Research Article

Dan Huang, Zhi-De Hu, Tian-Yuan Liu, Bo Lu, Zhi-Chao Zhen*, Ge-Xia Wang*, and Jun-Hui Ji* Seawater degradation of PLA accelerated by water-soluble PVA

https://doi.org/10.1515/epoly-2020-0071 received September 23, 2020; accepted October 16, 2020

Abstract: In order to promote the degradation of PLA in seawater, a series of seawater-degradable polyester blends PVA/PLA were prepared by blending biodegradable polylactic acid (PLA) with water-soluble modified polyvinyl alcohol (PVA) in this paper. ADR 4370S was introduced to bring a certain degree of improvement in compatibility of PVA/PLA blends. The results of degradation test in natural seawater for 180 days show that the weight loss of PVA/PLA blends in seawater is much higher compared with that of pure PLA. PVA can be used as an effective hydrolysis accelerator for PLA matrix, helping to significantly reduce the molecular weight of PLA. The channels caused by dissolution/swelling of PVA facilitate the entry of water and microorganisms into the materials to contact with PLA, thereby promoting the degradation process of PLA matrix itself. Thus, both dissolution/swelling of PVA and degradation of PLA occur in PVA/PLA blends, and

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the degree of rapid dissolution of PVA in the early stage determines the degree of degradation of PLA.

Keywords: seawater degradation, PVA modification, polylactic acid, solubility, hydrolysis accelerator

1 Introduction

The current marine plastics pollution and its huge negative impacts on marine environment have become heated public issues all over the world (1-8). Today, many countries/regions around the world have successively issued policies to "ban plastic" and "limit plastic." The existing measures focus on reducing, reusing, and recycling plastics aiming to stop the plastic-waste problem on land before they are washed into the oceans. However, the high dependence of mankind on plastic products makes it impossible for us to completely prevent the generation of plastic waste from the source. From a long-term perspective and considering the material itself, the development and application of degradable plastic products in seawater, instead of general refractory plastics, is an effective way to solve the problem of environmental pollution.

Biodegradable materials, especially biodegradable aliphatic polyesters and co-polyesters, are highly anticipated materials in recent years (9), not only because they have excellent thermal, mechanical, and processing properties comparable to those of general plastics, but also because they are susceptible to hydrolysis by water and microorganisms, resulting in a complete microbial enzymatic degradation to produce CO₂ and H₂O when placed in compost or soil for several months (10-13). After decades of development, many types of biodegradable polymers have been synthesized and become commodity products. Biodegradable polyesters have gradually developed into mature products (12). Among them, polylactic acid (PLA) is undoubtedly the most popular and widely used (14), not only because of its excellent tensile strength and modulus, high barrier properties, and transparency, but also because it is a completely green material that can be produced from renewable

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natural resources such as corn, sugarcane, or tapioca starch (15–18). PLA has applications in many fields such as disposable packaging, tableware, and medical treatment and is considered to be one of the most promising bio-based and biodegradable polymers (14).

However, the degradation performance of PLA in seawater is frustrating. Deroiné et al. (19) studied the degradation of dog-bone specimens of PLA $(180 \times 10 \times 4 \text{ mm})$ in the natural seawater in the Lorient harbor, France. It is found that the molecular weight of PLA remained unchanged after 6 months. Bagheri et al. (20) immersed PLA films with an average thickness of 320 ± 20 um in the artificial seawater (AB Reef Salt, Aqua Medic, Germany) at 25°C under fluorescence light (16 h light and 8 h dark) for 1 year and found that the PLA films did not show any significant weight loss under tested conditions. Tsuji and Suzuyoshi (21,22) compared the degradation performance of crystalline and amorphous PLA films (50 µm thickness) in natural seawater and laboratory static seawater at 25°C. The results showed that the molecular weight of PLA films, whether crystalline or amorphous, only slightly declined after being placed in natural seawater and laboratory static seawater for 5 weeks and 10 weeks, respectively. In order to investigate the degradation over a longer time range and the influence of different environmental factors in the water body on the degradation performance of polyester, we studied the degradation performance of PLA in 6 different water bodies, such as static seawater, static river water, distilled water, sterilized seawater and lab-prepared seawater at room temperature, and natural seawater (Bohai Bay, China) in 52 weeks. The results revealed that PLA did not show any significant degradation in any water bodies (23).

PLA, which exhibits excellent degradation performance in controlled industrial composting, shows almost no degradation in the ocean. This can be explained as: on the one hand, PLA has a higher T_{σ} of about 60°C, which is glassy in low-temperature seawater and is not conducive to the entry of water molecules (24); on the other hand, compared to the composting environment (with higher temperature 58-65°C and number of microorganisms more than $10^9 \,\text{CFU}\,\text{mL}^{-1}$) (25), the temperature in seawater is relatively low (with the annual average water temperature on the sea surface about 17.4°C) (26), and the specific microbial species and number are less $(0-10^{6} \text{ CFU mL}^{-1})$ (27), resulting in obvious inhibition of the hydrolysis process. PLA is currently the most popular biodegradable product, and how to improve its degradation rate in seawater is of great significance.

In order to accelerate the degradation of PLA in seawater, Chen et al. (28) immersed tensile bars from

injection molding of starch/PLA blends (12.42 cm length \times 1.18 cm width \times 0.31 cm height, with weight ratio of 61.7/38.3) in the static seawater at 25°C; the results indicated that the rapid degradation and leaving of starch promoted the degradation of PLA to a certain extent, making the number molecular weight $M_{\rm p}$ of PLA decrease from 1.9×10^4 to 1.5×10^4 g mol⁻¹ after 12 months in seawater. Although the starch/PLA blends were degradable in seawater and the degradation rate had been improved, the final overall weight loss after 12 months was only 13%, which was far lower than the mass fraction of starch contained. In addition, the introduction of starch also caused a significant decrease in the mechanical properties of the starch/PLA blends. Guzman-Sielicka (29) prepared two series of starch-PLA-CaCO₃-glycerin and starch-PLA-gelatin-glycerin blends with different proportions. After 4 weeks, all thin sheets (0.5 mm thickness) quickly turned into fragments, with a maximum weight loss up to 73%, but the remaining components were still not completely degraded after 4 months. These results all signify that the introduction of fast biodegradable starch as the second component can promote the degradation of PLA in seawater to a certain extent, but the overall degradation rate is still very slow. And the introduction of fillers also causes the loss of mechanical properties of the material.

Polyvinyl alcohol (PVA) is the only commercial water-soluble and biodegradable polymer material currently. Compared with other synthetic water-soluble polymers, PVA not only has excellent mechanical properties, but also can be biodegraded by some microorganisms (e.g., members of the genera Pseudomonas, Sphingomonas, and Sphingopyxis) under both aerobic and anaerobic conditions (30). These microorganisms capable of degrading PVA are mainly distributed in specific environments such as wastewater, especially PVAcontaining wastewater discharged from textile and paper mills, but are less distributed in seawater, of which the number is lower compared to those that can degrade aliphatic polyesters (30-34). Nevertheless, it has to be admitted that there are indeed microorganisms with the ability to degrade PVA in seawater and there is still a chance of PVA degradation in the marine environment. For example, Nogi et al. (35) searched for PVA-degrading microorganisms and isolated a new strains of genus Thalassospira, in seawater, which belongs to rod-shaped bacteria and is widely distributed in the ocean, waste oil ponds, and oil-polluted seawater. Blends containing PVA are potential seawater degradation materials. Novamont in Italy reported the blend of modified starch with modified PVA and claimed that this material can

be completely degraded in seawater within 4-12 months (36). In the preliminary work, we introduced PVA into the biodegradable PCL matrix and conducted a 3-month natural seawater degradation performance test on the PVA/PCL blends (37). It was found that PVA could be used as an effective hydrolysis accelerator for the PCL matrix, and the channels left by the rapid dissolution of PVA helped water and microorganisms to enter and contact with PCL, thereby promoting the biodegradation process of the PCL matrix itself. The PVA/PCL blends in seawater showed a higher weight loss than pure PCL. Through the adjustment of the degree of alcoholysis. the degree of polymerization, and the ratio of PVA, the overall seawater degradation performance of the PVA/PCL blends could be effectively controlled. Inspired by this, the introduction of water-soluble PVA into a PLA matrix may help to accelerate the degradation of PLA in seawater.

In this paper, blends were prepared by using biodegradable polyester PLA as the resin matrix and introducing modified PVA0588 and 1788 with excellent water solubility as degradation accelerators with adding of a certain amount of compatibilizer to improve the compatibility of the two polymers. Through the analysis of morphology, weight loss, molecular weight change, and ¹H NMR spectroscopy, the degradation performance of the material in seawater for 180 days is characterized. We hope that water-soluble PVA can be used as an effective hydrolysis accelerator for the PLA matrix and improve the degradation performance of PLA in seawater, which make PLA completely sustainable, with both green "birth" and green "death" fate.

2 Materials and methods

2.1 Materials

PLA (grade 4032D) pellets were obtained from Nature works. PVA0588 and PVA1788 were purchased from Sinopec Sichuan Vinylon Works. The two PVAs have the same degree of alcoholysis of 88% and different degrees of polymerization (500, 1,700), and the molecular weights are 2.2×10^4 g mol⁻¹ and 7.5×10^4 g mol⁻¹, respectively. 1,4-Butanediol and food-grade sorbitol were purchased from Xilong Scientific Co. and Roquette China Co., Ltd, respectively. Blend compatibilizer ADR 4370S was purchased from BASF.

2.2 Modification of PVA

PVA, 1,4-butanediol, and sorbitol (10 wt%) were added to the mixer in order and stirred until they were well-mixed. The premix was sealed and plasticized in an oven at 50°C for 3 h, and then the modified PVA was obtained by melt extrusion. According to the melting characteristics of PVA, the extrusion temperatures of PVA0588 and PVA1788 are selected as 180°C and 200°C, respectively.

2.3 Preparation of sample specimens

The modified PVA, PLA, and 0.5 wt% ADR 4370S were well-mixed and then melt-extruded to obtain a polyester mixture with a PVA:PLA mass ratio of 30:70 or 50:50. Then, the modified PVA (0588 and 1788), PLA, and PVA/PLA blends (with or without compatibilizer) were processed into standard tensile test specimens (effective length $G_0 = 25 \pm 1$ mm, width $b = 4.0 \pm 0.4$ mm, and thickness $d = 2.0 \pm 0.2$ mm) on an injection molding machine. The injection temperature and mold temperature are selected as 200°C and 50°C for modified PVA0588, respectively, and 220°C and 50–70°C for other samples, respectively. All samples are injected at a pressure of about 700 bar. The weight of each specimen which was within 1.5–2.0 g was tested and recorded before degradation.

2.4 Water conditions

The natural seawater degradation experiment was carried out in the Bohai Bay, China (38°40′20″N, 117°38′41″E). The characteristic parameters of natural seawater from October 2018 to April 2019 are summarized in Table 1, which have a certain fluctuation caused by seasonal changes. Among them, the seawater temperature shows the most obvious fluctuation between -1.7° C and 18.5°C. The pH and salinity do not change significantly, with average values of 8.17‰ and 28.6‰, respectively. The monthly average values of CFU fluctuate between 10 and 10³, which is much lower than the value in compost (>10⁹ CFU mL⁻¹) (25).

2.5 Degradation experiment

The specimens of PVA, PLA, and PVA/PLA blends (30:70 and 50:50, w/w) were marked, weighed, and placed in the Bohai Bay at a depth of 150 cm. Three samples of each type were regularly taken out from the seawater and then cleaned with ultrasonic cleaning technology to remove

Date of sampling	Temperature ^a (°C)	рН ^ь	Salinity ^b (‰)	Microbial counting ^b (CFU mL^{-1})	
				PCA ^c	PDA ^d
24.10.2018	15.3-18.5	8.37	27.2	392	0
30.10.2018	13.5-17.0	8.13	28.5	610	0
06.11.2018	11.1–15.6	8.14	29.5	2600	10
15.11.2018	9.5-14.6	8.05	28.5	532	0
23.11.2018	9.2-14.5	8.08	28.5	188	1
08.12.2018	4.0-10.0	8.11	28.6	448	0
23.12.2018	_	8.27	27.9	_	_
22.01.2019	-1.0 to 6.5	8.44	29.0	33	0
21.02.2019	-1.7 to 3.9	7.94	29.6	40	0
22.04.2019	6.2-12.4	8.12	28.8	49	0

Table 1: Parameters of seawater in the Bohai Bay, China

^a Data obtained from the National Marine Environmental Forecasting Center. ^b Data obtained by measurements. ^c"PCA" refers to "Plate Count Agar" that is a kind of culture medium specifically for bacteria. ^d"PDA" refers to "Potato Dextrose Agar", which is a kind of culture medium specifically for fungi.

biofilms. After being rinsed with distilled water, they were dried in a vacuum oven at 50°C for 48 h for further study.

2.6 Property testing

- The salinity of seawater samples was measured with a handheld salinity meter from HengXing (model AZ8371; Taiwan), taking the average of three measurements.
- 2. The pH of seawater samples was monitored with a Mettler pH meter, taking the average of three measurements.
- 3. The number of microorganisms in seawater was determined via a plate count method. During the experiment, 1 mL of sampled seawater was drawn for gradient dilution, and then 20 mL plate count agar or potato dextrose agar were poured, respectively, and finally incubated at 37°C for 72 h to count the viable bacteria.
- 4. The weight changes of the samples before and after degradation were studied by a weight loss test and averaged over three specimens.
- 5. The water absorption rate (ε) of PVA1788 was obtained by separately weighing the mass of PVA1788 taken from natural seawater before and after drying, and then calculating according to the following Eq. 1, taking the average of the three specimens.

$$\varepsilon = \frac{W_{\rm w} - W_{\rm d}}{W_{\rm d}} \times 100 \tag{1}$$

where W_w and W_d denote the wet and dry weight of PVA1788 specimens, respectively.

- 6. The partial morphological changes (surface and interior) were observed with a JCM-6000 (JEOL) scanning electron microscope (SEM) by applying a rapid freeze-fracture method to form the cross-section.
- The tensile strength and elongation at break of samples were monitored by a WDW-10 microcomputer-controlled electronic universal material testing machine and averaged over three specimens. Dumbbell-shaped samples were stretched at a stretching rate of 50 mm min⁻¹ at 25°C.
- 8. Molecular weight and distribution of each sample were analyzed with a Waters 1515 gel permeation chromatography (GPC) system at different sites for each of the three specimens. $CHCl_3$ was used as the mobile phase, and its flow rate is 1 mL min^{-1} .
- 9. In order to analyze the overall structure of samples, the ¹H NMR spectra were recorded on a Bruker AMX-300 apparatus, using DMSO-d₆ as the solvent. Chemical shifts were given in parts per million referenced to tetramethylsilane.

3 Results and discussions

3.1 Water solubility of modified PVA in natural seawater

PVA contains many hydrophilic hydroxyl groups, and the intermolecular and intramolecular hydroxyl groups are

easy to associate and form strong hydrogen bonds. This not only makes the melting temperature and decomposition temperature even close and lead to thermal decomposition during melt during processing (38,39), but also gives obvious obstacles to the water solubility of PVA (40). Considering that plasticizers such as polyols can form hydrogen bond complexes with PVA, thereby inhibiting the crystallization of PVA, increasing melt fluidity, and improving the thermoplastic processing performance of PVA, we used food-grade sorbitol and 1,4-butanediol as plasticizers to modify PVA (37). Modification effect is investigated through the characterization of thermal and mechanical properties and water solubility. As shown in Table 2, comparing the properties of PVA before and after modification, it can be found that both melting temperatures (T_m) are significantly reduced (37). Between them, the tensile strength of PVA0588 decreases but the elongation at break increases, and water solubility is further improved. In addition, contrary to PVA1788 before modification, modified PVA1788 can be melt-processed into standard tensile test specimens and still has excellent mechanical properties and good water solubility. The above results have proved that the introduction of plasticizers increases the melt fluidity, thereby successfully improving the thermoplastic processability of PVA, which can be melt-processed while the water solubility is further improved. Therefore, modified PVA0588 and modified PVA1788 with excellent water solubility are selected for further melt blending and extrusion with PLA.

Considering that the water solubility of PVA is highly susceptible to temperature, we investigate the water solubility of modified PVA in natural seawater. It is found that the water solubility of modified PVA0588 and 1788 in natural seawater shows significant differences. The modified PVA0588 with a lower molecular weight has completely dissolved and disappeared in the first sampling after 6 days, while the dissolution process of the modified PVA1788 exhibits two stages. The first is the linear weight loss caused by the early rapid dissolution process of 30–50 wt%, and then the weight loss reaches the plateau caused by the water-absorbing swelling process (corresponding to a high water absorption of 100%), as shown in Figure 1. Therefore, PVA1788, which possesses good water solubility at room temperature, mainly shows water-absorbing swelling and only partially dissolves away in this natural seawater degradation experiment (temperature from -1.7° C to 18.5°C).

3.2 Seawater degradation of PVA/PLA blends

Since the compatibility of two phases in blend systems not only affects the mechanical properties of blends, but also influences its degradation properties (41), we added a small amount of ADR during the melt extrusion process to improve the compatibility of the PVA/PLA blends. As shown in Figure 2, comparing the SEM images of the cross-sections of two PVA/PLA blends before and after adding ADR, it is observed that the blends have different degrees of phase separation. In the system containing



Figure 1: Weight loss and water absorption of modified PVA1788 in natural seawater.

Table	2:	Properties	of P	PVA0588	before	and	after	modification	(37))
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PVA		<i>T</i> _m (°C)	Tensile strength (MPa)	Elongation at break (%)	Water solubility (days)
0588	Before modification	194	95	3	6
	After modification	177	33	217	4
1788	Before modification	190	_	_	_
	After modification	163	63	89	8

 $T_{\rm m}$ is the melting temperature; water solubility is measured by the time required for PVA to completely dissolve in distilled water at room temperature; '--' indicates that unmodified PVA cannot be processed into standard tensile test specimens for poor melt fluidity.

PVA0588, when the PVA content is 50 wt%, it shows better compatibility compared with the content of 30 wt%. However, the compatibility in the system containing 50 wt% PVA1788 is worse, compared with the content of 30 wt%. On the one hand, PVA may form hydrogen bonds with the oxygen atoms of the ester groups, and partial miscibility can be achieved between PVA and PLA (42,43); on the other hand, during melt processing at the same temperature, PVA0588 has the same melt viscosity as PLA, making it easier to mix the two phases evenly. After adding 0.5 wt% ADR 4370S, the micro voids produced by phase separation become less and slightly smaller in size. Especially in the PVA1788/PLA = 50/50 system (4a, 4b), the massive agglomeration of PVA has almost disappeared.

Tensile test is performed on the PVA/PLA blend specimens, and the measured mechanical properties are shown in Table 3. The tensile strength and elongation



Figure 2: SEM images of the cross-section of PVA/PLA blend specimens: (1) PVA0588/PLA = 30/70, (2) PVA0588/PLA = 50/50, (3) PVA1788/PLA = 30/70, (4) PVA1788/PLA = 50/50, (1a-4a) the cross-section of the sample without compatibilizer, (1b-4b) the cross-section of the sample with compatibilizer.

at break of modified PVA0588 are 31.7 MPa and 314.4%, respectively, and those of PVA1788 are 37.9 MPa and 181.3%, respectively. Compared with the corresponding values in literature (37), the tensile strength of this modified PVA is lower, but the elongation at break increases significantly, which is related to the degree of plasticization. After adding PVA0588 with better toughness, compared to pure PLA (tensile strength 76.5 MPa, elongation at break 9.1%), the blends sacrifice part of the strength while significantly improving the toughness, especially the elongation at break of the system containing 50 wt% PVA0588 increases to 111.9%, which is consistent with the compatibility results of the previous SEM analysis. On the contrary, in the system containing PVA1788, when the PVA content is 50 wt%, the tensile strength and elongation at break are significantly reduced. After adding 0.5 wt% of ADR 4370S, the mechanical properties of the blends are improved to varying degrees. The tensile strength of blends with a PVA content of 30 wt% does not increase significantly, but the toughness increases. When the PVA content is 50 wt%, the tensile strength and elongation at break of blends are significantly improved. In summary, after adding 0.5 wt% ADR 4370S to the PVA/PLA blends, the compatibility has been improved to a certain extent, and the PVA/PLA blends obtain a more uniform structure.

3.2.1 Morphology

The morphology of PLA and PVA/PLA blends after degradation in natural seawater for 180 days is shown in Figure 3a. There is no significant change in pure PLA. However, the PVA/PLA blend specimens become brittle and easily crushed, resulting in a complete loss of mechanical properties, and significantly changed morphology is also observed. Because PVA0588 is very easy to dissolve, white spots left after dissolution appear on the surface



Figure 3: (a) Surface morphology after degradation. The letters A, B, and C represent PLA, PVA0588/PLA, and PVA1788/PLA, respectively; The numbers 1 and 2 represent the mass ratios of PVA/PLA: 30/70and 50/50, respectively. (b) Side view of PVA0588/PLA = 50/50specimens (B2).

of the blend specimens containing PVA0588, and a large area of dissolution/degradation gap appears on the side (see Figure 3b), resulting in a large degree of internal hollowness. Because PVA1788 is partially dissolved and swelled in natural seawater, many cracks appear on the surface of the blend specimens containing PVA1788, and the overall specimens show a certain degree of bending deformation. With the increase of PVA content, these changes become more obvious.

Scanning electron microscopy was used to observe the surfaces and cross-sections of the specimens before and after degradation, as shown in Figure 4. It is found

Table 3: Mechanical	properties of PLA and PVA	A/PLA blends before degradation
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Sample	Tensile strength ^a (MPa)	Elongation at break ^a (%)	Tensile strength ^b (MPa)	Elongation at break ^b (%)
PLA	76.5 ± 2.3	9.1 ± 3.0	_	_
PVA0588/PLA = 30/70	31.9 ± 3.3	61.1 ± 28.4	31.3 ± 7.6	173.3 ± 19.0
PVA0588/PLA = 50/50	24.4 ± 2.5	111.9 ± 42.9	30.6 ± 0.4	277.9 ± 4.6
PVA1788/PLA = 30/70	38.2 ± 1.6	4.2 ± 0.6	39.2 ± 3.6	8.3 ± 0.6
PVA1788/PLA = 50/50	15.6 ± 1.5	3.7 ± 1.8	24.8 ± 4.2	9.0 ± 2.7
Modified PVA0588	31.7 ± 1.6	314.4 ± 24.7	_	_
Modified PVA1788	37.9 ± 1.1	181.3 ± 20.7	_	_

^aBefore adding ADR 4370S. ^bAfter adding ADR 4370S.



Figure 4: SEM images of PLA and PVA/PLA specimens after immersion in natural seawater for 180 days: (1) PLA, (2) PVA0588/PLA = 30/70, (3) PVA0588/PLA = 50/50, (4) PVA1788/PLA = 30/70, (5) PVA1788/PLA = 50/50, (1a–5a) surfaces of the specimens before degradation, (1b–5b) surfaces of the specimens after degradation, (1c–5c) cross-sections of the specimens before degradation, (1d–2d, 4d–5d) cross-sections of the specimens after degradation, and (3d) internal surface of the specimens.

that after 180 days in natural seawater, no obvious changes are observed on the surface and cross-section of pure PLA after degradation (1b and 1d), which is consistent with the report in literature (19). The specimen of PVA0588/PLA = 30/70 exhibits holes and cracks (2b and 2d) caused by the dissolution of PVA0588 on the surface and inside. As the content of water-soluble PVA0588 increases, when the content of PVA0588 is 50 wt%, the hole density on the surface becomes denser (3b), and dense holes are also observed on the internal surface of the specimen, which means the holes left by PVA dissolving extend from the surface to the inside. It is precisely because of the existence of holes extending from the outside to the inside that countless channels leading to the interior of specimens are formed. These channels promote the entry of water and microorganisms, thereby causing the dissolution or/and degradation of the interior of specimens.

Compared with the systems containing easily watersoluble PVA0588, different micro-morphological changes are observed in PVA1788/PLA blends after being placed in natural seawater for 180 days. A few holes (4b) caused by the dissolution of PVA appear on the surface of PVA1788/PLA = 30/70; however, obvious cracks appear on the surface and inside of the specimen, due to the swelling of PVA1788 in the hard matrix of PLA. With the increase of PVA1788 content to 50 wt%, the cracks and holes on the surface widen and deepen, as well as deep and large holes appear inside, which is consistent with the observation results of the macro morphology in Figure 3. It is not difficult to imagine that the holes and cracks generated by the dissolution or water-absorbing swelling of PVA0588 or PVA1788 will help water and microorganisms entering inside to contact PLA, thereby promoting the degradation process of the PLA matrix itself.

3.2.2 Weight loss

As shown in Figure 5, the weight loss of pure PLA specimens is not significant after being immersed in natural seawater for 180 days, which is consistent with literature (44). When water-soluble PVA is introduced, the weight loss increases significantly, and with the increase of PVA content, the rate of weight loss increases, which is consistent with the results of morphological changes analysis. When the PVA content is 30 wt%, the total weight loss does not exceed 10%, which may be because water molecules cannot penetrate deeply, owing to the continuous PLA phase acted as a barrier to prevent dissolution of PVA. When the PVA content reaches 50 wt%, the weight loss curves of blends corresponding to PVA0588 or PVA1788 in natural seawater exhibit a linear upward



Figure 5: The percentage of weight loss of PLA and PVA/PLA blends in natural seawater over time.

trend in the first 6 days, and then tend to rise gently. Between them, for the system containing the better water-soluble PVA0588, the weight loss rate is faster, and the weight loss quickly reaches 39.7% on the 6th day and finally reaches the highest weight loss percentage of 45.4% after 180 days. Similarly, for the system containing PVA1788, the weight loss quickly reaches 25.6% on the 6th day and finally reaches 33.5% after 180 days. In summary, it can be inferred that the weight loss process of the PVA/PLA = 50/50 systems in natural seawater exhibits two stages: the first stage is the linear weight loss caused by the rapid dissolution process of modified PVA; the second stage is the slow weight loss caused by the degradation process of PLA. This seems to reflect that the water-soluble PVA has a certain promotion effect on the weight loss of PLA degradation in natural seawater, and this promotion effect may become more obvious over time.

3.2.3 Molecular weight change

In order to verify the effect of the holes and cracks left by the dissolution/swelling of PVA in blends on promoting the seawater degradation of PLA, we study the molecular weight changes of PLA in blends after degradation. PLA was extracted from the blends by using chloroform, and GPC tests were performed on the PLA in chloroform at 40°C. As shown in Figure 6, pure PLA before degradation shows an unideal single peak. Pure PLA after degradation slightly shifts to a lower molecular weight relative to before degradation, which signifies that the PLA specimens undergo bulk degradation in seawater to a certain extent. The unimodal peaks of PLA in blends shift to a



Figure 6: GPC curves of pure PLA before degradation, pure PLA and PLA in blends after natural seawater degradation for 180 days.

lower molecular weight more obviously, with PVA0588/ PLA = 50/50 shifting most obviously, which means that the degradation degree of PLA in blends is higher than that of pure PLA.

In order to compare with the degradation degree of PLA in blends, the peaks of pure PLA can be approximately treated as a unimodal peak to obtain the average molar mass and PI value for further analysis. As shown in Table 4, $M_{\rm n}$, $M_{\rm w}$, and PI values obtained from the GPC tests are summarized. The initial M_n and PI of pure PLA are $6.6 \times 10^4 \,\mathrm{g \, mol^{-1}}$ and 2.2, respectively. After being immersed in natural seawater for 180 days, the molecular weight of pure PLA decreases slightly (from 6.6×10^4 to $4.8 \times 10^4 \,\mathrm{g}\,\mathrm{mol}^{-1}$), while the molecular weight distribution increases slightly (from 2.2 to 2.5). The molecular weight of PLA in blends is significantly reduced to different degrees compared with the initial value, and the systems with higher PVA content have a more obvious downward trend. Among them, the M_n of PLA in PVA0588/PLA = 50/50 decreases by 70%, from 6.6×10^4 to 2.0×10^4 g mol⁻¹. It is noteworthy that the molecular weight distribution of PLA in blends decreases significantly. This may be because the holes and cracks caused by the dissolution or swelling of PVA act as channels for water molecules and microorganisms, while promoting the degradation of the PLA phase, and the small molecules and oligomers produced during the degradation process can easily diffuse out without autocatalytic effect, thereby reducing the molecular weight distribution. The above results show that blending water-soluble PVA with PLA to achieve water solubility is indeed effective in promoting the degradation of PLA in seawater. In this way, compared with pure PLA, PLA in the blends exhibits a

Table 4: Changes in the molecular weight and distribution of purePLA and PLA in blends after degradation in natural seawater for180 days

Sample	$M_{\rm n} imes 10^{-4}$ (g mol ⁻¹)	$M_{n} imes 10^{-4}$ (g mol ⁻¹)	PI	M _n / M _{n0} (%)
Pure PLA ^a	6.6	14.7	2.2	100
Pure PLA ^b	4.8	12.0	2.5	72.7
PLA-1	2.8	4.2	1.5	42.4
PLA-2	2.0	3.3	1.6	30.3
PLA-3	3.6	5.6	1.6	54.5
PLA-4	2.7	4.1	1.5	40.9

^a Before degradation. ^bAfter degradation; PLA-1 to PLA-4, respectively, represent PLA in the blend of PVA0588/PLA = 30/70, PVA0588/PLA = 50/50, PVA1788/PLA = 30/70, PVA1788/PLA = 50/50 after degradation.

faster weight loss in natural seawater, which is consistent with the previous results inferred from weight loss.

3.2.4 ¹H NMR

By analyzing the chemical compositions and relative proportions of the blends before and after degradation, we can further obtain the relative degree of the two processes of PVA dissolution and PLA degradation in the blend systems. A small amount of the blends before and after degradation were dissolved in deuterated DMSO and characterized by ¹H NMR. The ¹H NMR spectra of the blends are compared with those of pure PLA and modified PVA. As shown in Figure 7, the ¹H NMR spectra of the blends before degradation correspond to the characteristic peaks of pure PLA and modified PVA. It is worth noting that two obvious quartets (5.42-5.47 and 5.18-5.23 ppm), both of which attributed to the -CH of PLA, are actually detected in the blends, especially in the systems containing PVA0588 with better compatibility. This may be because the oxygen atoms on some of the ester bonds in PLA form intermolecular hydrogen bonds with the hydroxyl groups of PVA, which to a less extent causes the deshielding of the $\beta_{\rm H}$ resonance and makes the proton peak of -CH shift to the low field, from 5.18-5.23 to 5.42-5.47 ppm. After being immersed in seawater for a long time, the peaks corresponding to the plasticizers (g, f) in the ¹H NMR spectra of the blends and the quartet (a, 5.42-5.47 ppm) of -CH in PLA disappear. Although the ¹H NMR spectra of the blends after degradation contain both the characteristic peaks of PLA and PVA, it can be clearly observed that the relative peak intensity between the characteristic peaks of PLA and PVA changes to a certain extent. Furthermore, we integrated the -CH characteristic peaks of PLA and -OH characteristic peaks of PVA and calculated according to Eq. 2 to obtain the relative mass fractions of PVA (w_{PVA}) before and after degradation, which are summarized in Table 5.

$$w_{\rm PVA} = \frac{44 \times I_{\rm e}}{44 \times I_{\rm e} + 72 \times I_{\rm a}} \tag{2}$$

The relative mass fractions of PVA in PVA0588/PLA = 30/70 and PVA1788/PLA = 50/50 decrease significantly, which means that the departure caused by the dissolution of PVA is mainly responsible for the degradation process of the blends in natural seawater. In the PVA0588/PLA = 50/50 system, most of the middle is dissolved and left, and the w_{PVA} in the internal or out skin of remaining part (from 51.34% to 41.72% and 38.96%,



Figure 7: ¹H NMR spectra of PLA, modified PVA, and PVA/PLA blends before and after natural seawater degradation for 180 days: (a) modified PVA0588; (b) modified PVA1788, * represents the solvent DMSO absorption peak, letter h is the absorption peak of acetone, and other letters represent the characteristic peaks of different groups in the sample, respectively.

respectively) is lower than other systems, which indicates that while the PVA is dissolved and left, the degradation of PLA is also proceeding to a large extent, in accordance with the GPC results. In the PVA1788/PLA = 30/70

system, w_{PVA} only slightly increases, which is because PVA1788 is wrapped by PLA and hardly dissolved, but it swells due to water absorption. The cracks caused by swelling promote the degradation of PLA to a certain

Sample	Before degradation w _{PVA} (%)	After degradation w _{PVA} (%)
PVA0588/PLA = 30/70	44.97	16.92
$PVA0588/PLA = 50/50^{a}$	51.34	41.72
$PVA0588/PLA = 50/50^{b}$	51.34	38.96
PVA1788/PLA = 30/70	38.98	40.67
PVA1788/PLA = 50/50	52.05	25.46

Table 5: Changes in the relative mass fractions of PVA in the blends before and after degradation in natural seawater

^aInternal. ^bOuter skin.

extent, but the molecular weight of PLA only drops to 3.6×10^4 g mol⁻¹, which is still not easy to further degrade and leave. Combining the previous results of weight loss and molecular weight, it can be concluded that the degree of PVA dissolution in the early stage of the blends in natural seawater determines the degree of PLA degradation in the later stage. In the blends mainly undergoing the dissolution of PVA in natural seawater, PLA is distinctly degraded, corresponding to a significant decrease in molecular weight.

4 Conclusions

In order to promote the degradation of PLA in seawater, we introduced the water-soluble PVA as a degradation accelerator into the hard-to-hydrolyze PLA matrix, and an appropriate amount of compatibilizer was added to improve the compatibility of the two polymers. PLA/PVA blends were prepared by simple melt blending and a 180-day seawater degradation performance test was conducted in natural seawater. The results of weight loss and molecular weight changes demonstrate that the weight loss rate of PVA/PLA blends in natural seawater is significantly increased, and the degradation rate of the PLA phase is also obviously improved compared with pure PLA. The weight loss process of PVA/PLA blends in natural seawater includes two processes: the dissolution/swelling of PVA and the degradation of PLA. The degree of rapid dissolution of PVA in the early stage determines the degree of slow degradation of PLA, and the above two processes complement and promote each other. As observed in SEM, the holes left by the dissolution or the cracks caused by swelling of water-soluble PVA promote the entry of water and microorganisms, thereby promoting the degradation of PLA, and when the PVA content increases, the promotion effect is more obvious. It is worth noting that in the current time scale, the weight loss percentages of PVA/PLA blends have not been observed to exceed the initial percentages of PVA, and the compatibility of the PVA/PLA systems needs to be further improved, which not only affects the mechanical properties but also the degradation performance. Longer experimental time and further improvement of compatibility as well as making a profound study for the biodegradability of PVA in seawater may be required in the following research.

Acknowledgments: The authors would like to thank the National Natural Science Foundation of China (Project No. 51973228) and Youth Innovation Promotion Association, CAS (2018033) for financial support.

The author also thanks Shujun Zhao for his help in experimental sampling.

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