Characterization of Structure and Properties of Polylactic Fiber

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ABSTRACT: Polylactic fiber (PLA) is a new environment-friendly fiber and has been produced by different plants with wide application, while there are few studies on the difference of the structure and property of PLA fibers produced from these plants in China. The main content in present article is to conduct elementary analysis, gas chromatography mass spectrum, IR spectroscopy, ultraviolet, X-ray, differential scanning calorimetry (DSC), TG, SEM, and tensile tests to obtain the common structure and properties of PLA fibers and to prove that there are no significant difference between the 13 kinds of PLA fibers made by 13 plants in China. The elementary analysis method is used to test the contents of C, H, and O elements, and it has good accordance with the theoretical results. Gas chromatography mass spectrum method proves that the functional groups of PLA fiber are lactide and acetaldehyde as well as 2,3-pentanedione. IR spectroscopy depicts that significant absorbing peaks exist as —C=O—, —C—O—, —OH— within absorbing wavelength zones. There are no characteristic absorbing peaks of ultraviolet spectrum. Crystallinity and orientation degree in full wave at half maximum and in area are calculated based on X-ray. The peak melting point and pyrogenation peak point are obtained by DSC and TG testings. The tensile property and the surface morphology by SEM are conducted and some typical faults in the surface are observed. In addition, the coefficient of variance of these experimental results between 13 kinds of PLA fibers show that their structure and properties are similar. J Appl Polym Sci 000: 000–000, 2012

Key words: polylactic fiber; lactide; elementary analysis; crystallinity; thermal

INTRODUCTION

It is a known fact that environment had to be protected by adopting eco-friendly materials, which necessitates the development and investigation of biodegradable polymers. Polylactic (PLA) fiber is a new environment-friendly fiber and has wide application, while now there also has no qualitative standard methods and will cause the difficulties in identifying PLA fiber for inspection. So, it is necessary to study identifiable characteristics of PLA fiber to provide relying experimental results to obtain the general properties of PLA fibers made in China. PLA fiber is polymerized by lactic acid into lactide, which contains the L-lactic and D-lactic acid to provided polymer with high mechanical strength.[1–3] It is one of the most popular biodegradable polymers materials for its better physical property and thermoplastic and biological properties. Moreover, the degradation products of PLA fiber are nontoxic, which enhances practical applications in biomedicine.[4,5] So, PLA fiber is currently being commercialized for a wide applications; especially, successful efforts are being made to tailor PLA with specific architectural characteristics.[6,7] There are many researchers who have been focusing on the preparation and process of PLA fiber,[8] while few works were on the investigation of structure and properties of PLA fibers.[9]

Therefore, the article aims to analyze element contents, functional groups, thermal, and physical properties to present. It is greatly helpful in analyzing the marker functional groups and physical properties of PLA fiber being significantly different with other fibers. It is useful in having a deep recognition of PLA fiber, and especially in the inspection of textile fibers.

MATERIALS AND METHODS

A total of 13 kinds of PLA fibers were selected from 13 plants in China, and their specifications were listed in Table I.

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TABLE I
Specification of 13 Kinds of Polylactic Fiber

Sample no.	Linear density (dtex)	Company
1	1.67	Shanghai Defulun Company
2	1.33	Haining XinnengI Textile Company
3	1.67	Haining XinnengII Textile Company
4	3.33	Ningbo Huanqiu Company
5	2.22	Defulun Company
6	3.33	Jiangyin JinxinII Company
7	1.67	Suzhou Taiyuanfang Company
8	1.33	Jiangyin JinxinI Company
9	1.67	Shenzhen guanghuaweiyespu Company
10	2.22	Shenzhen guanghuaweiyefil Company
11	3.33	Jiaxing Pulilaigreenfil company
12	1.67	Jiaxing Pulilaicoffeefil company
13	1.67	Shuixin Textile Company

These PLA fibers were tested for elementary analysis, gas chromatography mass spectrum, IR spectroscopy, ultraviolet testing, X-ray, differential scanning calorimetry (DSC), TG, SEM, and tensile tests. Elmentar Vario EL III was to test the elementary contents of C, H, and O elements, purged with helium gas and the temperature set as 950°C; GCMS–QP2010 was to show the significant functional groups, purged with helium gas and the temperature set as 600°C; NICOLET5700 IR spectroscopy tester was to feature marker functional groups; Hitachi U-4100 Ultraviolet tester was for testing ultraviolet absorbing ability; Rigaku D/Max-2550 X-ray tester was for measuring crystallinity and orientation degree; the LLY-06 tensile tester was used to conduct stretching experiments on each kind of PLA fiber, and set as follows: the gage length as 10 ± 0.5 mm and speed as 10 mm/min and preset load as 0.01 ± 0.001 cN/dtex; scanning electric microscope (SEM) had been conducted to study surface photograph of fibers, and each kind of PLA fiber was tested for 100 fiber specimens and to capture typical surface faults; thermal properties of fiber was investigated by the NETZSCH DSC204 DSC, purged with nitrogen gas 20 mL/min and scanned from 18 to 220°C at a heating rate of 10°C/min; pyrogenation property was also conducted by NETZSCH TG 209, purged with nitrogen gas and scanned from 20 to 500°C at a heating rate of 10°C/min. To show the common structure and properties of 13 kinds of PLA fibers, average value and correlation of variance (CV) value are calculated to prove the small difference between the 13 kinds of PLA fibers from 13 different plants.

RESULTS AND DISCUSSION

Elementary analysis

The experimental elementary contents of C, H, and O elements were listed in Table II by Elmentar Vario EL III. The theoretical elementary contents of C, H, and O were 50, 5.56, and 44.44% according to the structural formula of PLA fiber H-(—$C_3H_4O_2$–)$_n$-OH, when degree of polymerization n was very large. If authors have considered the effects of end groups of —H and —OH, the content of C was less than 50%, H and O were both larger than 5.56 and 44.44%, respectively.

To analyze whether or not there are significant differences between the 13 kinds of PLA fiber from 13 plants in China, the authors have processed the results of contents of C, H, and O of the 13 kinds of PLA fibers by statistical methods as average values and CV values of elementary analysis. It can be seen from Table II that content of C was 49.83% and CV was 0.29%, and content scope of C was within 49.83 ± 0.088% at the 0.05 level with two-tailed evaluation. The relative error of content of C was not larger than 0.5%. It showed that there existed good accordance between theoretical and experimental results. In addition, content of H was within 5.63 ± 0.027% at the 0.05 level with two-tailed evaluation and CV was 0.78%, and content of O was within 44.54 ± 0.10% at the 0.05 level with two-tailed evaluation and CV was 0.38%. Their relative errors were less than 0.2%. These results of contents of C, H, and O elements indicated that these PLA fibers were very pure and had little blending structure, and the 13 PLA fibers were similar.

Analysis of gas chromatography mass spectrum

The typical spectrum curve of functional groups was cut into two visible parts between 0–10 and 10–22 min and shown in Figure 1 by GCMS–QP2010, and the three kinds of functional groups of PLA fiber featured from the GCMS experimental results were listed in Table III.

TABLE II
Elementary Contents of Polylactic Fiber

Sample no.	1	2	3	4	5	6	7	8	9	10	11	12	13	Average	CV (%)
Content of C (%)	49.7	49.84	49.86	49.69	49.67	50.04	49.53	49.96	49.94	49.91	49.8	49.97	49.86	49.83	0.29
Content of H (%)	5.61	5.61	5.62	5.66	5.64	5.70	5.59	5.71	5.68	5.66	5.59	5.57	5.60	5.63	0.78
Content of O (%)	44.69	44.55	44.52	44.66	44.69	44.26	44.87	44.33	44.38	44.43	44.61	44.46	44.54	44.54	0.38

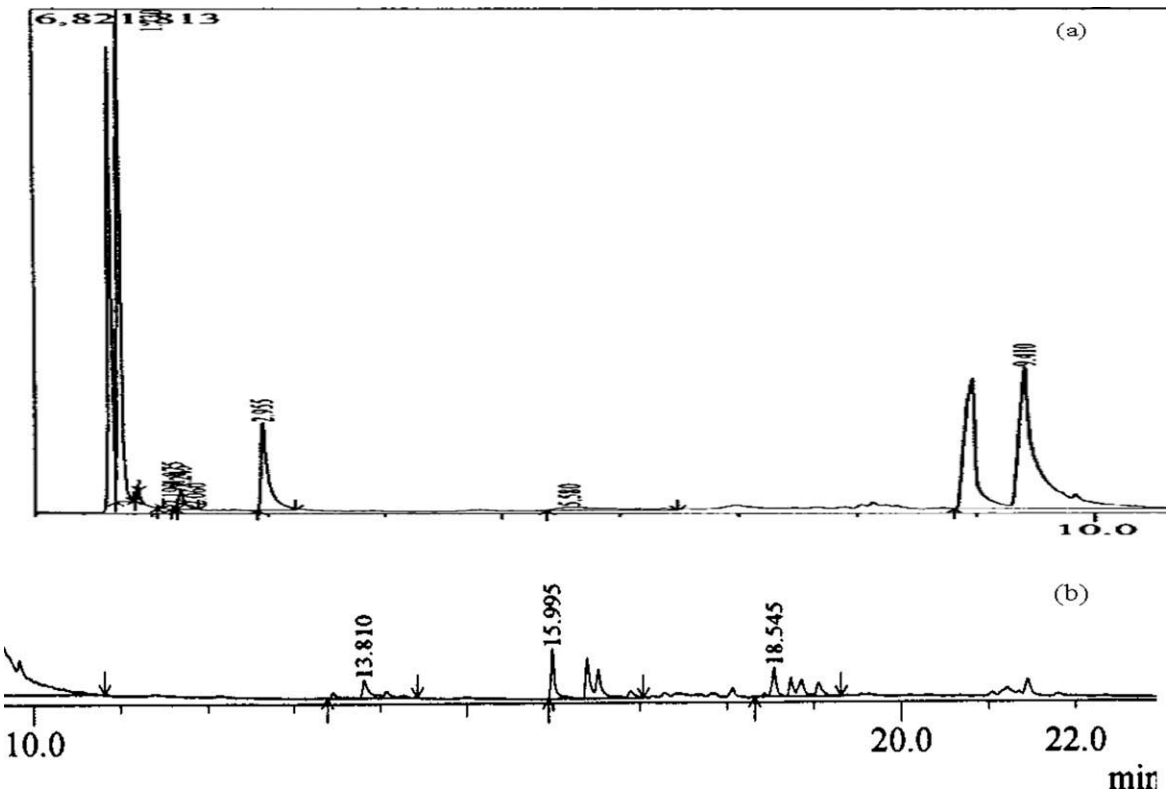

Figure 1 Curve of gas chromatography mass spectrum from 0 to 10 min (a) and 10–22 min (b).

The results of gas chromatography mass spectrum method proved that the functional groups of PLA fiber were lactide and acetaldehyde as well as 2,3-pentanedione. Their accumulated total contents were all larger than 70%. The percentage of lactide was largest, and the other two groups were the pyrolysis matters. It expressed that the main group of PLA fiber was lactide, whose polymerization was PLA fiber. The three kinds of groups were the marker characters of PLA fiber and could be used to differentiate with other fibers, such as PET, PA, and PAN fibers.

Analysis of IR spectroscopy

The typical spectrum of marker peaks were given in Figure 2 based on NICOLET5700 IR spectroscopy tester.

It could be seen from Figure 2 that there were significant absorbing peaks for PLA fibers from 650 to 3400 cm^{-1} wavelength. The absorbing peaks related the functional group dynamic status, and the corresponding groups were listed in Table IV. It was obvious that PLA fiber was the one of polyester category because it had features of —C—O, C=O, C—C, O—H, C—H groups. This was the fingerprint zone to be used to distinguish with other fibers. Moreover, PLA fiber had group zones where C=O, C—H, C—H_3 groups were marker. Moreover, 13 kinds of PLA fibers had the same peaking peaks from 650 to 3400 cm^{-1} wavelength, which explained that they had the same significant functional groups.

Analysis of ultraviolet spectroscopy

The typical spectrum of ultraviolet spectrum of PLA fiber was presented in Figure 3 by Hitachi U-4100 Ultraviolet tester, and the wavelength ranged from 240 to 380 nm.

The authors have found that it was very interesting that there was a minimum absorbing peak in the ultraviolet zone for PLA fiber, which was located

TABLE III
Content of Functional Groups of PLA Fiber

Sample no.	1 (%)	2 (%)	3 (%)	4 (%)	5 (%)	6 (%)	7 (%)	8 (%)	9 (%)	10 (%)	11 (%)	12 (%)	13 (%)
Lactide	53.15	62.56	58.06	46.03	73.18	63.77	64.68	70.15	65.80	59.35	50.76	50.03	40.71
Acetaldehyde	24.75	20.72	10.42	21.53	10.29	7.08	19.85	16.76	26.69	14.34	26.24	19.25	34.61
2,3-Pentanedione	8.40	6.28	5.34	21.74	5	5	5.87	3.80	4.63	4.12	3.13	3.65	2.00
Total percentage	86.30	89.56	73.82	89.30	88.47	75.85	90.40	90.71	97.12	77.81	80.13	72.93	77.32

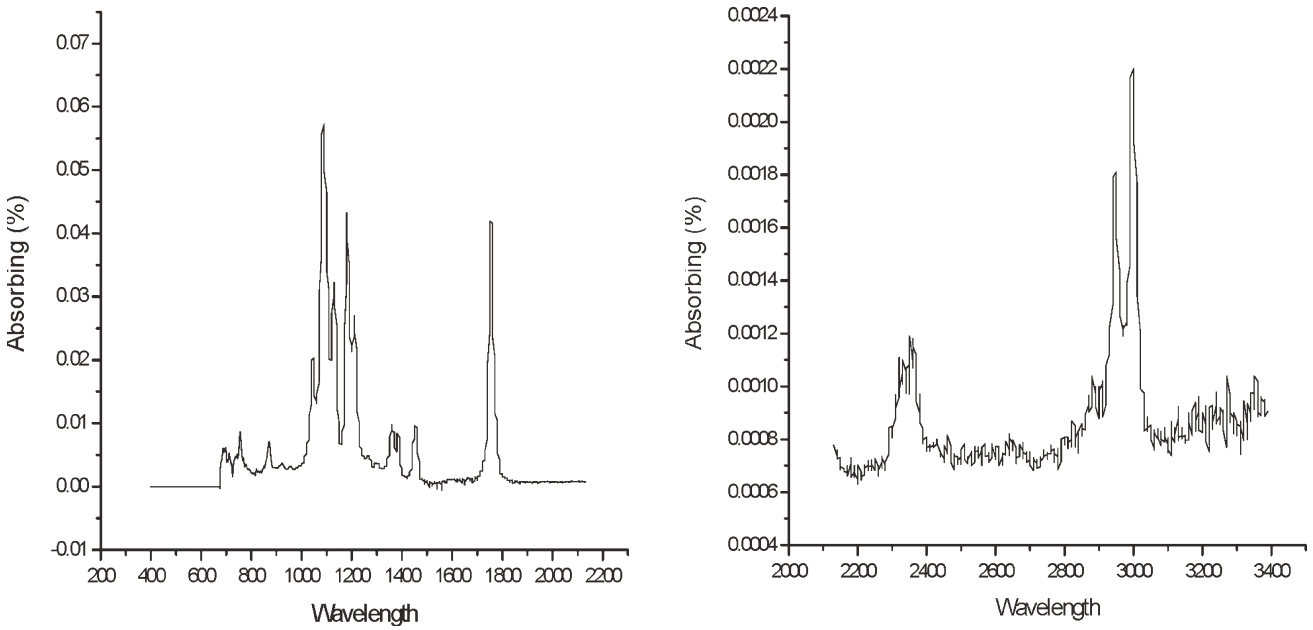

Figure 2 Total of 650–2200 cm^{-1} spectrum (left) and 2200–3400 cm^{-1} spectrum (right).

about 260 nm and the absorbing percentage value being less than 8%. It meant that PLA fiber was a good new fiber, which could be selected to be proof-ultraviolet products. It is the absorbing peak of groups just like in the IR spectroscopy. However, the curve did not provide the significant peaks of functional groups. So, it could not be used to have an identification of PLA fiber with other fibers, while it could be used as good anti-ultraviolet light materials.

Analysis of crystallinity and orientation degree

The typical crystallinity and orientation degree spectrum of X-ray spectrum of PLA fiber was illustrated in Figure 4(a,b) by Rigaku D/Max-2550 X-ray tester.

The experimental crystallinity of PLA fiber was 61.72% and orientation degrees were 93.36 and 84.30% in full wave at half maximum and in area calculations based on X-ray. It was used to explain that PLA fiber had higher strength to be used as products. In addition, their CV were 11.09 and 3.99% for FWHM and 8.36% for area integration. It indicated that structure of PLA fiber in processing and production were stable, and the 13 PLA fibers had similar crystalline and orientation properties.

TABLE IV
Function Groups of PLA Fibers by IR Spectroscopy

	Peak (cm^{-1})	Group vibration status
Fingerprint zone:	700–900	C—C stretching
650–1300 cm^{-1}	1000–1060	O—H bending
	1060–1200	—C—O— stretching
	1200–1300	C=O bending
	1300–1400	C—H bending
Group zone:	1400–1500	—CH_3— bending
1300–4000 cm^{-1}	1700–1800	C=O stretching
	2200–2400	C—H stretching
	2800–3200	C—H stretching

Analysis of differential scanning calorimetry

The typical melting curve and characteristics of melting zone of PLA fiber were shown in Figure 5 and Table V by NETZSCH DSC204. In the melting zone, three characteristics were featured, including the starting melting point, the melting peak point, and the end melting point.

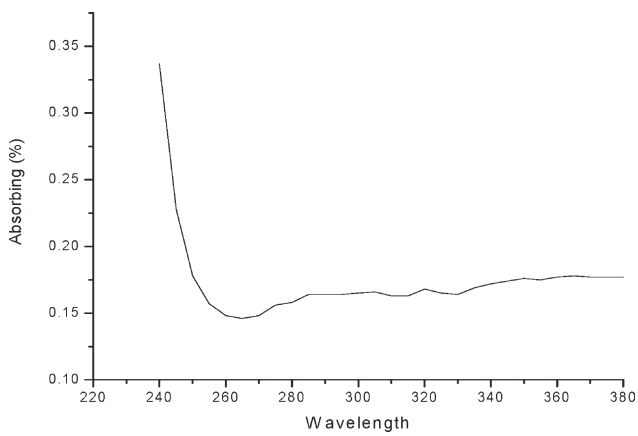

Figure 3 Total of 240–380 nm spectrum of ultraviolet of PLA fiber.

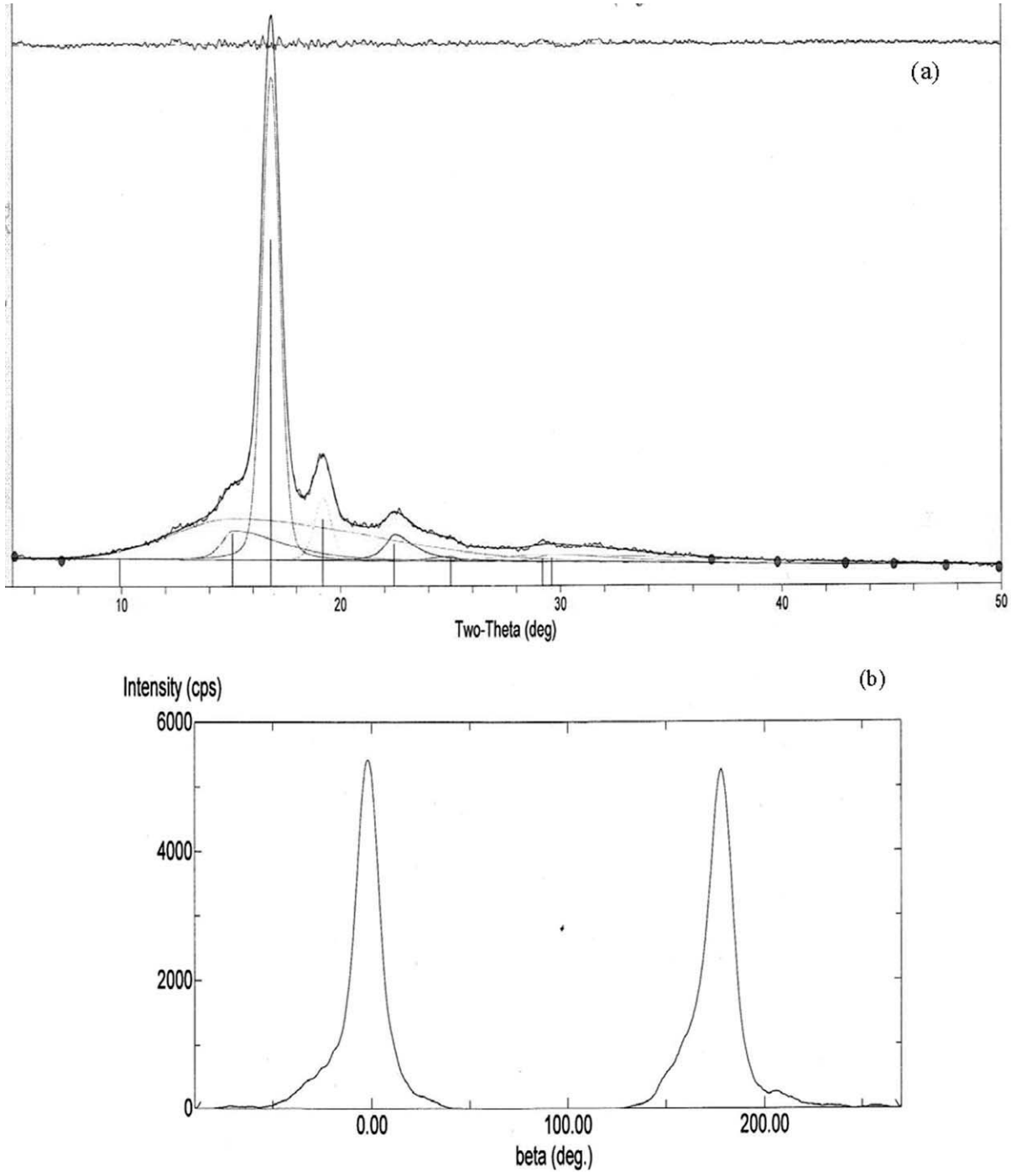

Figure 4 Crystallinity spectrum (a) and orientation degree spectrum (b) of X-ray spectrum of PLA fiber.

It was seen from Table V that the average values and correlation coefficient CV of the starting melting point, the melting peak point, and the end melting point were 145.58°C and CV = 8.45%, 162.58°C and CV = 4.93%, and 167.82°C and CV = 4.53%, respectively. It showed that the melting zone of PLA fiber ranged from 145.58 to 167.82°C, and the temperature span was relatively narrow. It addressed that 13 PLA fibers also had melting properties for similar structure of crystalline. The small melting span could be explained that the crystallinity of PLA fiber was high and the typical functional groups were concentrated, which were proved by the testing results of gas chromatography mass spectrum and X-ray. To analyze the characteristic melting peak point, the statistic method was used to obtain the melting peak point span being 162.58 ± 4.84°C at the 0.05 level with two-tailed evaluation. These results proved that the melting properties of these PLA fibers are similar.

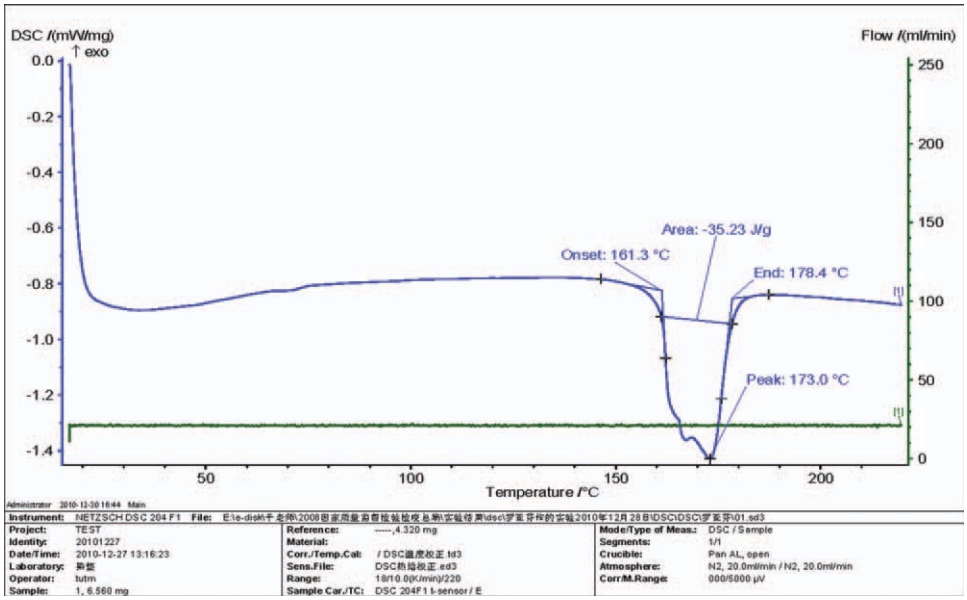

Figure 5 Melting curve of differential scanning calorimetry of PLA fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Analysis of pyrogenation

The typical pyrogenation curve and characteristics of pyrogenation zone of PLA fiber were listed in Figure 6 and Table VI by NETZSCH TG 209. In the pyrogenation zone, four characteristics were featured, including the starting pyrogenation point, the pyrogenation peak point, the end pyrogenation point, and residual mass ratio.

It was seen from Table VI that the average values and correlation coefficient CV of the starting pyrogenation point, the pyrogenation peak point, and the end pyrogenation point were 321.37°C and CV = 2.45%, 348.10°C and CV = 1.48%, and 356.58°C and CV = 2.15%, respectively. It showed that the pyrogenation zone of PLA fiber varied from 321.37 to 356.58°C, and the temperature span was relatively small. The residual mass ratio of PLA fiber under temperature 500°C was not larger than 5.5%, which indicated that PLA fiber was almost fully decomposed. To analyze the characteristic pyrogenation peak point, the statistical method was used to obtain the pyrogenation peak point span being 348.10 ± 3.10°C at the 0.05 level with two-tailed evaluation. It further added that the typical functional groups were concentrated, which was proved by the testing results of gas chromatography mass spectrum. In addition, the small CV for starting pyrogenation point, the pyrogenation peak point, and the end pyrogenation point were not more than 3%, which further exhibited that these 13 PLA fibers were similar.

TABLE V
Results of Melting of PLA Fiber by DSC

	Melting zone of PLA fiber			
Sample	Starting melting point (°C)	Melting peak point (°C)	Ending melting point (°C)	Heat content (J/g)
1	161.3	173.0	178.4	35.23
2	156.8	169.2	174.0	30.10
3	137.3	152.2	160.6	21.72
4	128.4	155.6	161.1	18.56
5	137.4	162.7	168.0	24.05
6	159.6	172.8	177.3	34.86
7	155.8	168.8	172.8	29.56
8	158.8	169.2	173.0	28.71
9	136.9	163.6	167.1	26.21
10	133.6	153.2	158.4	20.81
11	135.1	154.9	159.2	23.26
12	135.6	152.0	157.7	24.64
13	155.9	166.3	174.1	37.30
Average value	145.58	162.58	167.82	27.31
CV	0.0845	0.0493	0.0453	0.217

Analysis of tensile property

The tensile property of 13 kinds of PLA fiber was tested by strength tester, and each kind of PLA fiber was tested for 100 fiber specimens, and the total average value and CV of 13 kinds of PLA fibers' average values were listed in Table VII.

It could be seen from Table VII that the average tensile strength, elongation, and tensile work of PLA fiber were 2.44 cN/dtex, 37.51%, and 0.54 cN/dtex, respectively. These results of tensile property showed that PLA fiber were used in many products for proper strength and elongation. Moreover, the CV of the three tensile characters tensile strength were not more than 25. They were smaller compared

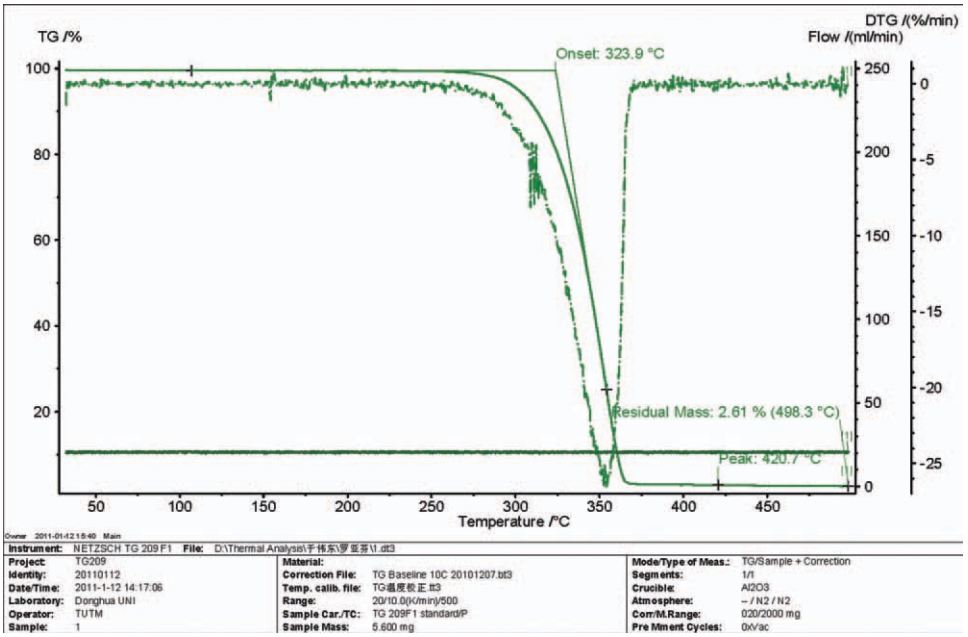

Figure 6 Pyrogenation curve of TG of PLA fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with other fibers such as CV of tensile strength of PET fiber larger than 25%. It further showed that structures of PLA fibers were concentrated and similar between the 13 kinds of PLA fibers.

Analysis of surface by SEM

The authors have found that there existed obvious characteristics of PLA fiber when it was magnified by 2000 times. The typical surfaces of PLA fiber by SEM were shown in Figure 7. The best surface was smooth and has less small particles, seen as Figure 7(a). 13 kinds of PLA fibers were all tested and each kind of PLA fiber was tested for 100 fiber specimens and to capture typical surface faults. The authors have found that the 13 kinds of PLA fibers all had the common surface faults. It had to be smooth for PLA fiber morphology for spinning; while they were quite rough or had bad faults whose typical faults included spiral, groove, cross stria, apophysis, crack, particle, and concave, seen from Figure 7(b–h). These faults might be caused by the polymer processing conditions, and would significantly influence the mechanical property and handle of products, while they addressed that the surface of PLA fibers were easily damaged in spinning. It was caused by the polymerization of the basic polymerized unit—lactide, which was easily decomposed in high humid environment.

TABLE VI
Results of Pyrogenation of PLA Fiber by TG

	Pyrogenation zone of PLA fiber			
Sample	Starting pyrogenation point (°C)	Pyrogenation peak point (°C)	Ending pyrogenation point (°C)	Residual mass ratio (%)
1	323.9	352.6	366.8	2.61
2	301.9	342.8	346.2	2.61
3	324.8	351.8	367.2	1.11
4	330.0	352.2	366.1	0.31
5	316.8	343.6	349.3	1.17
6	328.9	355.5	360.3	0.00
7	318.7	340.0	350.2	4.20
8	315.7	346.0	350.8	5.38
9	320.8	351.5	359.3	1.81
10	320.7	346.5	352.4	0
11	318.4	341.8	350.4	3.28
12	323.9	346.8	351.9	0
13	333.3	354.2	364.6	1.32
Average value	321.37	348.10	356.58	
CV	0.0245	0.0148	0.0215	

CONCLUSIONS

The main content in present article was to analyze element content and functional group as well as properties, and the experimental results would be

TABLE VII
Tensile Testing Results of 13 Kinds of PLA Fibers

Tensile	Average value	CV (%)
Tensile strength	2.44 cN/dtex	14.7
Elongation	37.5%	9.7
Tensile work	0.54 cN/dtex	21.3

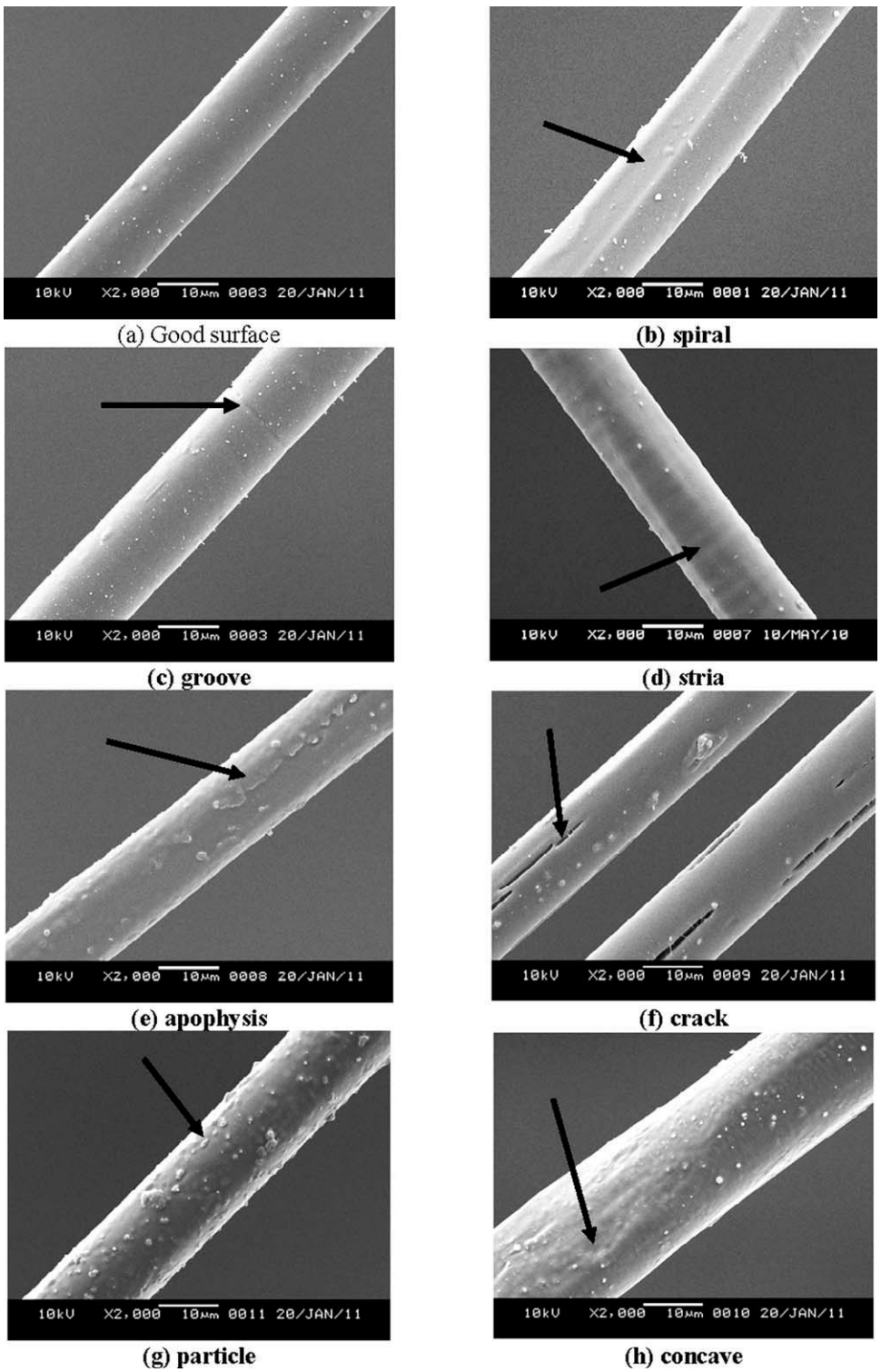

Figure 7 Surface morphology of PLA fiber by SEM.

greatly helpful in the qualitative analysis of PLA fiber. The conclusions can be drawn as follows:

1. The elementary analysis method showed that the contents of C, H, and O elements are 49.83, 5.63, and 44.54%, respectively; it had good accordance with the theoretical results.
2. Gas chromatography mass spectrum method proved that the functional groups of PLA fiber were lactide and acetaldehyde as well as 2,3-pentanedione, and whose total content was larger than 70%.
3. IR spectroscopy depicted that there existed significant absorbing peaks by —C=O—, —C—O—,

—OH— within 1000–1300 cm^{-1}, and —C=O— within 1000–1300 cm^{-1}.

4. The absorbing peak of ultraviolet spectrum was 260 nm wavelengths.
5. Crystallinity was 61.72% and orientation degree was 93.36 and 84.30% in full wave at half maximum and in area calculations based on X-ray.
6. The peak melting point by DSC and pyrogenation peak point by TG were 162.58 and 348.10°C, respectively.
7. The tensile strength and elongation were 2.44 cN/dtex and 37.5%, respectively.
8. There existed some typical fault on the surface by SEM, including spiral, groove, cross stria, apophysis, crack, particle, and concave.
9. 13 kinds of PLA fibers from different plants in China had similar structure and properties for small CV.

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