS AND DISCUSSIONS

Orthogonal design^{22–24} is a mathematical method used for planning multifactor tests. It is a balanced arrangement of pairs or groups and applied broadly in many fields to optimize test designs. In this study, spinning temperature, spinning distance, and species and content of the antioxidant were selected as targets for investigation. All other factors, such as electrospinning pressure, electrospinning voltage, and ambient temperature, were maintained. Each of the abovementioned four factors could be changed at three levels. The L9 (3^4) orthogonal array was used to arrange the tests.²⁵ The number “4” stood for four factors and “3” for three levels. If every factor and level were considered, there would be 81 experiments. However, because factors and levels were collocated evenly, there were only nine experiments. Balanced collocation ensured that three levels of one factor appear three times each and that the various levels’ collocations between two factors appearing to be the same happened only once. Effects of the four factors on relative molecular mass were then examined. Details of the three levels of each factor are shown in Table I.

TABLE III
Number-Average Relative Molecular Mass (M_n) and Polydispersity Index (M_w/M_n) of PLA before and after Powdering and PLA Fibers after 1, 5, 10, and 15 min Electrospun

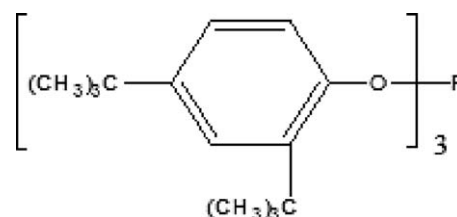
	PLA					
	Before powdering	After powdering	After 1 min	After 5 min	After 10 min	After 15 min
M_n	61,208	53,384	24,294	16,598	12,781	7058
M_w/M_n	1.86	1.90	2.14	2.14	1.94	2.43

Nine experiments, in accordance with the L9 (3^4) orthogonal array, were performed. Results of the effects of the four factors on the relative molecular mass of PLA fibers are presented in Table II,²⁶ where M_{1j} represents the sum of the results of row "j" if the level is 1. For instance, M_{11} is the sum of the results of the first row (temperature) when the level is 1 ($26,349 + 7922 + 8856 = 14,376$). R_j represents the difference between the largest and the smallest M_{ij} values of row "j." For example, 9879 is the difference between 16,694 and 6815. A large value of R_j indicates that the effect of factor j on the molecule weight of PLA is significant. Based on the R_j value in Table II, $11,168 > 10,001 > 9879 > 1384$. Thus, the effect of the four factors on the relative molecular mass of PLA fibers can consequently be listed in the following order: content of antioxidant > distance > temperature > species of antioxidant.

The abovementioned order is such because influential factors of PLA degradation include antioxidant, temperature, and heat time. A comparison of the relative molecular mass of Sample 5 ($M_n = 21,769$ from Table II) and the blank sample [$M_n = 7058$ from Fig. 2(b) and Table III] shows that antioxi-

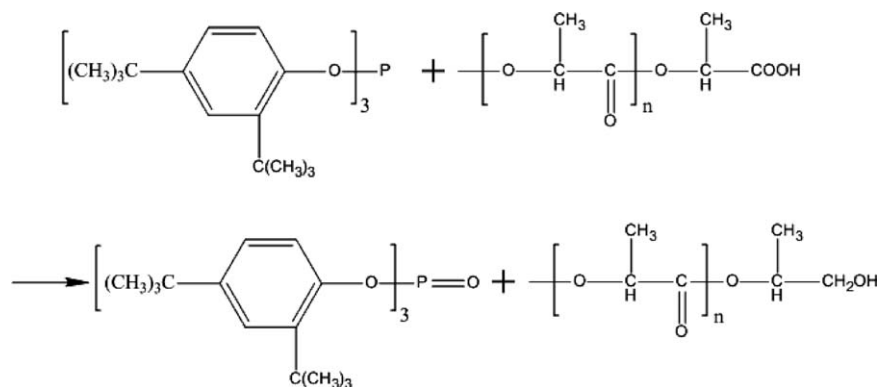
dants can delay the degradation of PLA. Degradation is initiated by the end carbonyl. When the ratio of the end carbonyl to PLA molecules is smaller, PLA degradation is slighter.

Antioxidant 168 is a phosphite ester-type antioxidant. Its molecular formula is

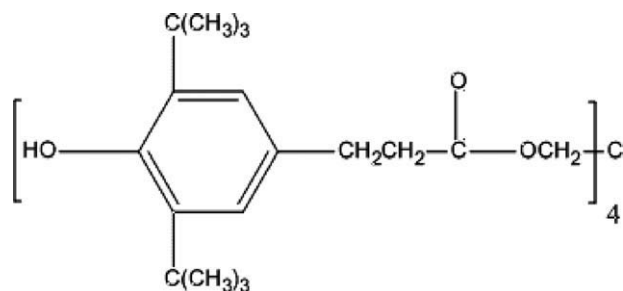


Like Formula (1), antioxidant 168 has intense reducing action, which captures the oxygen atom of PLA and deoxidates the end carbonyl to end hydroxyl. At the same time, antioxidant 168 changes to a corresponding organic phosphate. The deoxidation process decreases the ratio of the end carbonyl in the system to a certain extent, which prevents the degradation of PLA.

Formula (1)



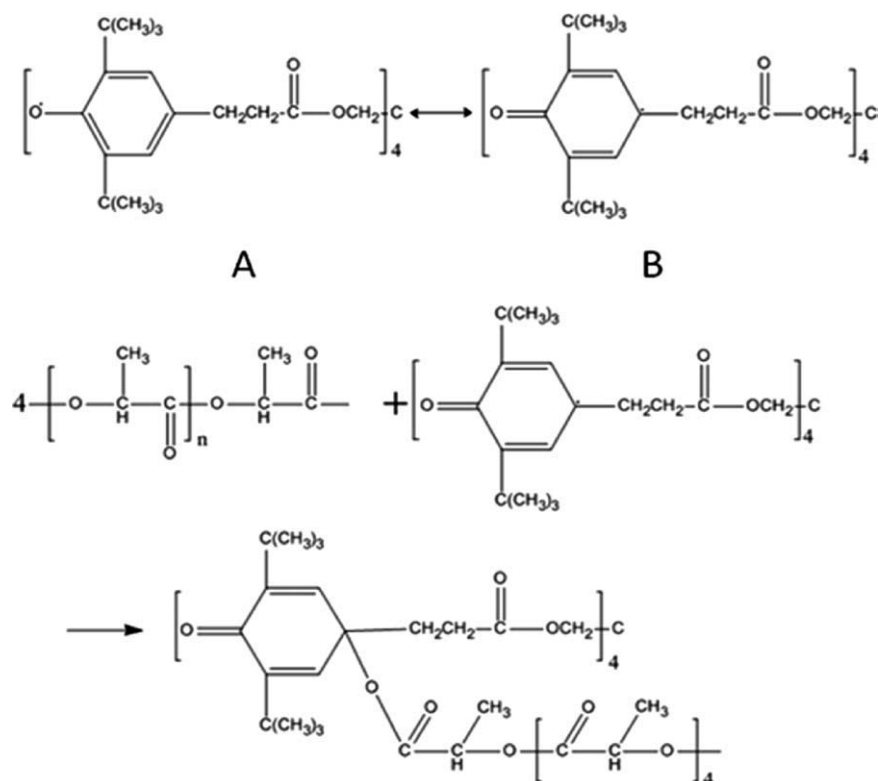
Antioxidant 1010 is a hindered phenolic antioxidant. Its molecular formula is



Hydrogen atoms in the hydroxyl groups easily disintegrate from the molecule because the hydroxyl group suffers from the steric effect of the benzene ring and the substituent group on the benzene ring. Like Formula (2),

the antioxidant 1010 molecule loses a hydrogen atom to form an aryl radical, as shown in Formula (2) A. The aryl radical formed is unstable, which easily changes to a stable aryl radical, as shown in Formula (2) B. The activity point is the benzene ring. When PLA melt is under high temperature and air, thermo-oxidative degradation happens. The antioxidant 1010 acts on the chain-free radical producing from thermo-oxidative degradation. It captures the chain-free radical produced from the thermo-oxidative degradation of PLA to form a stable polymer. The thermo-oxidative degradation of the PLA conforms to the reaction mechanism of the chain-free radical.²⁷ Antioxidant 1010 reduced the activity of the chain-free radical produced from the thermo-oxidative degradation of the PLA. Thus, the reaction of the chain degradation was terminated.

Formula (2)



The decrease of the end carbonyl group in the system or the inactivation of chain-free radical, led by the antioxidant, obviously reduces the degradation of PLA. Thus, the antioxidant can affect thermal degradation and oxidation degradation extensively.

However, to conclude that more antioxidant contents can lead to greater inhibition of molecular degradation, as heating time is also an important factor, is presumptuous. As shown in Figure 2(b) and Table III, the relative molecular mass of resulting fibers, along with an extension in time, decreased from 24,294 to 7058. The heating time affected the degradation of PLA. When the antioxidant content was 0.1%, the antioxidant decreased the ratio of the end carbonyl in the system and the activity of the chain-free radical. As such, the degradation of PLA decreased and the relative molecular mass was biggest ($M_n = 18,507$). PLA is a long-chain polymer. Long chain twists with itself and/or other long chains. The entanglement effect leads the PLA chain to move difficultly equaling to big viscosity. The long chain breaks down into short chain due to the thermo-oxidative degradation. Short chain has no entanglement effect or twists unobviously. So the chains move easily equaling to small viscosity. With an increase in antioxidant content, the degradation of PLA is decreased. The length of PLA chain is still very long and the entanglement effect is obvious. Hence, viscosity was enlarged and mobility of PLA

melts was decreased. At the same time, the required time for the PLA melts to flow out of the cylinder and stay in the barrel increased with an increase in corresponding heating time. PLA had a longer degradation time. When the content of the antioxidant was 0.3%, which caused an increase in viscosity, the PLA melts stayed in the barrel for a longer time and decreased the relative molecular mass. Thus, M_{ij} ($j = 4$) was $18,507 > 12,039 > 7339$ (Table II), suggesting that the antioxidant content at 0.1% would result in the least degradation of PLA fibers.

The effect of spinning distance on the degradation of PLA was achieved by influencing the tensile force of flying melt in the electric field. The bigger was the spinning distance, the smaller was the tensile force. PLA melts gathered on the edge of the spinning head to form superfine fibers under tensile force. When the spinning distance was bigger, the tensile force under the same voltage was smaller. Therefore, residence time on the high-temperature spinning head was longer, which increased the degradation of PLA melts. As shown in Table II, M_{ij} ($j = 2$) is $17,920 > 12,046 > 7919$. When spinning distance was 12 cm (i.e., the shortest distance), the relative molecular mass was at the maximum.

Two aspects of temperature effect could be observed on PLA relative molecular mass, namely, (1) high temperature promotes the degradation of PLA and the decrease of the relative molecular mass

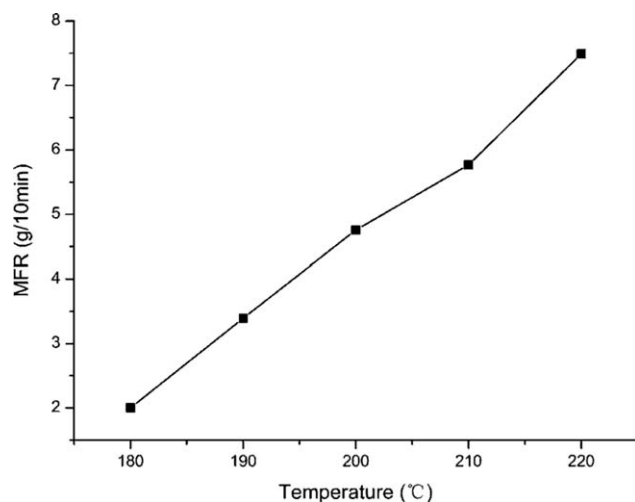


Figure 4 MFR of PLA at different temperature.

and (2) viscosity becomes small as temperature rises. Figure 4 shows the melt flow rate (MFR) of PLA at different temperatures. With a rise in temperature, the MFR of PLA increases. As such, the viscosity becomes small. Residence time of PLA melts in the barrel decreases and the corresponding relative molecular mass becomes larger because of the decrease in PLA degradation time. When the spinning temperature is low, the viscosity is large and the mobility of the PLA melts is poor. At the same time, the required time for the PLA melts to stay in the barrel increases, leading to an increased degradation of PLA melt. Beside decreasing MFR and residence time of PLA, the high-spinning temperature could lead to increased degradation too. To conquer the dilemma, our experiments showed that M_{ij} ($j = 1$) was $16,694 > 14,376 > 6815$ (Table II), suggesting that when the temperature is at 210°C (i.e., the mid-value), the relative molecular mass is at the maximum. In summary, the degradation of PLA is lowest under the $A_2B_1C_1D_1$ conditions.

As shown as above, the change of distance and temperature leads to the change of relative molecular. Moreover, the change of relative molecular leads to the change of viscosity. The decrease of viscosity can affects the relative molecular mass at the same

TABLE IV
Error Analysis of Orthogonal Experiment of Relative Molecular Mass of Melt Electrospinning Fibers

Factors	DOF	DEVSQ	S/F	F ratio	Significance
A (temperature)	2	160,121,365		51.746	*
B (distance)	2	151,567,755		48.982	*
C (species of antioxidant)	2	3,094,353		1.000	
D (content of antioxidant)	2	188,649,248		60.966	*
Error	2	3,094,353			

$F_{0.01}(2,2) = 99.0, F_{0.05}(2,2) = 19.0, F_{0.1}(2,2) = 9.00.$

time. Because of the decrease of viscosity the melt flow more quickly, which lead to the time of melt in the high-temperature cylinder decrease, so the thermo-oxidative degradation will cause the relative molecular mass become a little bigger in another aspect. In other words: distance and temperature are independent factors. Relative molecular and viscosity are dependent variables. Moreover, relative molecular and viscosity influence reciprocally.

Error analysis of the orthogonal design can distinguish whether the effect of factor levels on experimental results really comes from factor levels or from experimental error. It enhances the precision of the analysis. This article made the following error analysis. According to the previous experiment, Factor C, the species of the antioxidant, had a very minus effect on the degradation of PLA compared with other factors. Therefore, C was taken as the error standard in the analysis. Table IV is the error analysis of the orthogonal experiments on relative molecular mass of melt electrospinning fibers. Where DOF (degree of freedom) is the degree of freedom of each factor, DEVSQ (sum of squares of deviation/quadratic sum of deviation) S/F shows the quadratic sum of deviation between data point and corresponding sample average and F ratio is the variance ratio. The table shows that the change in D (the content of antioxidant) has the most marked effect on the degradation of PLA. The second entry in the table is A (temperature) and then B (distance).

TABLE V
Interaction of Every Factor

		B			D		
		12 cm	14 cm	16 cm	0.1%	0.3%	0.5%
A	200°C	26,349	7922	8856	26,349	7922	8856
	210°C	20,815	21,769	7498	21,769	7498	20,815
	220°C	6597	6446	7403	7403	6597	6446
B	12 cm				26,349	6597	20,815
	14 cm				21,769	7922	6446
	16 cm				7403	7498	8856

$R_{A \times B} = 42,797; R_{A \times D} = 41,840; R_{B \times D} = 44,250.$

Based on Table V (the interaction of *A* and *B*, *A* and *D*, and *B* and *D*), the order of effect is $R_{B \times D} > R_{A \times B} > R_{A \times D} > R_D > R_B > R_A > R_C$. The interaction between *B* and *D* is greater than that between *A* and *B* and between *A* and *D*. All effects of interaction on the experimental results are larger than those of the single factor. The relative molecular mass of the fiber is at the maximum under the B_1D_1 condition according to the analysis of the interaction between *B* and *D*, which matches the results in the analysis of the single factor.

CONCLUSIONS

In summary, using an orthogonal design method, the effects of four factors (i.e., melt temperature, spinning distance, and species and content of antioxidant) on the degradation of PLA fibers were compared at three levels. Results showed that the influence of the four factors on relative molecular mass could be listed in the following order: content of antioxidant > distance > temperature > species of antioxidant. The best conditions for electrospinning were under 210°C, with a 12 cm distance between the spray head and the collecting plate. The species of the antioxidant was antioxidant 1010, with a content of 0.1%. Error analysis showed that changes in temperature, distance, and content of antioxidant influenced the experiment results significantly. All effects of interaction on the experimental results were larger than those of the single factor.

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