Photo-Aging of Biodegradable Polylactic Acid Microplastics

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Abstract. Microplastic (MPs) pollution has became a serious issue. Photoaging is one of the main ways to produce MPs. Polylactic acid (PLA) is the most commonly used biodegradable plastic in industry, however, the current reports on the quantitative data of biodegradable PLA MPs produced by photoaging were little known. Therefore, this study selected PLA MPs as representative MPs to explore photoaging of biodegradable MPs. The results showed that PLA MPs were broken by photoaging, resulting in an increase in the total particle numbers and a decrease in average particle size. The numbers of particle in PLA MPs increased from 4.39×10^6 particles/L to 6.74×10^6 particles/L, and the average particle size decreased from 22 μm to 17 μm. C=O and C-O on PLA MPs surface were broken, which further confirmed that PLA MPs were degraded and broken after photoaging. This work is helpful to better understand the impact of light on the aging of biodegradable MPs and to assess the environmental risk of biodegradable MPs.

1 Introduction

Plastic pollution has became a global environmental pollution problem alongside ocean acidification, global warming and ozone depletion[1]. The annual output of plastic in the world reached 400 million tons in 2022[2]. Most plastic products have a short service life and lack a proper recycling and disposal mechanism, they are easy to enter into natural water bodies such as rivers, lakes and oceans. Plastics in the environment can be degraded into microplastics (MPs) with a particle size smaller than 5 mm under long-term physical wear, chemical degradation and biodegradation[3]. MPs exist widely in the atmosphere, water and soil[4,5], and they can be transported over long distances under the action of wind and ocean currents, thus spreading all over the world[6]. In order to minimize the damage to the environment caused by traditional non-biodegradable plastics, biodegradable plastics have been widely used in recent years and their production has increased year by year. It was estimated that the output of biodegradable plastics will reach 2.4 million tons in 2025[7]. Polylactic acid (PLA) is the most commonly used biodegradable plastic in industry. In the next ten years, the output of PLA plastics will increase to 9.5×10^5 tons/year[8]. Biodegradable plastics can only be degraded completely under specific conditions, so they may be more likely to be partially degraded due to the degradability of PLA plastics, resulting in greater environmental risks. Some studies have shown that PLA plastics could produce more MPs than traditional plastics[9]. Photoaging is one of the main ways to produce MPs, but the current reports on the quantitative data of PLA MPs produced by photoaging were missing to a large extent. In this paper, the biodegradable PLA MPs with uneven particle size were selected to qualitatively analyze the PLA MPs produced and quantitatively analyze the PLA MPs in different particle size ranges before and after photoaging. The results of this study can provide more powerful theoretical support for the environmental risk assessment of PLA MPs after photoaging.

2 Materials and Methods

2.1 Materials and Characterization

PLA MPs were purchased from Shanghai Yangli Mechanical and Electrical Technology Co., Ltd., and the morphology of PLA MPs was characterized by scanning electron microscope (SEM, Hitachi, Japan). Ten SEM images were imported into Image J software, and the PLA particles were manually counted and PLA particle size was manually measured, so as to obtain the PLA MPs particle size distribution. The surface functional groups of PLA MPs were characterized by Fourier transform infrared spectroscopy (ATR-FTIR, PerkinElmer, UK) and the zeta potential of PLA MPs suspension was characterized by Malven Zetasizer Nano-ZS (Malven, UK). The pH of PLA MPs suspension was measured by pH meter (ThermoFisher, USA).

2.2 Preparation of Aged PLA

The PLA MPs were prepared into 25 mg/L suspensions with deionized water. Then, these photolysis tubes which contained MPs suspension (25 mg/L, 50 mL) were transferred to a photoreaction apparatus (Shanghai Bilang, China) for photoaging experiment to simulate the aging behavior of PLA MPs in natural environment. The MPs were aged continuously for 55 h under simulated sunlight (1000W xenon lamp).

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2.3 Characterization of the Particle Numbers and Size of PLA MPs

The PLA MPs before and after photoaging were subjected to ultrasonic 10 min in water bath, and the particle numbers and particle size of PLA MPs were determined by Coulter particle counter (BeckmanCounter, USA). The special quality control product of the particle counter (2 μm, BeckmanCounter, USA) was used to correct the instrument parameters and accuracy firstly, the particle counter selected a 70 μm small hole tube for sample determination according to the particle size range of PLA. The volume mode was used to analyze and detect the particle concentration of PLA MPs and the electrolyte volume and analytical volume were 30 mL and 500 μL respectively. The background particle concentration in the electrolyte (0.9% NaCl injection) was determined. If the numbers of particle detected were less than 50, the 1 mL sample could be added to the 30 mL electrolyte, and then the particle numbers and particle size of PLA MPs could be determined, and the particle size distribution of PLA could be obtained at the same time. The PLA MPs were divided into several particle size ranges, and the numbers of PLA particle in each particle size range were obtained.

2.4 Characterization of Functional Groups on the PLA MPs Surface

The PLA MPs after photoaging were transferred to the ultrafiltration centrifuge tube (50 mL, 100 KD) to separate MPs. The centrifugation procedure was set as follows: rotational speed was 5000 rpm and the time was 5 min. The PLA MPs particles on the filter membrane were collected and the surface functional groups of PLA MPs were characterized by ATR-FTIR spectrometry.

2.5 Statistical Analysis

Particle number, particle size, zeta potential and pH were repeated three times, and the results were expressed as mean and standard deviation. SPSS 26.0 software was used for independent sample T-test, when p value < 0.05, it was significant.

3 Results and Discussions

3.1 Characterization of Particle Size of PLA MPs

The SEM image (Fig. 1A and Fig. 1B) showed that PLA MPs were irregular shape and the particle size was uneven. The PLA MPs particle size distribution obtained by Image J showed that the PLA MPs particle size distribution was wide, most of the particles were concentrated in the range of 5-30 μm, and the proportion of 10 μm particles was the highest (Fig. 1C). The quantitative data of PLA MPs by particle counter also showed that the particle concentration of 10 μm was the highest, and the particle size distribution of PLA MPs was basically the same as that obtained by Image J (Fig. 1D), indicating that the particle counter could be used to quantify PLA MPs accurately and the particle size distribution of PLA MPs could be obtained at the same time.

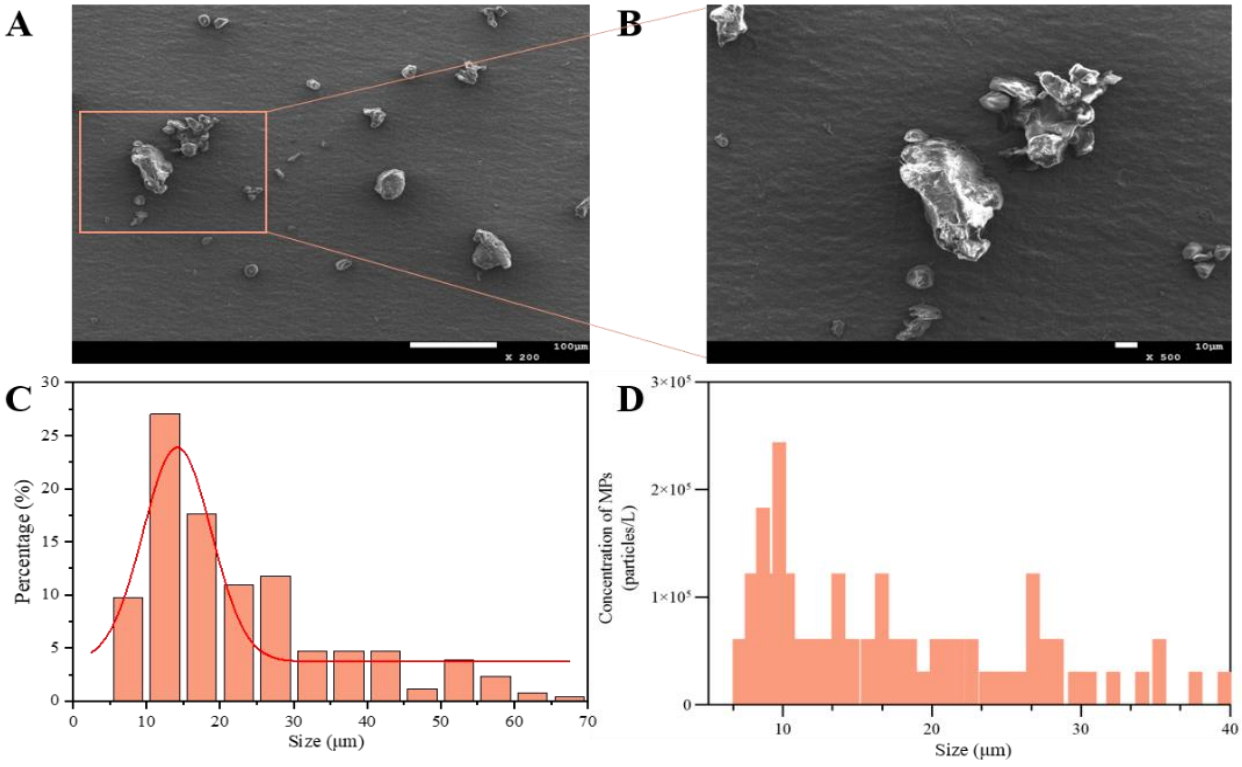

Fig. 1. Characterization of particle size of PLA MPs. (A) PLA MPs SEM image in deionized water; (B) Orange region magnification of SEM image; (C) Particle size distribution of PLA MPs obtained from SEM image; (D) Particle size distribution of PLA MPs in deionized water obtained by particle counter.

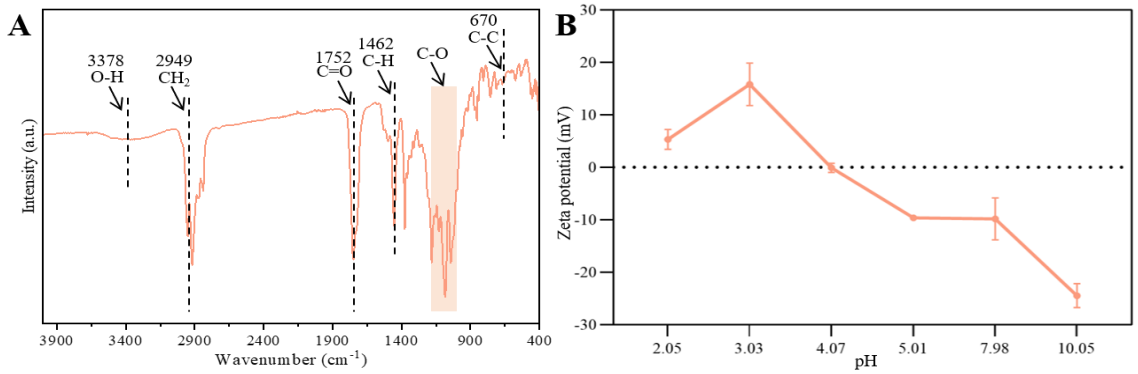

Fig. 2. Characterization of surface chemical properties of PLA MPs. (A) ATR-FTIR spectrum of PLA MPs; (B) Isoelectric point of PLA MPs in deionized water.

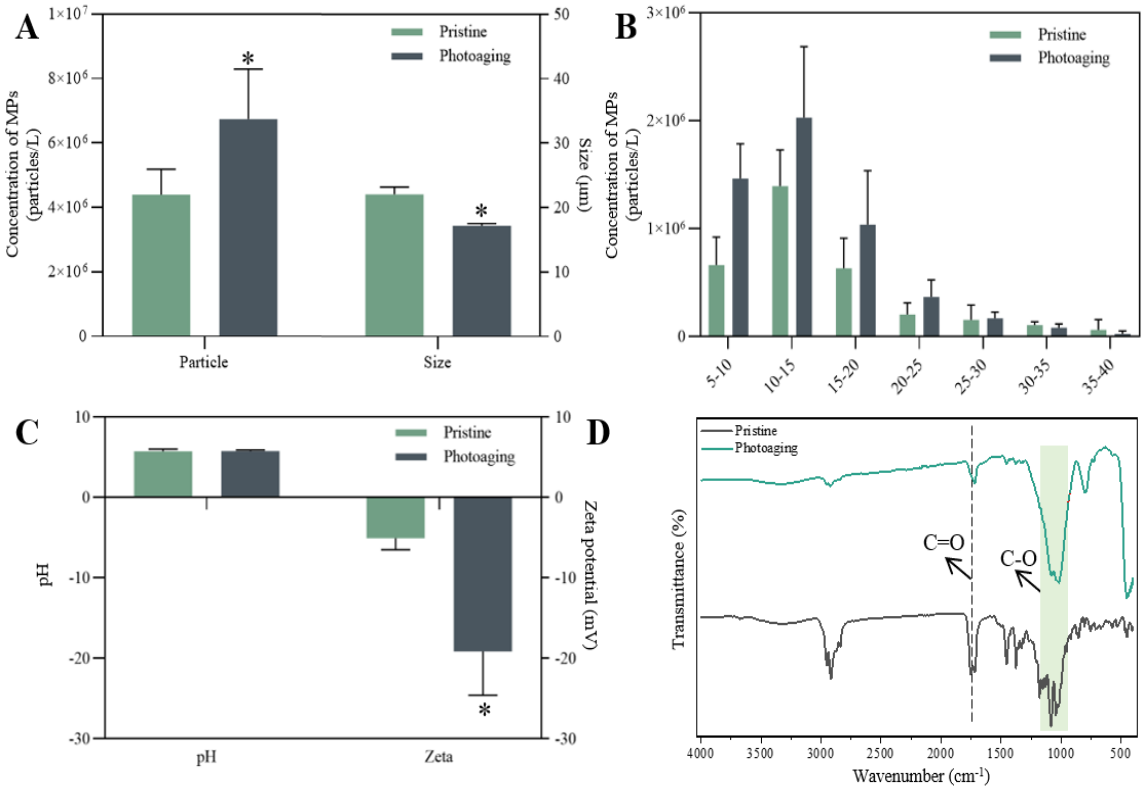

Fig. 3. The aging effect of light on PLA MPs. (A) The change of the particle numbers and size of PLA MPs before and after photoaging; (B) The size distribution of PLA MPs before and after photoaging; (C) The change of pH and zeta potential of PLA MPs suspension before and after photoaging; (D) The ATR-FTIR spectrum of PLA MPs before and after photoaging.

3.2 Characterization of Surface Chemical Properties of PLA MPs

It could be seen that MPs were typical PLA polymers from the FTIR spectra (Fig. 2A). The peaks at 3378 cm^{-1}, 2949 cm^{-1}, 1752 cm^{-1}, 1462 cm^{-1} and 670 cm^{-1} corresponded to O-H, CH_2, C=O, C-H and C-C of PLA MPs, respectively. In addition, the orange region in the Fig. 2A corresponded to the C-O of PLA MPs. By measuring the zeta potential of PLA MPs suspension under different pH, the results showed that the zeta potential of PLA MPs in deionized water was positive when pH was less than 4, and the zeta potential of PLA MPs in deionized water was negative when pH was greater than 4, so the isoelectric point of PLA MPs in deionized water was about 4.

3.3 Photoaging of PLA MPs

The effect of light on the physical and chemical properties of PLA MPs was shown in Fig. 3. After photoaging, the numbers of particle in PLA MPs increased from 4.39×10^6 particles/L to 6.74×10^6 particles/L, and the average particle size decreased from 22 μm to 17 μm, indicating that photoaging broke PLA MPs, resulting in an increase in the proportion of small particles (Fig. 3A). The particle size distribution of PLA MPs before and after photoaging (Fig. 3B) showed that the numbers of particle in the range of 30-40 μm decreased after photoaging and the numbers of particle in the range of 5-25 μm increased, which further confirmed that the PLA MPs were broken after photoaging, and the particles in the particle size range of 30-40 μm

were broken into a large number of particles in the range of 5-25 μm. After photoaging, the pH of PLA MPs suspension did not change significantly, and the surface electronegativity increased (Fig. 3C). The ATR-FTIR spectra of PLA MPs (Fig. 3D) showed that the peak of C=O on the surface of PLA MPs and the peak of C-O in the green frame disappeared greatly after photoaging, indicating that photoaging caused the breaking of C=O and C-O bonds in PLA MPs, resulting in the degradation of PLA MPs. Therefore, this study showed that PLA MPs were not completely degraded by photoaging, resulting in the production of a large number of smaller MPs, which may bring greater environmental risks than traditional plastic.

4 Conclusion

In this work, biodegradable PLA MPs were selected to explore the aging effect of light on it. The main results are as follows:

(1) The PLA MPs in the size range of 30 μm-40 μm were broken by photoaging and produced a large number of PLA MPs in the size range of 5 μm-25 μm, resulting in an increase in the total numbers of particle and a decrease in average particle size. After photoaging, the surface electronegativity of PLA MPs increased.

(2) PLA MPs were degraded after photoaging, which led to the breaking of C=O and C-O, and the particle size of degraded PLA MPs became smaller, which may bring greater environmental risk.

Acknowledgments

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