Photo-aging of brominated epoxy microplastics in water under simulated solar irradiation†

Xuefeng Hu, Hao Xie, Yujie Li and Chao Wang

Microplastics have become an increasingly concerning pollutant in aquatic environments, and photodegradation is their main degradation pathway in water. Gaining insight into the transformation process of microplastics will enhance our understanding of their behavior and destiny in natural environments. This paper studied the aging process of BER microplastics in aquatic environments under simulated sunlight and investigated the changes in the physical and chemical properties of microplastics and the changes in the leachate. During the photodegradation process, BER-MPs underwent extensive oxidation and reduction in particle size, and the originally smooth surface developed numerous voids, accompanied by yellowing. Introduction of O atoms in the molecular chains increased their hydrophilicity, resulting in the polymer chains breaking away from the plastic particles and dissolving in water. Also, once BER was excited by light, environmentally persistent free radicals are produced on its surface. Moreover, the breaking of C–Br bonds occurred during the photodegradation process of BER-MPs, which suggested that tetrabromobisphenol A would be transformed during the photoaging process of BER even if it was covalently bound to BER.

1 Introduction

Epoxy resin (EP), a thermosetting resin, is known for its excellent processing, mechanical, and physical properties.1 As of 2020, China’s epoxy resin production capacity was 2.216 million tons per year, with an annual output of 1.695 million tons.2 As the use of epoxy resin in electronic appliances, transportation, sporting goods, and other sectors has gradually expanded, the performance requirements for epoxy resins have continued to evolve.3 However, epoxy resins are inherently combustible materials and pose a great fire hazard. To enhance its safety, flame retardants are added to EP, modifying and boosting its flame retardant properties. Among these, brominated flame retardants (BFRs) are the most widely used, owing to their high hazard. To enhance its safety, flame retardants are added to EP, modifying and boosting its flame retardant properties. Among these, brominated flame retardants (BFRs) are the most widely used, owing to their high flame retardant efficiency, low effective dosage, and low cost.4

They remain one of the largest categories of organic flame retardants globally. Despite the ban on some brominated flame retardants (BFRs) by the Stockholm Convention on Persistent Organic Pollutants and various countries due to their high toxicity, many new types of brominated flame retardants (novel BFRs, such as decabromodiphenyl ethane, 1,2-bis(2,4,6-tribromophenoxy) ethane, and so on)5 have been introduced as alternatives. However, due to their low cost and effectiveness, the use of BFRs continues in certain developing countries or underdeveloped countries.6 Tetrabromobisphenol A (TBBPA), accounting for about 60% of the global BFR market, is one of the most widely used BFRs. Annually, an estimated 200 000 tonnes of TBBPA are consumed as an additive in the manufacture of various products.7 TBBPA can interact with plastics by either physical mixing or chemical bonding.8 TBBPA can be chemically bonded to EP to generate brominated epoxy resins, reducing the possibility of TBBPA leaching during use. Fig. S1† illustrates the structural formula for this brominated epoxy resin. In a previous study, we investigated the photoaging behavior of ABS (acrylonitrile-
butadiene–styrene microplastics) formed by the physical mixing of TBBPA and acrylonitrile–butadiene–styrene resin in aqueous solution,\textsuperscript{10} and this experiment will further explore the photoaging behavior of BER-MPs (brominated epoxy resin microplastics) generated after chemical bonding of TBBPA and EP in aqueous solution.

As people’s living standards and economic conditions improve, the rate at which products containing brominated epoxy resin (BER) are upgraded is naturally accelerating.\textsuperscript{11,12} This leads to an increasing number of BER-containing products being discarded in the environment. Since these products contain a significant amount of Brominated Flame Retardants (BFRs), improper disposal can cause serious harm to the ecosystem. Particularly during incineration, a large number of toxic and harmful gases are emitted, which can have a detrimental impact on living organisms. Furthermore, during the production, processing, use, and disposal of BER products, particles of BER with smaller sizes are inevitably produced. Plastics with particles smaller than 5 mm are defined as microplastics (MPs).\textsuperscript{13} and in this context, they are referred to as brominated epoxy microplastics (BER-MPs). Due to the small size, strong adsorption capacity, and high persistence of microplastics (MPs), they are easily ingested by aquatic organisms of different trophic levels, thereby affecting the growth, development, reproductive capacity, and behavioral characteristics of organisms, and even altering the structure and stability of aquatic ecosystems.\textsuperscript{14} Therefore, it is crucial to further investigate the behavior of BER-MPs in the environment.

MPs undergo aging and degradation under the combined effects of environmental conditions such as light, mechanical wear from wind and waves, pyrolysis, hydrolysis and biodegradation.\textsuperscript{15,16} Photodegradation in the aqueous environment is the main process of MP aging, and during this process, microplastics undergo several changes.\textsuperscript{17,18} These changes, in turn, affect the environmental behavior of MPs.\textsuperscript{14} For instance, MPs composed only of carbon and hydrogen atoms, such as PE, PP and PS,\textsuperscript{19} experience branching, crosslinking, and the formation of oxygen-containing functional groups (aldehyde groups, carbonyl groups, etc.) under aerobic conditions due to oxidation and chain breaking. These oxygen-containing functional groups possess unsaturated double bonds, making them more susceptible to photoirradiation. PET and other MPs containing heteroatoms are prone to ester bond breakage through hydrolysis, followed by further photodegradation.\textsuperscript{20} Different additives also contribute to varying photoaging properties. Wu\textsuperscript{21} found that the antioxidant Irgafos 168 present in PP food packaging items like lunch boxes and tea cups greatly hinders the photoaging of PP microplastics in artificial seawater. While there has been a lot of research on the photodegradation of microplastics,\textsuperscript{10,22–24} there is still limited research on BER. To date, most of the research on BER focuses on hydrothermal decomposition,\textsuperscript{25–27} flame retardant properties,\textsuperscript{28,29} and leaching and degradation of BFRs in BER,\textsuperscript{30,31} and there is less research on its photoaging in the water environment.

In this study, BER-MPs were selected as the research object to systematically study the photoaging behavior of BER-MPs in the water environment under simulated sunlight irradiation. The changes in the physical and chemical properties of BER-MPs during aging, such as surface morphology, elemental abundance and functional groups, as well as surface chemical composition, etc., were detected. Additionally, the leachate during photoaging was characterized.

2 Materials and methods

2.1 Materials

The BER-MPs were purchased from Kaimei Chemical Technology Co., Ltd, and the structural formula is shown in Fig. 1 for more information refer to Text S1.† All of the MP samples were washed with ultrapure water and anhydrous ethanol (3 times) to remove surface impurities, then placed in a 60 °C electric thermostatic drying oven to dry, and stored in a ziplock bag before the experiments. CH\textsubscript{3}CH\textsubscript{2}OH was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. DMSO-d\textsubscript{6} was purchased from Shanghai McLean Biochemical Technology Co., Ltd. Ultrapure (MilliQ) water was supplied by Chengdu Haokang Technology Co., Ltd.

2.2 Photoaging of BER-MPs

100 mg of BER-MPs and 50 mL of ultrapure water were added to a quartz tube, and then placed in an XPA-7 photochemical reactor for photoaging studies. The simulated sunlight was provided by a 350 W xenon lamp (light intensity at the sample location is 330.5 ± 0.5 W m\textsuperscript{-2}, measured by using a solar power meter (Sanpometer, China)) in the middle of the photochemical reactor, a rotation speed of 1000 rpm was maintained during the entire photoaging process, and the reactor should be kept rotating throughout the aging process to ensure that the light received by each quartz tube was uniform. The quartz tube was taken out at selected time intervals (0 h (BER-MP0), 500 h (BER-MP1) and 1000 h (BER-MP2)), and a solvent filter was used to pass the reaction solution through a 0.22 μm aqueous filter membrane. Suction filtration was performed to obtain BER-MP particles with different aging degrees and their leaching solution. The obtained BER-MP particles are placed in a freeze-
drying machine for freeze-drying, and then collected in a zip-lock bag for subsequent characterization. The leaching solution was stored in a refrigerator for further characterization. The control group was subjected to dark conditions, and aged MPs were collected and identified by freeze-drying after 500 hours (BER-MP3) and 1000 hours (BER-MP4) of the dark reaction, respectively.

2.3 Characterization of light aged BER-MPs

Scanning electron microscopy (SEM, Zeiss Sigma 300, Zeiss Group, Germany), coupled with energy dispersive spectroscopy (EDS, Inca Energy X-Max20, Oxford instruments, UK), analysis were employed to investigate the surface morphology and element abundance of pristine and aged BER-MPs. Ultraviolet-visible spectroscopy (UV-vis, Shimadzu UV-2600, Japan) was used to analyze the light absorption properties of aged microplastics. Gel permeation chromatography (GPC, Agilent GPC 50, US) was used to measure the molecular weight of BER-MP particles and leachate. Surface functional groups of microplastics were determined by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR, INVENIO, Bruker, Germany). The surface chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS, AXIS SUPRA, Shimadzu, UK). Electron paramagnetic resonance (EPR, E500, Bruker, Germany) was used to determine the presence of environmentally persistent free radicals (EPFRs) on the surface of the BER-MP. The 3D excitation-emission matrix (3D-EEM) spectra (Edinburgh FS5, UK) were used to analyze the changes in the composition of the leachate. A nuclear magnetic resonance spectrometer (NMR, AVANCE NEO 600 MHz, Bruker, Germany) is used to record the $^1$H NMR and $^{13}$C NMR spectra of the leachate of BER-MPs photoaged for 1000 h. More characterization methods are given to Text S2.†

3 Results and discussion

3.1 Characterization of light aged BER-MPs

3.1.1 Physical properties of microplastics. SEM analysis of the surface morphology changes in BER-MPs before and after photoaging was carried out, and the results are shown in Fig. 2. The original BER-MP0 was a massive particle with a smooth and flat surface (Fig. 2a and b), and a size of about 140.6 μm was then calculated through the scale of the SEM image. After 500 h of photoaging, the surface morphology of BER-MP1 underwent an obvious change, from the original block to a sheet with a certain thickness, cracks and holes began to appear on the surface of the polymer. For the BER-MP2 sample, the surface morphology is similar to BER-MP1, but the thickness of the sheet is smaller than BER-MP1.

Fig. 2  SEM images of BER-MP0 (a and b), BER-MP1 (c and d) and BER-MP2 (e and f).
The surface of microplastics, where the breakage of surface polymer chains leads to a decrease in the molecular weight of particulate matter. Subsequently, during the light reaction process, oxygen atoms are introduced into the molecular chains, causing an increase in the molecular weight of the particulate matter. At the same time, the introduction of oxygen atoms increases the hydrophilicity of the polymer chains, causing them to separate from the plastic particles and dissolve in water with an increased molecular weight during the initial photochemical reaction period. As the photochemical reaction progresses, the water-soluble molecular chains degrade rapidly, resulting in a decrease in molecular weight in the leachate. This leads to an initial increase followed by a decrease in the molecular weight of the leachate. In addition, Table S1† shows the GPC data of microplastics during dark reactions. During dark reactions, the PDI slightly decreases while the molecular weight of the particles slightly increases. A decrease in the PDI usually indicates that polymer samples have better molecular weight control and a more uniform molecular weight distribution. The changes in GPC data during dark reactions may be related to prolonged mechanical stirring.

3.1.2 Chemical properties of microplastics. FTIR spectra were used to analyze the changes in functional groups of microplastics. Fig. 3a depicts the FTIR spectra of BER-MPs during the photoaging process. These absorption bands indicated the presence of various functional groups in both the pristine and aged BER-MP samples. The similarity in the FTIR spectra suggested that the basic structure of the BER-MP remained intact after aging, with no significant degradation or chemical changes. However, there were some differences between the spectra of the pristine and aged samples. The bands at 2969/2934 cm⁻¹ and 2870 cm⁻¹ belonged to the stretching vibrations of C–H in –CH₃ and –CH₂–, respectively. Four characteristic absorption peaks at 1581/1531/1462/1446 cm⁻¹ correspond to the aromatic ring C=C skeleton vibrations. The out-of-plane rocking vibration of –CH₃ and the bending vibration of –CH₂– were located at 1385 cm⁻¹ and 1327 cm⁻¹, respectively. The characteristic absorption peak at 1243 cm⁻¹ corresponded to the asymmetric stretching vibration of the aromatic ether group (C=O–C), those at 1162/1059/999 cm⁻¹ were assigned to the stretching vibration of C–O, and those at 927/870/790 cm⁻¹ corresponded to the characteristic absorption of epoxy groups at both ends of the BER-MP molecular chain. In the aged BER-MP sample, the intensity of these absorption peaks all slightly increased compared to that of the pristine sample, which indicated that photo-oxidation resulted in a decrease in the molecular weight of the BER-MP fragments produced during light irradiation. Furthermore, digital photos showed that the original BER-MP0 particles can be seen to be white (Fig. S1a†); however, after photoaging for 500 h (Fig. S1b†) and 1000 h (Fig. S1c†), BER-MP1 and BER-MP2 underwent obvious color changes, and with the extension of photoaging time, their yellowing phenomenon became more and more obvious. During the entire dark reaction, the BER-MP particles did not undergo significant color changes. The ultraviolet-visible absorption spectra of microplastics at different reaction times were measured (Fig. S2†), revealing that the photoreaction significantly enhanced the absorbance of visible light by the microplastics, further confirming the phenomenon of yellowing in microplastics. The yellowing phenomenon of MPs may be caused by the oxidation of the BER structural units to chromophore substances (C–O, C=O, etc.) during photolysis.† This showed that light can promote the aging process of BER-MPs.

Table 1  GPC analysis of BER-MPs and their leachate at different photoaging times, 

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<th>M_w (g mol⁻¹)</th>
<th>M_n (g mol⁻¹)</th>
<th>M_p (g mol⁻¹)</th>
<th>M_z (g mol⁻¹)</th>
<th>M_{z+1} (g mol⁻¹)</th>
<th>PDI</th>
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<tr>
<td>BER-MP0</td>
<td>33 180</td>
<td>15 951</td>
<td>30 468</td>
<td>54 122</td>
<td>75 933</td>
<td>2.080120</td>
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<tr>
<td>BER-MP1</td>
<td>31 590</td>
<td>14 815</td>
<td>28 321</td>
<td>54 192</td>
<td>78 918</td>
<td>2.132298</td>
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<tr>
<td>BER-MP2</td>
<td>32 473</td>
<td>15 323</td>
<td>29 590</td>
<td>54 398</td>
<td>77 580</td>
<td>2.119233</td>
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<tr>
<td>BER-MP1 (leachate)</td>
<td>34 366</td>
<td>17 655</td>
<td>30 917</td>
<td>55 078</td>
<td>76 317</td>
<td>1.946531</td>
</tr>
<tr>
<td>BER-MP2 (leachate)</td>
<td>31 544</td>
<td>15 530</td>
<td>27 910</td>
<td>53 370</td>
<td>77 003</td>
<td>2.031165</td>
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The surface morphology and size (about 56.8 μm) changes in microplastics during the dark reaction (Fig. S3†) was mainly attributed to the fragmentation by mechanical forces. However, this was a negligible surface change compared to the more pronounced BER-MP fragments produced during light irradiation. Possibly due to light penetrating the surface during photoaging. The development of cracks or pits in aging microplastics can create additional adsorption sites, enhancing the retention of contaminants. The surface morphology and size (about 38.6 μm) and a significantly lower thickness. Its surface exhibited numerous cracks and small holes (Fig. 2e and f), possibly due to light penetrating the surface during photoaging.
treatment increases C–H, C==C, C–O–C, and C–O on the BER surface in the photoaging process, which may be due to the oxidation or degradation of other functional groups. The characteristic absorption peaks generated at 734/638/569 cm\(^{-1}\) belonged to the vibrations of the C–Br bond in the BER-MP molecule.\(^{29}\) After the photoreaction, the C–Br bond became obvious, which may be due to the fracture of the C–Br bond in the photoreaction, which weakened the symmetry of the group, enhanced the dipole moment change during vibration, and strengthened the absorption strength.\(^{30,31}\) In the EDS results (Table S2\(^{†}\)), the content of the Br element decreased significantly with the increase in illumination time, which also indicated that C–Br bond breaking would occur during the photoaging process. After photaging (BER-MP1 and BER-MP2), two new characteristic absorption peaks were generated at 1743 cm\(^{-1}\) and 1162 cm\(^{-1}\), which belonged to the stretching vibration of C==O (ref. 27) and C–O, respectively. But they did not appear in the ATR-FTIR spectra in the original (BER-MP0) and dark control (BER-MP3 and BER-MP4) samples. The results indicated that the BER-MPs were oxidized during photoaging, and more oxygen-containing functional groups were produced on their surface. EDS results of BER-MPs before and after photoaging are shown in Fig. S4 and Table S1.\(^{†}\) The results showed that, compared with the original microplastics, the O element in BER-MPs increased slightly after aging. According to the GPC findings, it was deduced that the oxygen element content would initially increase and then fall. However, the decrease in O/C for BER-MP2 could be linked to heterogeneous oxidation on the surface of BER-MPs during aging, leading to varying O/C ratios within a single microplastic fragment.\(^{42}\)

The carbonyl index (CI) was employed to quantitatively assess the degree of aging of microplastics at different aging times. It was determined by calculating the ratio of the maximum carbonyl peak at 1728 cm\(^{-1}\) to the reference peak at 2934 cm\(^{-1}\). Fig. 3b shows that under the condition of photoaging, the CI of BER-MPs continued to increase with the extension of aging time, and the growth rate was extremely fast, while in the dark reaction group, the CI of BER-MPs increased slightly after aging for 500 h, and then it did not change significantly with the aging time. The results showed that the aging process of BER-MPs would be accelerated under simulated sunlight irradiation, and more oxygen-containing groups would be generated. While under the condition of the dark reaction, the aging rate was quite slow.

XPS characterization revealed further changes in the surface chemical composition of BER-MPs before and after aging (Fig. 4). Fig. 4a shows the total spectrum of BER-MP elements before and after photoaging. C, O and Br elements were detected in all samples. As shown in Fig. 4b, in the spectrum of the C 1s of pristine BER-MP0, there were four peaks at binding energies of 284.6 eV, 285.87 eV, 288.73 eV and 291.71 eV. Among them, the peak at 284.6 eV usually belonged to C–C and C–H. The peak at 285.87 eV corresponded to C–O (epoxy group and hydroxyl group) and C–Br bonds.\(^{43}\) The characteristic peak at a binding energy of 288.73 eV belonged to C=O. The peak at 291.71 eV was attributed to the \(\pi-\pi^*\) vibration of the benzene ring.\(^{44}\) After photoaging, the binding energies of the C 1s peaks of BER-MP1 (500 h) and BER-MP2 (1000 h) were basically unchanged compared with those of BER-MP0, but O=C=O peaks at 288.59 eV (BER-MP1) and 288.61 eV (BER-MP2) appeared,\(^{44}\) indicating that BER-MPs were oxidized in the process of photoaging, which was consistent with the results of infrared analysis. However, the spectrum of BER-MP4 after a 1000 h dark reaction exhibited little change compared with the BER-MP0’s C 1s spectrogram. The spectrum of O 1s of BER-MPs is shown in Fig. 4c, which could be well deconvoluted into three peaks. For BER-MP0, its peaks at 531.74 eV, 532.82 eV and 533.1 eV belonged to C==O, C–OH and C–O–C groups, respectively.\(^{45,46}\) After photoaging, it could be found that the peak area of C==O increases gradually, which also provided evidence for the oxidation of BER-MP0 in the photoaging process. In Fig. 4d, there were two peaks at binding energies of 70.2 eV and 71.2 eV, corresponding to Br 3d\(_{5/2}\) and Br 3d\(_{3/2}\), respectively,\(^{44}\) indicating the existence of C–Br bonds, corresponding to a Br atom covalently bound to a carbon atom. During the light reaction, the peak shifted to a low energy level, while during the dark reaction it hardly changes from the original peak position. Combined with the results of ion chromatography detection (Table 2), Br\(^{−}\) appeared in the solution after the photoreaction, and it was speculated that the C–Br bond in the polymer undergoes heterolytic cleavage. That was, when the bond was broken, the shared electron pair between the two atoms is completely transferred to the Br atom to generate Br\(^{−}\). As a result, the
valence electron density of bromine increased, and the binding energy decreased.

Fig. 5 shows the EPR detection of the presence of persistent free radicals on the surface of microplastics. The results showed that there were no EPFRs on the original BER-MP0, but after the photoaging, the EPR spectrum of BER-MP1 and BER-MP2 displayed an obvious single peak with a $g$-factor of 2.0028, which was characteristic of the typical C-centered organic radicals, and the signal intensity of BER-MP2 was significantly higher than that of BER-MP1, indicating that signal intensity gradually increased with the increase in photoaging time. However, no similar phenomenon was observed in the dark control group (BER-MP3 and BER-MP4). These results suggested that simulated sunlight photoirradiation induced the formation of EPFRs on BER-MPs, and the $g$-factor remained constant (2.0028) during the entire photoaging process, indicating that the EPFRs are the same type (C-centered organic radicals).

3.2 Characterization of the BER-MP aging leachate

3D-EEM was used to investigate the changes in the composition of the leachate. Fig. 6 shows the fluorescence EEM of leachate from microplastics at different reaction times, with four fluorescence peaks appearing during the photoreaction. These peaks may be the result of small particles adhering to the MPs themselves or released additives. Among them, peak B (Ex/Em = 225/280–305 nm) corresponds to phenolic substances, peak T (Ex/Em = 225/280–350 nm) corresponds to microbial byproducts, and peak A (Ex/Em = 260/380–460 nm) and peak C (Ex/Em = 350/400–480 nm) correspond to humic acid-like substances (photochemical products of microplastics). Peaks A and C showed enhanced fluorescence after illumination, indicating an increase in humic acid-like substances (photochemical

![Fig. 4 XPS spectra of BER-MP0, BER-MP1, BER-MP2 and BER-MP4. (a) full spectra, (b) C 1s spectra, (c) O 1s spectra, and (d) Br 3d spectra.](image)

![Fig. 5 EPR spectra of BER-MPs before and after aging.](image)

![Table 2 Ion chromatograms of BER-MP leaching solutions at different reaction times](table)

<table>
<thead>
<tr>
<th>Release of Br$^-$ (mg L$^{-1}$)</th>
<th>Proportion of total Br (%)</th>
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<tr>
<td>BER-MP1</td>
<td>13.86 1.33</td>
</tr>
<tr>
<td>BER-MP2</td>
<td>35.88 3.45</td>
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products of microplastics), suggesting that light exposure promotes the photodegradation of microplastics.

In order to better understand the changes in the chemical structure of BER-MPs during photoaging, NMR analysis was carried out on the aged leaching solution of BER-MP2 after photoaging for 1000 h. The $^1$H NMR and $^{13}$C NMR spectra of the BER-MP2 leachate are shown in Fig. 7. The $^1$H NMR spectrum (Fig. 7a) showed that the peak values of the chemical shift at 0.84–3.50 ppm corresponded to the proton on the saturated alkyl carbon. The peaks at 4.04, 4.38, and 4.52 ppm corresponded to protons in the $\alpha$-position attached to O (e.g. $-\text{CH}_2-\text{O}/-\text{CH}-\text{OH}$). The signal at 5.76 ppm corresponded to the proton in the hydroxyl group. The 1 : 1 : 1 signal at 7.02, 7.10, and 7.19 ppm was attributed to the proton in the aromatic ring, corresponding to the removal of a Br atom from the benzene ring of TBBPA in the BER-MP structure. The resonance at 7.95 ppm was assigned to the proton in the $\alpha$-position linked to the carbonyl group ($\text{C}=\text{O}$). The peak at 11.17 ppm was attributed to the proton on the carboxyl group ($-\text{COOH}$). The $^1$H NMR analysis of BER-MP2 indicated that oxidation occurred during the photoaging process, leading to the formation of oxygen-containing functional groups. Additionally, the photoaging process involved the cleavage of C–Br bonds, consistent with the findings from the EDS analysis. The $^{13}$C NMR spectrum of BER-MP2 is shown in Fig. 7b, and the signal at 40.06 ppm corresponded to unsubstituted saturated alkyl carbon. The signal at 62.79 ppm was aliphatic carbon attached to oxygen. The weak peak at a chemical shift of 69.79 ppm was attributed to the C atom attached to the hydroxyl group.

According to the $^{13}$C NMR spectrum of BER-MP2, its structure did not change significantly during the entire photoaging process.

TBBPA bound to BER plastic through chemical bonds, so TBBPA was difficult to be released in solution directly. However, the ATR-FTIR and NMR results indicated that the TBBPA debromination product was formed. Ion chromatography (IC) was employed to confirm the release of Br$^-$ during the photoaging of BER-MPs. Table 2 displays the ion chromatographic outcomes of the leaching solution from BER-MPs at various reaction durations. It was evident from the data that the concentration of Br-discharged into the solution rose as the reaction time lengthened, indicating that the microplastic additive TBBPA released Br-into the water.
4 Conclusion

This study investigated the long-term photoaging behavior of BER MPs in water environments under laboratory conditions. Microplastics can generate more and smaller microplastic particles through photooxidation and mechanical wear in water environments. Photoaging alters the surface properties of BER MPs, leading to the generation of more oxygen-containing...
functional groups. Under light exposure, the oxidized microplastics enter the water in the form of long chains, accompanied by the breaking of C–Br bonds. Additionally, exposure of MPs to sunlight leads to the formation of a large amount of EPFRs on the surface. Analysis of the leaching solution revealed an increase in humic-like substances in the aged leaching solution promoted by light exposure. The aging behavior of microplastics in the aquatic environment and the production of EPFRs and MP-DOM under light aging deserve further study, which will help in assessing the environmental risks posed by MPs.

Data availability

The data supporting this article have been included as part of the ESI†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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