ISSN 1560-0904, Polymer Science, Series B, 2024. © Pleiades Publishing, Ltd., 2024.

DESTRUCTION OF POLYMERS

Hydro-Thermal Degradation: A New and Rapid Method for Evaluating the Bio-degradation Performance of Poly(lactic acid)

Qiang Peng[a], **Rongqiu Li**[a], **Sijie Yin**[a], **Qiaolin Tang**[a], **Rong Sun**[a],
Guanjun Chang[a], **and Ming Kang**[a],*

[a]*College of Materials and Chemistry, Southwest University of Science and Technology,*
Mianyang, Sichuan, China

**e-mail: dyw510@126.com*

Received December 26, 2023; revised April 3, 2024; accepted April 4, 2024

Abstract—In order to evaluate the bio-degradation performance of different kinds of poly(lactic acid) (PLA) rapidly, a new method, called hydro-thermal degradation was developed. Four kinds of commercial grade PLA were analyzed by both bio-degradation and hydro-thermal degradation with their degradation performance investigated via weight loss (%), infrared spectra (IR), size-exclusion chromatography (SEC), and X-ray diffraction measurements (XRD). The experimental results showed that the bio-degradation performance, which would take several years to degrade totally, could degrade in a short time (2 h) at 170°C by the hydro-thermal degradation. The order of the degradation rate is Revode101 > Revode210 > Revode190 > Revode290, corresponding with the structure characteristics of them. Thus, this new method provides a simple and effective way to degrade the PLA rapidly and to evaluate its bio-degradation performance.

DOI: 10.1134/S156009042460089X

INTRODUCTION

Now with the rapid development of technology, the damage to the environment has gradually emerged. With the increasing environmental pollution, degradable materials have gradually been emphasized by countries. The degradable material is an environmentally friendly material, has begun to gradually substituting the fossil plastics. One of the most prominent is poly(lactic acid) (PLA), which can be obtained from natural sources, such as sugar and starch, etc., and has been used in many fields, including bio-medical engineering and the packaging industry [1–3]. The use of biodegradable polymer material has important significance in relieving the waste plastic pollution and eliminating issues such as land filling, sorting and reprocessing due to their biodegradability.

PLA degrades to nontoxic compounds through simple random fracture of the ester bonds [4]; it can be degraded by biological degradation [5], composting degradation [6], photo-oxidation degradation [7], thermal degradation [8], hydrolysis [9], etc. Standards for the composting ability of bio-based polymeric materials have been developed by the American Society for Testing and Materials (ASTM), the International Standards Organization (ISO) and the European Committee for Standardization [10]. So far, people's research on the degradation performance of poly(lactic acid) mainly focuses on biodegradation and hydrolysis, among which biodegradation includes composting and soil burial. Iozzino et al. [11], in the process of degrading PLA by bio-composting, it was found that the degradation rate of PLA after 35 days was about 0.45%, and the crystallinity of degraded PLA increased. Under the same degradation conditions, adding 3% fumaric acid to PLA could increase the degradation rate of PLA to 0.6%. Fabiolalniguez-Franco et al. [12] studied the hydrolysis and degradation process of PLA with 50% ethanol solution as solvent. Compared with pure water solution, the degradation rate of PLA exposed to 50% ethanol solution is faster, but if further utilization of lactic acid is needed, additional separation and purification steps need to be added, which reduces its economic benefits. Sambha'a et al. [13] conducted hydrothermal degradation experiments on PLA samples. The results revealed a decrease in the molecular weight of the polymer following hydrothermal treatment. Wolf et al. [14] investigated the hydrothermal degradation of poly(lactic acid) (PLA) when plasticized with polyethylene glycol (PEG). Their study revealed a strong correlation between the degree of hydrothermal degradation of PLA and the ambient temperature, as well as the duration of water exposure. Prolonged exposure to water above the glass transition temperature of PLA was observed to induce decomposition of the material.

In addition, the use of acid, alkali and catalyst may further cause equipment corrosion and other problems. ROCCA-SMITH research group [15] of the

Table 1. Relevant properties for the four kinds of PLA

PLA	M_n	M_w	$Đ$	T_m, °C
Revode101	58421	134766	2.31	135
Revode190	67222	156233	2.38	175
Revode210	60688	125818	2.07	161
Revode290	56016	131546	2.35	175

University of Burgundy in France studied the influence of liquid or gaseous water molecules on the hydrolysis and degradation of PLA films. Under the condition of low humidity (relative humidity 50%), PLA would not be hydrolyzed, but only physically aged. Under the condition of high humidity (relative humidity 100% or immersion in water), PLA is hydrolyzed, transparency decreases, and microstructure, crystalline phase and amorphous phase change. When the relative humidity is 100%, the degradation products of PLA (such as lactic acid, oligomer, etc.) will remain in the membrane, further catalyzing the hydrolysis reaction. Studies have shown that the best AmA yield can be obtained within 60 min at 250°C in a batch system in the hydrothermal method using pure water for waste fish offal. The application of lower temperature or reaction time leads to incomplete hydrolysis, while at higher temperature or reaction time, AmA degradation is dominant [16]. The same optimum conditions were also found in prawn shells; However, based on acid hydrolysis, only 25% of the total AmA content can be recovered [17]. Ling et al. [18] partially hydrothermally degraded the cotton fiber in polyester/cotton fabric at low hydrothermal temperature to obtain glucose and cellulose powder, while keeping the morphology and properties of polyester fiber unchanged, which can be used for secondary spinning. Zhang et al. [19] used copper sulfate as additive to hydrothermally degrade waste cotton fibers, and synthesized carbon microspheres with good morphology and rich oxygen groups (hydroxyl OH, carbonyl C=O, carboxyl COOH, etc.) in the hydrothermal range of ~280–330°C. The particle size of carbon microspheres was about ~0.5–5.0 μm.

The team of Rafael Auras [20] at Michigan State University reviewed more than two decades of research on the role of mass transfer in polylactic acid. They concluded that the molecular structure of PLA is intricately influenced by the mobility of molecular chains and the process of diffusion. Specifically, external factors such as temperature play a pivotal role in modulating the mass transfer properties of PLA. Elevated temperatures have been observed to augment the diffusion of gases and vapors, consequently inducing glass-to-rubber transition, plasticization, and degradation of the polymer. Furthermore, relative humidity (RH) represents another extrinsic factor impacting the diffusion of PLA molecules, with exposure to high RH leading to notable alterations in the molecular structure of the polymer and subsequent plasticization.

Nowadays although many studies have focused on crystallinity effects or composites, we know of no research about how to evaluate the bio-degradation performance of PLA rapidly. The aim of this work was to evaluate and compare the bio-degradation performance of four kinds of commercial PLA rapidly by a new strategy, named hydro-thermal degradation.

EXPERIMENTAL

Materials

Four commercial grade PLA were adopted in this work. They were produced by Zhejiang Haizheng Biological Material Co., Ltd. (China) with the commercial names of Revode101, Revode190, Revode210, and Revode290; their relevant properties are listed in Table 1. Besides, Revode101 and Revode210 have the D enantiomer content of 5% and Revode190 and Revode290 both are pure poly(L-lactic acid) (PLLA). The flow diagram of the experiment is presented in Fig. 1, using chloroform as the solvent to dissolve the PLA, and then pouring the solution into a dish to form films with thickness about 0.2 mm. The films were cut into 6 × 6 cm specimens for bio-degradation and 3 × 3 cm specimens for hydro-thermal degradation.

Degradation

Bio-degradation. Bio-degradation under real soil conditions was carried out in a soil located in Mianyang, China. Films (6 × 6 cm, thickness is 0.2 mm) were buried individually in the real soil at depths of 10 cm. At selected times, the samples were dug out, cleaned with distilled water, dried at 70°C for 4 h and then analyzed.

Hydro-thermal degradation. As a new and rapid method for evaluating the bio-degradation performance of PLA, hydro-thermal degradation was performed in a thermal water kettle (50 mL) which was made with a Teflon lining and steel casing. Three different solvent systems were adopted, hydrochloric acid solution (pH 1), distilled water (pH 7) and sodium hydroxide solution (pH 12), and the PLA films (3 × 3 cm, thickness is 0.2 mm) were put into the reactors with 25 mL medium separately. After being sealed, the reactors were placed in an oven for a predetermined period at 170°C; when completed, the reactors were removed from the oven and quenched by cold water to stop further degradation. The residual material was dried at 70°C for 4 h and then analyzed.

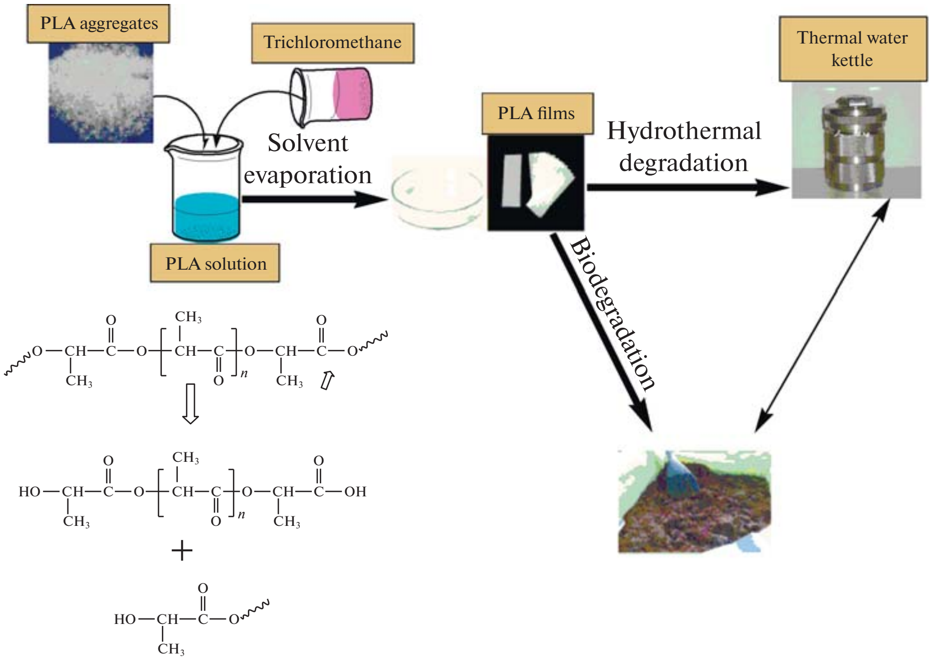

Fig. 1. Flow diagram of the experiment.

Methods of Investigation

The most common degradation processes of poly(lactic acid) can be divided into simple hydrolysis degradation and biodegradation. Firstly, the water of small molecules moves to the surface of the sample and diffuses around the ester bond or hydrophilic group. Under the action of acid and alkali in the medium, the ester bond of PLA is hydrolyzed and broken, and its relative molecular weight is reduced, and the molecular skeleton is broken, forming components with lower relative molecular weight, and water and carbon dioxide are produced under the action of microorganisms [21], so weight loss (%), molecular weight, the proportion of crystalline to amorphous regions and the chemical groups before and after degradation are common indices to describe the degree of bio-degradation. The percentage of weight loss was calculated from the following equation:

$$\text{weight loss (\%)} = 100 \times \frac{W_0 - W_d}{W_0}, \qquad (1)$$

where W_0 is the initial weight, and W_d is the weight after degradation.

The molecular weight was determined by a standard Size-exclusion chromatography (SEC) technique. A Waters 600 Multisolvent delivery system equipped with a Waters 717 auto sampler and a Waters 2410 RI detector, all produced by Waters Corp. (USA) was used to determine the molecular weights of the samples before and after degradation. Chloroform was used as an eluent at a flow rate of 0.8 mL/min at 30°C. Infrared spectra (IR) of the samples were obtained with an Avater 370 FTIR spectrophotometer produced by Nicolet Co. (USA), using KBr pellets. The crystal structure of the PLA were examined with a X Pert Pro diffractometer produced by PANalytical B.V. (Netherlands), using a X-ray diffraction system with CuK_α radiation ($\lambda = 0.15406$ nm), working voltage of 40 kV and current of 40 mA. The surface topography of the PLA before and after degradation were investigated with a TM-1000 SEM produced by Hitachi Ltd. Co. (Japan).

RESULTS AND DISCUSSION

Bio-Degradation

In order to evaluate the degradation performance of the four kinds of PLA in the natural environment, bio-degradation in soil was adopted. Table 2 and Fig. 2 show the weight loss (%) as a function of time (months) for all analyzed samples. PLA Revode101, with the D enantiomer content of 5% and the lowest density and T_m, showed the fastest rate of weight loss (%), reaching 9.52% after 3 months; the others lost 5.93, 6.98, and 4.76% corresponding to Revode190, Revode210, and Revode290, respectively. Revode290, being the pure poly(L-lactic acid) (PLLA) and with the highest molecular weight, T_m and density as shown in the Table 1, shows the slowest rate of degradation and only a small weight loss [22]. By prolonging the

Table 2. Statistical data on weight loss (%) versus time (months) for biodegradation of four polylactic acids in soil

Sample	Time, months	1st, %	2nd, %	3rd, %	Ave	σ, %
Revode101	1st	6.55	6.66	6.91	6.71	0.17
	2nd	8.01	8.17	8.50	8.23	0.21
	3rd	9.40	9.41	9.75	9.52	0.16
Revode190	1st	4.43	4.50	4.81	4.58	0.16
	2nd	4.83	4.90	5.21	4.98	0.17
	3rd	5.81	6.21	5.76	5.93	0.20
Revode210	1st	4.83	4.90	5.20	4.98	0.16
	2nd	5.33	5.35	5.71	5.46	0.17
	3rd	6.83	6.90	7.21	6.98	0.17
Revode290	1st	4.37	4.35	4.70	4.47	0.16
	2nd	4.44	4.48	4.82	4.58	0.17
	3rd	4.61	4.66	5.00	4.76	0.17

Ave is average value; σ is standard deviation.

time or raising the temperature of degradation, it would continue to degrade. The hydrolysis first occurred in the amorphous area and the surfaces of crystalline regions of the PLA, resulting in the decrease of the molecular weight and the increase of the active end groups. Due to the damage to the structure of the PLA, water molecules and some microbes could easily penetrate into the PLA for the further biodegradation [23]. Thus, the PLA with similar crystallinities may have the same weight losses at first. As Fig. 3 shows, Revode190 and Revode290 had similar X-ray diffraction scans and from Table 1, we can observe that they also had similar T_m, both of which were higher than Revode101 and Revode210, so the weight loss of Revode190 was equal to that of Revode290 after bio-degradation for 1 month and both were less than that of the Revode101 and Revode210. By prolonging the degradation time, the weight loss of Revode190 was higher than that of Revode290 because of the lower molecular weight. It can be seen that all four kinds of PLA degraded very slowly by bio-degradation, and it would take several years to degrade totally. Although the weight losses (%) were not large, it could also be concluded that the order of the weight losses was Revode101 > Revode210 > Revode190 > Revode290.

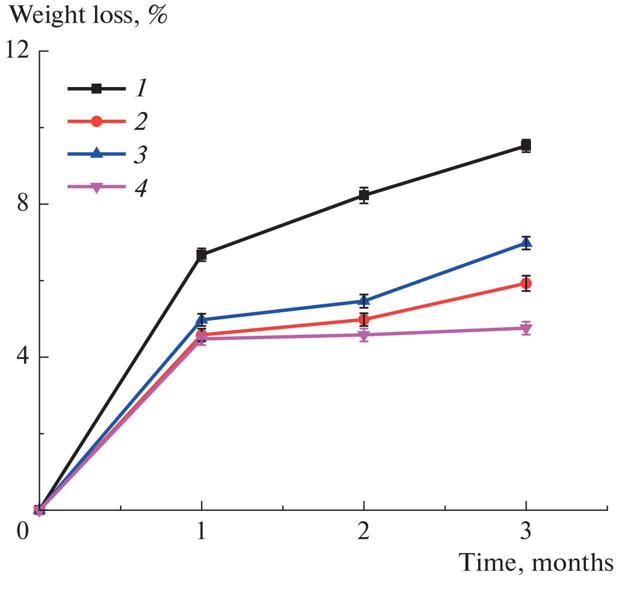

Fig. 2. Weight loss vs. time for the four types of PLA by bio-degradation in soil: (*1*) Revode101, (*2*) Revode190, (*3*) Revode210, (*4*) Revode290.

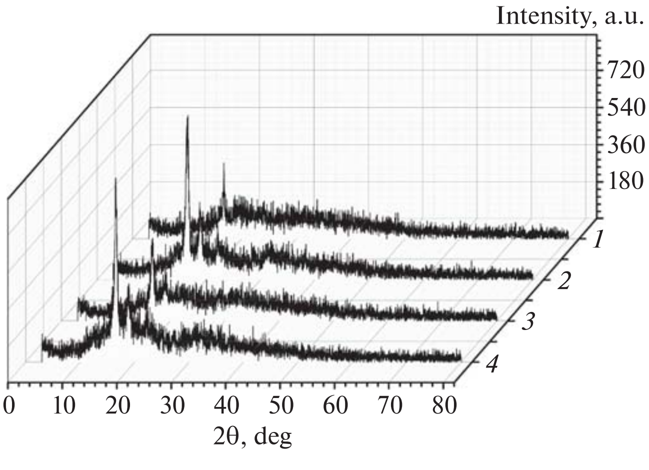

Fig. 3. The XRD patterns of the four types of PLA before degradation: (*1*) Revode101, (*2*) Revode190, (*3*) Revode210, (*4*) Revode290.

Table 3. Statistical data on M_w and M_n versus time (months) for biodegradation of four polylactic acids in soil

Sample	Time, months	M_w					M_n				
		1st	2nd	3rd	Ave	σ	1st	2nd	3rd	Ave	σ
Revode101	0	134800	132500	137100	134800	1878	57600	58000	59600	58400	864
	1st	86000	85400	89600	87000	1855	37900	39000	40100	39000	898
	2nd	77100	77500	81500	78700	1987	32600	31500	34300	32800	1152
	3rd	77100	74200	78600	75600	2123	32000	33900	31600	32500	1003
Revode190	0	130500	129900	134400	131600	1995	55100	57100	55800	56000	829
	1st	113100	116600	117400	115700	1867	54400	55900	56500	55600	883
	2nd	102200	102100	97800	100700	2051	42600	43600	44600	43600	817
	3rd	94500	92500	97400	94800	2012	39000	39100	41000	39700	920
Revode210	0	124300	124500	128600	125800	1982	59800	60500	61800	60700	829
	1st	112100	111900	108100	110700	1840	50500	50700	53000	51400	1134
	2nd	91200	91500	95400	92700	1913	41600	42800	44300	42900	1105
	3rd	86300	85000	89400	86900	1846	38600	38600	41000	39400	1131
Revode290	0	154000	156000	158600	156200	1883	66500	66500	68600	67200	990
	1st	143900	141800	139100	141600	1965	64800	64900	67100	65600	1061
	2nd	126500	129900	125200	127200	1982	54700	54100	56500	55100	1020
	3rd	122300	121000	125400	122900	1846	54900	52900	55400	54400	1080

Ave is average value; σ is standard deviation.

As a consequence of the degradation process, the polymeric chains undergo chain scission, resulting in a decrease of M_w and M_n. The change of molecular weight can intuitively reflect the PLA degradation degree. Table 3 and Fig. 4 illustrate the M_w (Fig. 4a) and M_n (Fig. 4b) of all samples as functions of the degradation time (months). The data showed obvious differences between the four kinds of PLA. In particular, Revode101 demonstrated a much faster degradation rate: the M_w decreased to 7.56×10^4 from 1.348×10^5 and M_n decreased to 3.25×10^4 from 5.84×10^4 after degrading for 3 months in real soil. Compared with Fig. 2, the molecular weights decreased more quickly than the weights, which is due to there being many hydrolysis sites at the beginning of the hydrolysis, so the hydrolysis of the ester bonds were random and the molecular weights decreased rapidly. These shorter

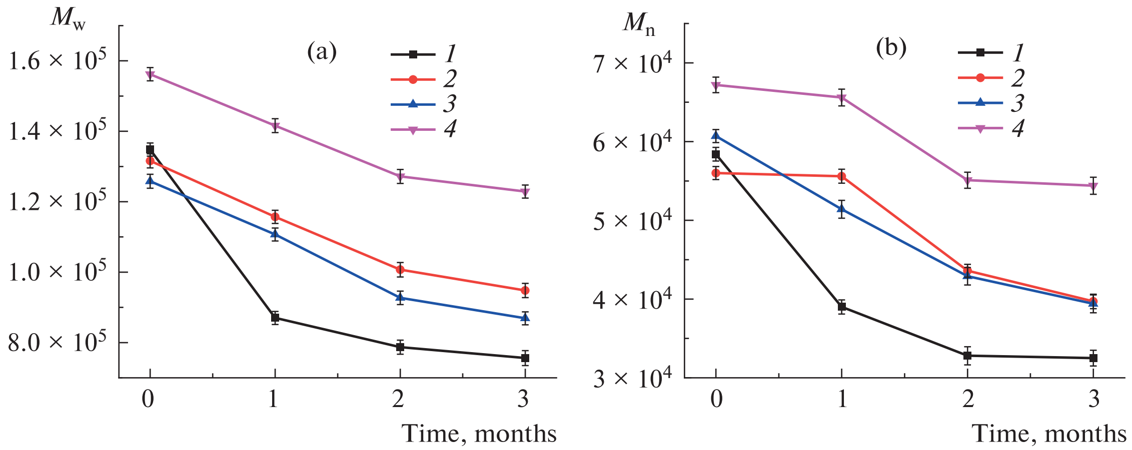

Fig. 4. The change of the molecular weights (a) M_w and (b) M_n of the PLA by bio-degradation: (*1*) Revode101, (*2*) Revode190, (*3*) Revode210, (*4*) Revode290.

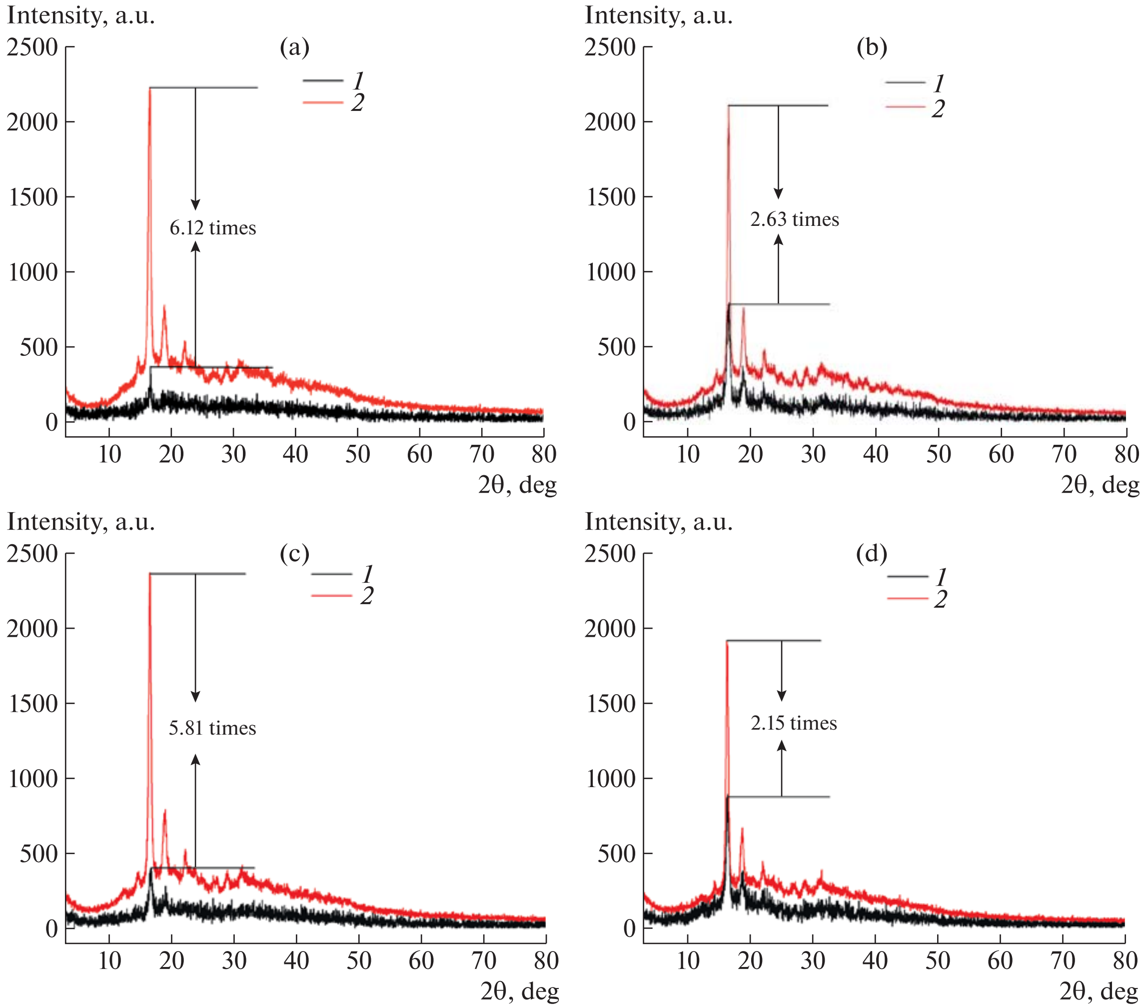

Fig. 5. The XRD patterns of the four types of PLA (*1*) before and (*2*) after bio-degradation for 3 months: (a) Revode 101, (b) Revode 190, (c) Revode 210, (d) Revode 290.

molecules originally generated still had a certain degree of polymerization and could stick together, so the weight losses were not obvious [17]. Although the M_w and M_n of the other three kinds of PLA also decreased, the molecular weights losses were obviously slower than Revode101 Obviously, the order of the molecular weights losses was Revode101 > Revode210 > Revode190 > Revode290.

The results of the XRD analyses of the samples are reported in Fig. 5. The analysis confirmed that the four kinds of PLA presented the typical diffraction pattern of crystalline molecular segments of PLA [24, 25]. As the polymer chains in the amorphous regions degraded, the amount of the amorphous regions decreased, so the proportion of crystalline to amorphous volume increased [26, 27]. From Fig. 5 it can be seen that after degradation for 3 months, the intensity of the XRD peaks became much stronger than in the initial samples, increasing by 6.12, 2.63, 5.81, and 2.15 times corresponding to Revode101, Revode190, Revode210, and Revode290, respectively. As predicted based on it having the greatest weight loss, the intensity of the XRD peaks of Revode101 changed the most. To compare the surface topography change of the samples, SEM images were obtained and the results are presented in Fig. 6. It was evident that Revode101 exhibited the greatest extent of surface deterioration and increase in roughness after bio-degradation for 3 months. On the contrary, the surfaces of the other three kinds of PLA exhibited less deterioration. The color change (the samples were initially transparent and became white and opaque after degradation) indicated the formation of corrosive holes, also showing the degree of degradation to some extent [4], which is Revode101 > Revode210 > Revode190 > Revode290.

On the whole, from the results of weight loss, SEC, XRD and SEM, the bio-degradation performance of

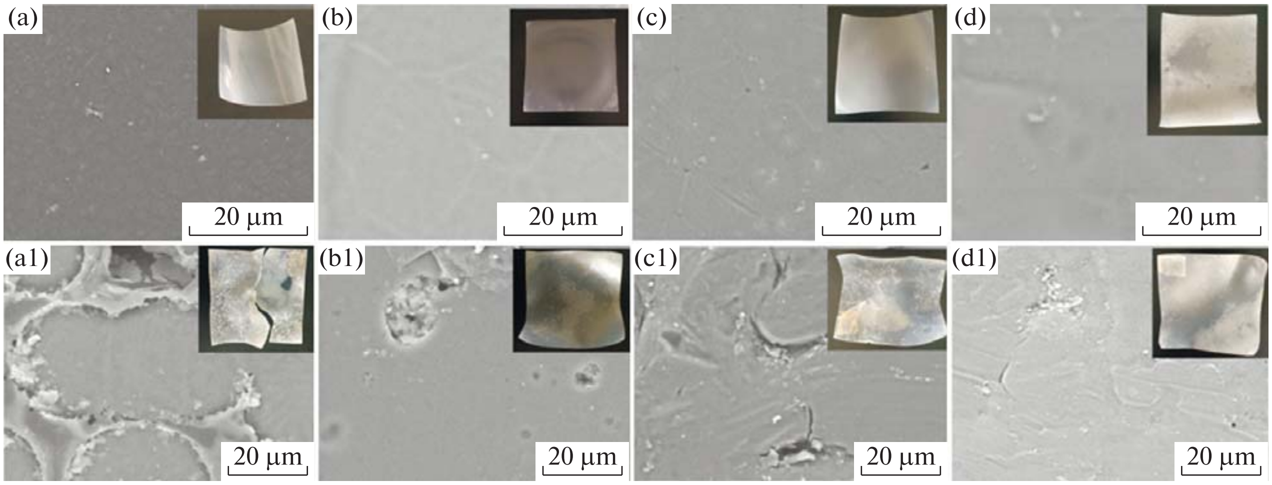

Fig. 6. SEM images of the four types of PLA films (a–d) before and (a1–d1) after bio-degradation for 3 months: (a, a1) Revode101, (b, b1) Revode190, (c, c1) Revode210, (d, d1) Revode290.

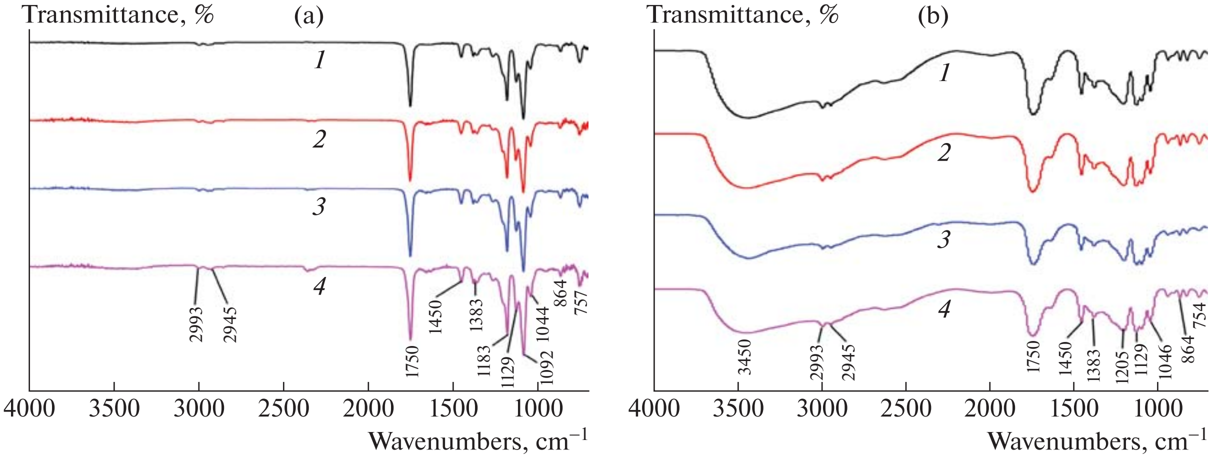

Fig. 7. The infrared spectra of the four types of PLA: (*1*) Revode101, (*2*) Revode190, (*3*) Revode210, (*4*) Revode290 (a) before degradation and (b) after hydro-thermal degradation.

the four kinds of PLA were in the order of Revode101 > Revode210 > Revode190 > Revode290, but it took a very long time. As indicated above, it would be very useful to develop a new and rapid method to evaluate the bio-degradation performance. Polylactic acid with relatively high molecular weight will decompose more slowly in the degradation process.

Hydro-Thermal Degradation

In order to evaluate the bio-degradation performance rapidly a new method, called hydro-thermal degradation, was adopted. Figure 7 shows the IR spectra of the PLA before degradation (Fig. 7a) and after degradation (Fig. 7b). In Fig. 7a, the peaks for all at the 2993 and 2945 cm^{-1} positions represent antisymmetric and symmetric stretching vibrations of CH_3 respectively. The peak at 1750 cm^{-1} represents the stretching vibration of carbonyl C=O. The peak at 1450 cm^{-1} represents the CH_3 antisymmetric bending vibratio and the peak at 1383 cm^{-1} represents the symmetric bending vibrations of CH. Those at 1183, 1092, and 1044 cm^{-1} represent the C–O–C stretching vibrations and the peak at 1129 cm^{-1} represents the stretching vibrations of C–O. The peak at 864 cm^{-1} represents the absorption of the ($O–CH–CH_3$) ester and that at 757 cm^{-1} represents the rocking vibration absorption of a $–CH_3$ group. Figure 7b shows that after degradation, a large O–H band appears at 3450 cm^{-1} and the peak at 1205 cm^{-1} represents the vibration absorption

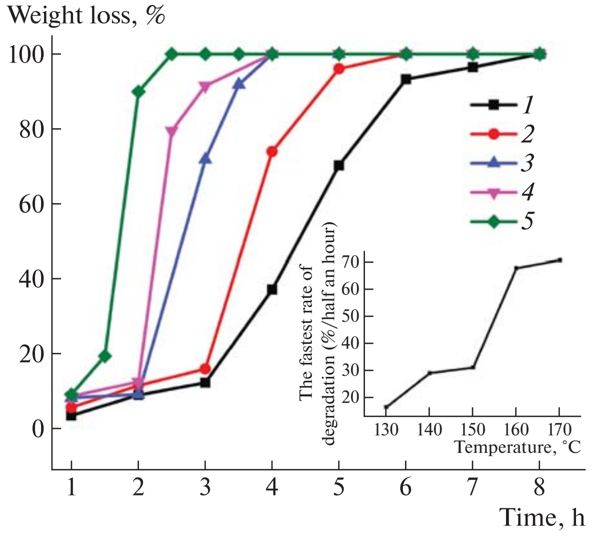

Fig. 8. Weight loss vs. time for PLA (Revode101) by hydro-thermal degradation at different temperature for 8 h: (*1*) 130, (*2*) 140, (*3*) 150, (*4*) 160, (*5*) 170°C. The inset is the fastest rate of degradation as a function of temperature.

of –COOH, which are all the characteristic absorption peaks of hydrolysates of the PLA. In addition, in Fig. 7b, the absorption peaks at 1750 cm^{-1} broadens and the peaks at 1092 and 1183 cm^{-1} nearly disappears, indicating the reduction or disappear of the ester bonds [4]. No obvious absorption peaks of pyrolysis products were observed, such as cyclic oligomer and lactide, indicating that the hydro-thermal degradation was mainly a hydrolytic degradation.

Figure 8 shows the weight loss (%) as a function of temperature for Revode101 in hydrochloric acid solution (pH 1). It can be seen that the samples degraded rapidly and the hydro-thermal degradation during the time measured all reached 100%. At the beginning of the hydrolysis, there were many hydrolysis sites so the hydrolysis of the ester bonds was random. These shorter molecules originally generated still had a certain degree of polymerization and could stick together, so the weight losses were not obvious. With the increase of temperature and the active end groups, the hydrolysis rate of the ester bonds also increased, so the weight losses became larger at the same time [28]. It only needed about 2 h to degrade totally when the temperature used was 170°C. The inset in Fig. 8 shows the fastest rate of degradation as a function of temperature (during the time period required to reach 100% degradation), increasing from 16.6 to 70.8% per half an hour with the rising of temperature from 130 to 170°C. As seen in the inset graph, when the temperature was below 130°C, the weight loss (%) of PLA (Revode101) was lower than 10% for half an hour and there were two plateaus and two steep multiple when the temperature was higher than 130°C. The reason is for Revode101, its melting point is 135°C, so when the temperature was increased from 130 to 140°C, the motion of the molecular chains occured and caused mutation of the weight loss. When the temperature was increased from 140 to 150°C, the motion of the molecular chains changed a little because of the viscosity between the molecular chains, so the weight loss was almost unchanged. When the temperature was increased to 160°C, the motion of the molecular chains was more freedom and the O–H and –COOH groups increased largely, which had the autocatalytic effect for the hydrolysis process, so the weight loss showed a sharp increase and reached almost 70% for half an hour. As temperature was increased successively, the weight loss showed a small increase in a high degree of the degradation [29, 30]. Obviously, increasing the temperature can effectively increase the PLA hydro-thermal degradation rate, so in our work, we took 170°C as the hydro-thermal degradation temperature for evaluating the degradation performance of PLA rapidly.

Table 4 and Fig. 9 show the weight loss (%) as a function of time (h) for the four types of PLA degraded in the different media at 170°C. It was clear that all four kinds of PLA degraded rapidly in hydrochloric acid solution (Fig. 9a, pH 1), distilled water (Fig. 9b, pH 7) and sodium hydroxide solution (Fig. 9c, pH 12). As shown in Fig. 9, in all 3 media, the four kinds of PLA had similar low weight losses (less than 20%) before 1.5 h. At 2 h, the weight losses of the residual PLA films in hydrochloric acid solution had increased rapidly and were 87, 43, 64, and 36% corresponding to Revode101, Revode190, Revode210, and Revode290, respectively (Fig. 9a). And it was obvious that the degree of the degradation was Revode101 > Revode210 > Revode190 > Revode290. Figures 9b and 9c showed the same order of degradation rates as in Fig. 9a. As many other studies have demonstrated, individual samples of PLA have different rates of degradation in acidic, neutral and alkaline solutions, with the order of degradation rate being alkaline solution > acidic solution > neutral solution [31, 32]. In our work, the same conclusions were obtained. For example, the weight losses (%) of Revode101 were 93, 87, and 70% in sodium hydroxide solution, hydrochloric acid solution and distilled water at 2 h, respectively. This has been attributed to the H$^+$ and OH$^-$ accelerating the hydrolysis rate of the ester groups. Thus, the degree of the degradation was also Revode101 > Revode210 > Revode190 > Revode290, which can be evaluated rapidly.

Table 4. Statistical data on weight loss (%) vs time (h) for the four types of PLA by hydro-thermal degradation at 170°C in different media

pH	Sample	Time, h	1st, %	2nd, %	3rd, %	Ave, %	Σ, %
1	Revode101	0.5	6	4	11	7	3
		1	7	8	12	9	2
		1.5	13	8	12	11	2
		2	86	85	90	87	2
	Revode190	0.5	2	6	1	3	2
		1	4	5	9	6	2
		1.5	13	16	10	13	2
		2	44	46	39	43	3
	Revode210	0.5	2	1	6	3	2
		1	6	3	9	6	2
		1.5	10	12	17	13	3
		2	61	63	68	64	3
	Revode290	0.5	2	1	6	3	2
		1	9	5	10	8	2
		1.5	14	17	11	14	2
		2	33	35	40	36	3
7	Revode101	0.5	6	6	12	8	3
		1	11	14	8	11	2
		1.5	16	18	23	19	3
		2	70	73	67	70	2
	Revode190	0.5	6	3	9	6	2
		1	6	6	12	8	3
		1.5	10	13	7	10	2
		2	35	39	34	36	2
	Revode210	0.5	5	2	8	5	2
		1	7	8	12	9	2
		1.5	9	12	15	12	2
		2	50	53	47	50	2
	Revode290	0.5	7	8	3	6	2
		1	8	11	5	8	2
		1.5	5	11	11	9	3
		2	25	29	30	28	2
12	Revode101	0.5	6	6	12	8	3
		1	7	5	12	8	3
		1.5	16	21	20	19	2
		2	91	96	92	93	2
	Revode190	0.5	1	6	2	3	2
		1	6	9	3	6	2
		1.5	5	10	6	7	2
		2	75	70	68	71	3
	Revode210	0.5	2	8	2	4	3
		1	6	10	5	7	2
		1.5	9	10	14	11	2
		2	88	94	88	90	3
	Revode290	0.5	4	5	9	6	2
		1	8	3	4	5	2
		1.5	5	2	8	5	2
		2	64	59	63	62	2

Ave is average value; σ is standard deviation.

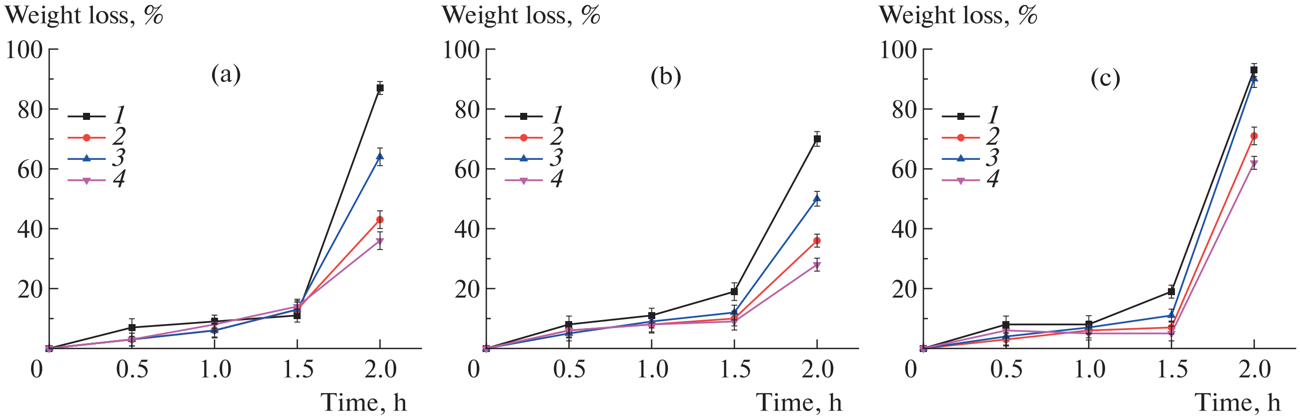

Fig. 9. Weight loss *vs.* time for the four types of PLA by hydro-thermal degradation: (*1*) Revode101, (*2*) Revode190, (*3*) Revode210, (*4*) Revode290 at 170°C in different media: (a) hydrochloric acid solution (pH 1), (b) distilled water (pH 7), (c) sodium hydroxide solution (pH 12).

CONCLUSIONS

A new method called hydro-thermal degradation was proposed in this paper for rapidly evaluating the degradation performance in soil of PLA. Four kinds of commercial grade PLA were adopted and their degradation performances were monitored by weight loss (%), IR, SEC, XRD, and SEM. The results showed that the degradation weight loss performance could be evaluated in 2 h at 170°C by the hydro-thermal degradation, with the order of PLA degradation rate being Revode101 > Revode210 > Revode190 > Revode290. We concluded that this new method, hydro-thermal degradation, is a promising way for rapidly evaluating the bio-degradation performance of all PLA. In future research endeavors, priority should be given to the mechanistic analysis of the hydrothermal method, aimed at enhancing the decomposition of PLA and the establishment of a robust mathematical model. These efforts will better inform the industrial lifecycle of biomass materials.

FUNDING

This work was supported by the Key Special Projects of the Ministry of Science and Technology in China (SQ2020YFF0409402).

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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