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The photodegradation processes and mechanisms of polyvinyl chloride and polyethylene terephthalate microplastic in aquatic environments: Important role of clay minerals

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ABSTRACT

It is well known that microplastics (MPs) may experience weathering and aging under ultraviolet light (UV) irradiation, but it remains unclear if these processes are impacted by natural components, such as clay minerals. In this study, we systematically investigated the photodegradation behaviors of polyvinyl chloride (PVC) and poly (ethylene terephthalate) (PET), two utmost used plastics, in the presence of clay minerals (kaolinite and montmorillonite). The results demonstrated that the clay minerals, particularly kaolinite, significantly promoted the MPs photodegradation, and the aging of PET was more prominent. The photodegradation was the most distinct at pH 7.0, regardless of the presence or absence of the clay minerals. The results of electron paramagnetic resonance and inhibition experiments of reactive oxygen species indicated that the minerals, particularly kaolinite, remarkably facilitated production of •OH, which was the key species contributing to the photodegradation of MPs. Specifically, UV irradiation facilitated the photo-ionization of MPs, producing hydrated electrons and MP radical cations (MP⁺). The Lewis base sites prevalent on the clay siloxane surfaces could stabilize the MP radical cations and prevent their recombination with hydrated electrons, which promoted the generation of •OH under aerobic conditions, and facilitated the degradation of MP. Two-dimensional (2D) Fourier transformation infrared (FTIR) correlation spectroscopy (COS) analysis and ultra-high-performance liquid chromatography coupled to a Q Exactive Orbitrap HF mass spectrometer were used to identify the sequential changes of functional groups, and the degradation products of the MPs. This study improves our understanding on the aging of MPs in the complex natural environment.

1. Introduction

Microplastics (MPs), as an emerging contaminant, have been detected in various environmental media and raised great concerns over their hazardous effects to ecosystems (He et al., 2018; Koelmans et al., 2016; Moore 2008; Wang et al., 2019a; Zhang et al., 2020b). MPs are commonly defined as plastic particles less than 5 mm in effective diameter, including polycarbonate (PC), polystyrene (PS), polyethylene (PE) and so on (Cole et al., 2015; Ding et al., 2020; Thompson et al., 2004). MPs are introduced to environment via waste disposal, engineering applications and other pathways, leading to relatively high level of MPs in the environment (Chen et al., 2020; Ding et al., 2021; Koelmans et al., 2016; Sintim and Flury 2017). MPs entering the environment will be subject to a series of natural processes, eventually leading to their degradation, and changes in molecular structure and particle characteristics, such as brittleness, density, size, and surface charge (Andrady 2011; Chubarenko et al., 2016; Ding et al., 2020; Kedzierski et al., 2018). These changes may eventually alter the environmental behaviors, ecological risks and biological effects of MPs (Ding et al., 2020; Mao et al., 2020; Zhu et al., 2019).

MPs may experience biotic (mainly microbial), thermal, and photodegradation in the environment, and photolysis induced by ultraviolet

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(UV) light irradiation is considered to be one of the main causes of nonbiological aging of MPs (Singh and Sharma 2008, Wang et al. 2020). UV irradiation induces the generation of reactive oxygen species (ROS) (e. g., hydroxyl radical (\bullet OH), superoxide anion radical ($O_2^{\bullet-}$), and singlet oxygen ($^{1}O_{2}$)), which result in the formation of oxygen-containing functional groups on MPs surface and the breakage of polymers (Zhu et al., 2020; Zhu et al., 2019). Many simulation studies have been executed to disclose the degradation of MPs in UV irradiation conditions. Remarkable photoaging of PC-MPs in aquatic environment were observed over the course of 640 h UV irradiation (Shi et al., 2021). However, these results were obtained in pure water without considering the impacts of natural components in the environment.

As the main inorganic component in soil and natural colloidal particles in surface water, clay minerals play key role in the fate and transportation of polar and ionizable compounds (Kaiser and Guggenberger 2000; Sassman and Lee 2005; Sheng et al., 2001). Clay minerals also contain active substances that mediate certain biological or non-biological reactions, and participate in the transformation and degradation of organic pollutants (Chen et al., 2019b; Zehhaf et al., 2012; Zehhaf et al., 2015). One of our recent studies reported that minerals played critical roles in mediating the environmental behaviors of MPs (Zhang et al., 2020c). In addition, several studies reported that some clay minerals in aqueous solutions promoted the photochemical transformation of organic pollutants (Gu et al., 2011; Jia et al., 2019; Liu et al., 2011; Rubasinghege et al., 2018; Werner et al., 2009; Wu et al., 2018). Xu et al. (2019a) reported that smectite clay accelerated the photo-transformation of tetracyclines under simulated sunlight. These findings suggested the photodegradation of tetracycline was mainly attributed to the Lewis base-catalyzed alkalization on the clay surface. Under alkaline conditions, the amino and phenolic groups in the tetracycline molecule became more electron-rich, and thus more susceptible to the electrophilic addition reaction of ¹O₂. It is speculated that the photodegradation of organic compounds may be related to the formation and activation of organic free radicals on the clay surface according to previous studies (Li et al., 2014; Xu et al., 2019a). However, the possible production pathways and underlying mechanisms are not fully understood. As clay minerals are ubiquitous soil minerals (Jin et al., 2019), it is imperative to investigate their impacts on the environmental behaviors of MPs.

Although a few efforts have been made to understand the interactions between MPs and clay minerals (Zhang et al., 2020d), there is a large knowledge gap about transformation of MPs mediated by clay minerals, which hinders our understanding about the overall fate and effects of MPs in the ecosystems. Polyvinyl chloride (PVC) and polyethylene terephthalate (PET), as common engineering plastics, are widely used in everyday life and industry (Chen et al., 2019a; Djapovic et al., 2021). They are found as macro- and microplastic litters in aquatic, marine, and soil environments (Zhang et al., 2021; Zhang et al., 2020a). However, the degradation of PVC- and PET-MPs is far from well understood. Therefore, this study aimed to clarify the degradation behaviors of MPs mediated by clay minerals (kaolinite and montmorillonite) in aqueous solutions under UV light irradiation. The changes in surface morphology, oxygen-containing functional groups, transformation products, and generation of ROS were inspected. Based on these results, we tried to disclose the photodegradation pathways of MPs and the mediating mechanisms of clay minerals. Furthermore, we evaluated the photodegradation rates under different pHs in the presence or absence of the minerals. The results would advance our understanding into the photochemical transformation of MPs in the environmental relevant conditions.

2. Materials and methods

2.1. Chemicals and materials

Two types of plastic samples, including the MPs of PVC and PET,

were purchased from the local market of Yangling, China. Clay minerals of kaolinite and montmorillonite were purchased from the Clay Minerals Society (West Lafayette, Indiana, USA). Other chemicals and materials were listed in the Supporting Information Text S1.

2.2. Photodegradation of MPs and determination of weight loss

Photodegradation reactions of the MPs were carried out in a constant-temperature (25 °C) photochemical reactor equipped (Fig. S1) with 500 W mercury lamp. The light intensity on each quartz tube was 100 mW/cm^2 , which is equivalent to the equatorial summer sunlight irradiation. (China Education Au-light., China). A given amount of the clay minerals (0.25 g) were dispersed in 40 mL of MilliQ water, in which 0.1 g of MPs were added. The mixture was adjusted to pH 3.0, 7.0, or 10.0 by titrating with 5 mM phosphate buffer, and then sonicated for 30 min to ensure the MPs were well-dispersed in the solutions. Thereafter, the mixture was placed in the photochemical reactor with continuous magnetic stirring to ensure uniform illumination. The MPs were exposed to UV irradiation for pre-determined durations, such as 0, 1, 3, 5 and 7 days. One control group (A), in which no mineral was added, was set up in dark. The second control (B), which contained the same components as the test groups, was also conducted in dark. The third control (C) also contained the same components as the test groups except that no mineral was added. After the reaction, the MPs were filtered, dried and further calculated the weight loss of MP (WL,%), which was shown in detail in Supporting Information Text S2. The filtered leachate was also collected to identify the organic degradation intermediates during photodegradation. Each treatment contained three parallel replicates, and the mean \pm standard deviation (SD) of three replicates were reported. The difference between the weight loss of MPs of the three parallel samples was checked using one-way analysis of variance (significance level, 0.05) from SPSS statistics software (SPSS Inc., USA).

A scanning electron microscopy (SEM, Nova Nano SEM-450, FEI) was used to observe the morphology of the MPs before and after treatment, and the size distribution was analyzed using Nano Measurer software. Two-dimensional (2D) Attenuated Total Reflectance-Fourier transformation infrared (ATR-FTIR, vertex70, Germany) correlation spectroscopy (COS) analysis and X-ray photoelectron spectroscopy (XPS, Thermo Kalpha, Japan) were applied to interpret the changes in surface functional groups of the MPs. More details are provided in Text S3 and Text S4.

2.3. Measurement of ROS

To further shed light on the photodegradation mechanisms of MPs, the aqueous suspensions of clay minerals and MPs, as well as the blank aqueous solution were irradiated for 7 d The blank aqueous solution kept in the dark was considered as blank control. $^{1}O_{2}$, $O_{2}^{\bullet-}$, and $\bullet OH$ were measured using an Electron Paramagnetic Resonance (EPR) spectrometer (Bruker EMXmicro-6/1/P/L spectrometer, Karlsruhe, Germany). More details of experiment and instrumental operation parameters of the EPR scavenger were adjusted according to the description in Text S5.

To further evaluate the roles of ROS, ROS scavengers including sodium azide (NaN₃, 10 mM), superoxide dismutase (SOD, 3 mg/L), isopropyl alcohol (IPA, 10 mM) and 2,4,6-trimethylphenol (TMP, 0.1 mM) were used for the inhibition experiments (Chin et al., 2004; Fu et al., 2016; Halladja et al., 2007). The exposure time of the quenching tests were the same as the test groups (0, 1, 3, 5 and 7 d). More information on ROS scavengers was described in Text S6.

2.4. Analysis and identification of degradation products of MPs

To identify the chemicals released by MPs due to photodegradation, the filtered leachates were identified by UltiMate 3000 Rapid Separation Liquid Chromatography system (Dionex, Germering, Germany) coupled to a Q Exactive HF Hybrid Quadrupole-Orbitrap mass spectrometer (HPLC-MS, Thermo Scientific, Bremen, Germany). Detailed information for measurements and the analytical methods are provided in Text S7.

3. Results and discussion

3.1. Photoaging of MPs mediated by clay minerals

Fig. 1 shows the SEM images of pristine MPs (PET- and PVC-MP) and the treated ones (duration of 1 d and 7 d) with or without the clay minerals (kaolinite and montmorillonite) at pH 7.0. The surfaces of the pristine PET and PVC-MPs were smooth (Fig. 1A and H), and negligible change was observed in the control groups which were kept in dark. However, cracks and pits were observed gradually on the surfaces of MPs as the reaction proceeded (Fig. 1). Fig. 1B-G display the surface morphology of PET-MPs before and after oxidation. In the absence of clay minerals, the cracks on the PET-MP surface were thicker and linked together after 1 d UV light exposure (Fig. 1B). When the photoaging continued for 7 d, fine cracks appeared along with the larger cracks, indicating that the composite film was partially broken due to decomposition (Fig. 1C). It is noticed that large holes and cracks appeared on the treated PET-MPs, and the smooth surface morphology was completely destroyed in the presence of clay minerals. As the surficial polymer was decomposed, the subsurface of PET-MP was exposed. The SEM images of PVC-MP before and after photodegradation are depicted in Fig. 1I–N. The morphology of PVC-MP also showed obvious changes and same trend upon exposure time. Overall, the MPs experienced greater surface changes in the presence of the minerals, suggesting the minerals promoted the photodegradation of MPs.

The degradation of MPs was measured and the results are shown in Fig. 2 and Table S1. In the control groups (A and B) which were kept in dark (Fig. 2), less than 3% of the original weight was lost, no matter with or without the clay minerals in the solutions, suggesting that the MPs were hardly degraded without UV light irradiation. However, the weight loss of the photoaged PET- and PVC-MPs increased greatly, which was in the range of 0–20.22% \pm 0.023 and 0–19.78% \pm 0.035, respectively, and it increased continuously with the irradiation duration, suggesting that MPs experienced distinct degradation under UV light irradiation (Table S1). It was worth noting that the presence of clay minerals significantly enhanced the photodegradation of MPs (Fig. 2). For example, the weight loss of PET-MPs in the presence of kaolinite (44.25% \pm 0.026) was distinctly higher than that of montmorillonite $(35.99\% \pm 0.027)$, and both were significantly higher than that without clays (p < 0.05, Table S1). The results indicated that the MPs photodegradation were highly dependent on the types of clays. Our previous study indicated that the adsorption of MPs on the minerals was negligible (Zhang et al., 2020d), suggesting the increased weight loss of MPs in the presence of minerals was not due to physical adsorption. Thus, it is



Fig. 1. SEM images of pristine MPs and MPs (i.e., A. pristine PET and H. pristine PVC; B–G. PET and I-N. PVC) after 1 d and 7 d of treatment with and without the presence of clay mineral at pH 7.0 (i.e., no clay (B, C, I, and J), kaolinite (F, G, M and N) and montmorillonite (D, E, K and L)).



Fig. 2. Weight loss of the MPs as a function of irradiation time in the presence or absence of clay minerals at pH 7.0. Error bars represent the standard variations from duplicate measurements.

assumed that the clays promoted the degradation of both MPs. To further evaluate the impacts of minerals on the weight loss of MPs, a $R=(\rm ML_{Clay}-\rm ML_{No\ Clay})/\rm ML_{No\ Clay}$ was calculated. For the same MP, the R values in the presence of kaolinite were higher than montmorillonite (Table S1), implying that kaolinite exhibited stronger effects than montmorillonite on the photodegradation of MPs. Among the two kinds of MPs, the photodegradation of PET was slightly but significantly higher than PVC in the presence of the minerals (p < 0.05, Table S1), suggesting that the clay minerals displayed stronger effects on PET photodegradation.

3.2. Mediating mechanism of clay minerals

Some recent studies suggested that the generated radicals in UV light irradiation primarily contributed to the MP photodegradation (Zhu et al., 2020; Zhu et al., 2019). To understand the impacts of the minerals on the photodegradation of MPs, the produced ROS (including ${}^{1}O_{2}$, $O_{2}^{\bullet-}$, and \bullet OH) were measured in the reaction systems. Fig. 3 shows that the main peaks of ${}^{1}O_{2}$ signals in the presence of kaolinite were stronger than montmorillonite and the control (no clay), suggesting that more ROS were generated due to the presence of kaolinite. It is noticed that no signals of \bullet OH and $O_{2}^{\bullet-}$ were observed in the dark, whereas strong characteristic signals were observed in the presence of both minerals. \bullet OH adduct was detected in the suspension of kaolinite under light irradiation at pH 7.0, while it was not detected in the control. However, \bullet OH signal was very weak in the montmorillonite suspension, which might be because of the low conversion rate (Buettner 1993; Zhu et al.,

2020). These findings indicated that •OH production was facilitated by kaolinite under the simulated UV irradiation at pH 7.0. Similarly, there was a strong $O_2^{\bullet-}$ signal in the kaolinite suspension, but it was very weak in the montmorillonite suspension. These results were consistent with the more promoted photodegradation of the MPs by kaolinite, and suggested that the generated \bullet OH and $O_2^{\bullet-}$ played important roles in the photodegradation of MPs (Kang et al., 2019; Zhu et al., 2019). Kaolinite is a 1:1-type phyllosilicate, with its alumina octahedral plane exposed to the air, whereas montmorillonite is a 2:1-type phyllosilicate and the alumina octahedral sheet is sandwiched between the two silica tetrahedral planes (Jin et al., 2019), making it unable to participate directly in surface reactions (Scheme S1). Lewis base sites are prevalent on aluminosilicate surfaces of clay minerals, producing deprotonated Si/Al hydroxide groups at the edge sites and permanent negative charges arising from isomorphic substitution (Xu et al., 2019b). The negative charges could prevent MP recombination with hydrated electrons. subsequently facilitating the production of ROS (Tian et al., 2015). Therefore, the different structures might explain the different catalytic effects of the clay minerals.

Fig. 4 illustrates that all the ROS scavengers depressed the weight loss of MPs, fortifying the important roles of ROS (Fig. 4). Among the four tested ROS scavengers, IPA and SOD, scavengers of •OH and $O_2^{\bullet-}$ respectively, exhibited the strongest inhibitory ability during MP photodegradation process, suggesting a more important role played by •OH and $O_2^{\bullet-}$ than by ${}^{1}O_2$, and ${}^{3}MP^*$, which was in accordance with the utmost promoted generation of •OH and $O_2^{\bullet-}$ by kaolinite. Previous studies also suggested that •OH was the most critical species in the



Fig. 3. EPR spectra obtained from photodegradation reaction of different microplastics with and without the presence of clay mineral at pH 7.0.



Fig. 4. Suppressed photodegradation of PVC-MPs with the presence of kaolinite at pH 7.0 by quenching photolysis-induced reactive species.

photodegradation of MPs (Zhu et al., 2020; Zhu et al., 2019). It was reported that the oxygen-containing color groups (such as peroxides) in MPs absorbed photons to generate •OH radicals, which caused the subsequent degradation of MPs under UV light irradiation (Kaczmarek et al., 2000). As shown in Scheme S1, UV irradiation causes the photo-ionization of MPs, producing hydrated electrons and MP radical cations (MP⁺) (Pickett 2011; Shi et al., 2021; Xu et al., 2019b; Zhu et al., 2020). The negative surface charges on the clay minerals could stabilize the MP radical cations and prevent their recombination with hydrated electrons, subsequently generating •OH radicals under oxic conditions (Joseph et al., 2008; Tian et al., 2015; Zhang et al., 2018).

3.3. Effect of solution pHs

The photodegradation efficiency of the MPs apparently increased as increasing solution pH in the range of 3.0 - 7.0, but then decreased as pH increased from 7.0 to 10.0 (Figs. S2 and S3), which was consistent with the SEM results of MPs at different pHs (Figs. S4 and S5). Meanwhile, at all the examined pH conditions, the photodegradation of MPs was higher in the presence of clay minerals (Fig. S3). Regardless of the presence or absence of clay minerals, the photodegradation of MPs was the highest at pH 7.0. (Fig. S2). As shown in Fig. S6 A, the signals of ${}^{1}O_{2}$ fluctuated with the change in pH values. However, the •OH and O₂•derived from the solution show strong pH-dependence, which was in agreement with previous studies (Jin et al., 2019; Joseph et al., 2008; Tian et al., 2015). As the pH increased from 3 to 7, the sign of •OH and O20- sharply increased, and were utmost in the presence of both minerals at pH 7.0, particularly in the presence of kaolinite (Fig. S6 B and C). This might be explained by the impact of the basal spacing of clay mineral and the contribution of O₂ (Joseph et al., 2008; Zhang et al., 2018). Acidic conditions cause changes in the interlayer spacing of clay minerals, which led to protonation of minerals and affect the conversion of organic matter (Soma and Soma 1989). The basal spacing of clay mineral increased with pH increased, which leads to protonation of clay, and then accelerated the reaction rate between minerals and the accumulation of •OH and O₂•- radicals (Soma and Soma 1989). However, varying pH has negligible impact on the basal spacing of clay mineral and oxygen in pH range 7–8. In addition, high pH greatly suppressed the productions of •OH and O₂•- (Fig. S6 B and C). At high pH conditions, the release rate of O_2^{2-} could be limited, thereby affecting the formation of H₂O₂, and ultimately the generation of •OH and O₂•- (Joseph et al., 2008). The impact of oxygen is more noticeable than the basal spacing of clay mineral at pH > 8, and raising pH significantly decreases the release rate of O_2^{2-} and increases the expenses of •OH (Buxton et al., 1988; Joseph et al., 2008). At pH=10, the release rate of O_2^{2-} could be limited,

thereby affecting the formation of H_2O_2 , and ultimately the generation of •OH and O_2 •– (Joseph et al., 2008). This result support that the minerals facilitated the photodegradation of MPs by promoting the generation of •OH and O_2 •–, which actively participated in MPs degradation.

3.4. Photodegradation mechanism of MPs

3.4.1. Changes in functional groups

Fig. 5 revealed that the changes in surface functional groups of the MPs due to UV light irradiation. The characteristic bands of the pristine PET-MP (0 d) exhibited high absorption intensities (Fig. 5): the typical peaks at 728, 873, 1110, and 1715 cm⁻¹ were observed, which are related to the C–O of ester bonds, the C–H of aromatic ring groups and the carbonyl group (C = O) or ketone moieties, respectively (Kang et al., 2019; Zhou et al., 2017). For the pristine PVC-MP, five major characteristic peaks (e.g., 2914, 2853, 1331, 1254, and 600 cm⁻¹) were observed (Miao et al., 2020a; Thi Kim Ngan et al. 2018). For instance, the apparent sighs at 2914 cm⁻¹ and 2853 cm⁻¹ are associated with the C–H and CH₂ of PVC (Ali et al., 2016; Domínguez-Jaimes et al., 2021; Zhao et al., 2018). The bands located at 1331 and 1254 cm⁻¹ and 600 cm⁻¹ are attributed to C–H bending from CH–Cl and bending vibrations of C–Cl of PVC (Ali et al., 2016).

Additionally, we found that the functional groups of the MPs changed significantly with the UV light irradiation time. For PVC, as shown in Fig. 5, an apparent signal was observed at around 1740 cm⁻¹ (C = O), which increased remarkably with the irradiation time (Miao et al., 2020a; Thi Kim Ngan et al. 2018). The intensities of signals at 2914 cm⁻¹ and 2853 cm⁻¹ decreased with time. Moreover, the intensities of the signals at 600, 1331 and 1254 cm⁻¹ also decreased significantly. It was notable that the peaks in hydroxyl region (-OH) $(3440 \text{ cm}^{-1}-3450 \text{ cm}^{-1})$ decreased firstly and then increased after 7 d of UV irradiation (Fig. S7A). This might be due to the release of plasticizer from MPs in the early stage of aging, and formation of oxygen-related functional groups on the surface of the plastic in the later stage (Shi et al., 2021). Similarly, compared with the untreated PET, the treated PET showed several discernible changes such as peak shifting (Fig. 5). Especially, a new peak at 3435 cm⁻¹ was formed on the photo-irradiated MPs (Fig. S7B), corresponding to the hydroxyl group (O-H), while this peak was absence in the pristine PET-MP. The peaks at 873 and 728 $\rm cm^{-1}$, as well as that of $\rm C = O$ at 1715 $\rm cm^{-1}$ increased remarkably in the treated MPs, suggesting distinct oxidation of MPs (Moore 2008). The peak at 1110 cm⁻¹ representing C—O group increased over the course of oxidative degradation.

The carbonyl index (CI) (1715 cm⁻¹/974 cm⁻¹) is another indicator used to quantitatively evaluate the aging of MPs during oxidation, which was suitable to reflect the changes in the properties of MPs during the aging process (Acuña-Bedoya et al., 2021; Domínguez-Jaimes et al., 2021). Fig. 6 shows that the CI value increased with the exposure duration with a significant correlation (p < 0.05). These results provided evidence that more oxygen containing functional groups were generated during the MPs aging process. It is worthy to note that the CI values in the presence of kaolinite (from 0.0151 ± 0.004 to 0.3504 ± 0.023) were higher than that of montmorillonite (from 0.0151 ± 0.004 to $0.2978 \pm$ 0.018) and no clay (from 0.0151 ± 0.004 to 0.2052 ± 0.035) (Fig. 6A). Moreover, the CI values of PET displayed an obvious change than PVC-MPs within 7 d UV exposure. Such results showed that MPs photodegradation was highly dependent on the properties of MPs and clays.

3.4.2. 2D-COS maps

Due to the limited information provided by the one-dimensional FTIR spectra, 2D-COS analysis was performed to further understand the changes of functional groups of the MPs (Fig. 7). For PVC, seven auto-peaks were identified at 600, 1331, 1740, 2853, 2914 and 3440 cm⁻¹ along the diagonal line. For the PET, six major auto-peaks (at 728, 873, 1110, 1715, 1256, and 3435 cm⁻¹) were also identified. Tables 1



Fig. 5. The ATR-FTIR spectra of the photodegradation of MPs (i.e., PET (A, B, and C) and PVC (D, E and F) with and without the presence of clay mineral (i.e., kaolinite (A and D) and montmorillonite (B and E)) at pH 7.0.



Fig. 6. Carbonyl index of PET- and PVC-MPs during 7 d of aging process under UV conditions at pH 7.0 (A. PET and B. PVC).

and 2 show that majority of the cross peaks in the synchronous maps of PVC and PET were positive, suggesting that these functional groups underwent synchronous changes (i.e., decrease in the intensity of bands) during the photodegradation.

Based on the Noda's rule (Dowrey et al., 2001; Lasch and Noda 2019; Noda 2006), asynchronous correlation spectroscopy revealed the order of specific chemical reactions during PVC and PET degradation. Table 1 reveal that the photodegradation of PVC could occur in the following order: 600 and 1331 cm⁻¹ (C—Cl) > 2853 cm⁻¹ (CH₂) > 2914 cm⁻¹ (C—H) > 3440 cm⁻¹ (O—H) > 1740 cm⁻¹ (C = O) (Scheme S2 A). As a first step, the C–Cl vibration (600 and 1331 cm⁻¹) of PVC was attacked readily by obtaining electrons directly from the solution (Zhao et al., 2018). Subsequently, the CH₂ (2853 cm⁻¹) was greatly impacted (Zhao et al., 2018), and then C = C was formed. Fig. S8 revealed that, with increasing exposure time, the intensity of the peaks related to C = C bond remarkably increased. Additionally, C—H bond and C—Cl bonds weakened. These results These results demonstrated that the long chain

structures were destructed (Figs. S8–S10). New components of O—H appeared in the regional O1s spectrum (Fig. S8), which was consistent with the results of FTIR. XPS results also showed that the intensity of O/C increased with irradiation time, supporting the generation of oxygen-containing groups (SI Table S2). As expected, PVC was oxidized by •OH to form C—OH (3440 cm⁻¹) and C = O (1740 cm⁻¹) (Kang et al., 2019; Miao et al., 2020a; Zhu et al., 2019).

Likewise, according to the sign of 2D-COS map of PET, the sequential order of the band change was derived: 1110 and 1256 cm⁻¹ (C—O of ester bonds) > 1715 cm⁻¹ (C = O) > 728 cm⁻¹ (C—H) > 873 cm⁻¹ (C—H) > 3435 cm⁻¹ (O—H) (Scheme S2 B). These results demonstrated that the degradation of PET firstly took place at the C—O of ester bonds, which was attacked by •OH (Wang et al., 2019c). Secondly, the peak of C = O increased distinctly, followed by the formation of C—H groups (728 and 873 cm⁻¹) and O—H groups (3435 cm⁻¹) of PET (Sun et al., 2018). Finally, low molecular weight alcohols were formed, which might be partially mineralized to CO₂ and H₂O (Miao et al., 2020a). The



Fig. 7. Synchronous and asynchronous 2D correlation maps constructed from time-dependent ATR-FTIR spectra of PET (A–D, I–L) and PVC (E–H, M–P) membranes with and without the presence of clay mineral (i.e., kaolinite (A, B, E and F) and montmorillonite (I, J, M and N)) at pH 7.0. Red color denotes positive correlation, and blue color means negative correlation; darker color demonstrates a higher intensity and thus a stronger positive or negative correlation. In 2D-CoS maps, the peaks located at the diagonal line are called autopeaks while cross peaks are located off-diagonal positions (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Table 1

2D-COS data on the assignment and sign of each cross-peak in Synchronous (Φ) and Asynchronous (Ψ , in the Brackets) Maps of PVC upon Exposure to UV light at pH 7.0 with increasing exposure time.

Peak Band Sign* assignments (cm^{-1}) 600 1331 1740 2853 2914 3440 600 C-Cl +(-) +(-) +(-) - (+) +(-)CH-Cl 1331 +(-) +(-) +(-)- (+) 1740 $\mathbf{C} = \mathbf{O}$ + +(-) +(-) (-) 2853 CH_2 + (-) -(+)+ 2914 C-H - (+) 3440 O-H

Note: "+" means a positive sign; "-" means negative sign.

Table 2

2D-COS data on the assignment and sign of each cross-peak in Synchronous (Φ) and Asynchronous (Ψ , in the Brackets) maps of PET upon exposure to UV light at pH 7.0 with increasing exposure time.

Peak (cm ⁻¹)	Band assignments	Sign*					
		728	873	1110	1265	1765	3435
728	C-H	-	-	+	+	+	- (-)
			(+)	(+)	(+)	(+)	
873	C-H		-	+	+ +)	+	- (-)
				(+)		(+)	
1110	C-O			+	+ (-)	+ (-)	- (+)
1265	C-O				+	+ (-)	- (+)
1765	$\mathbf{C} = \mathbf{O}$					+	-(+)
3435	O-H						+

Note: "+" means a positive sign; "-" means negative sign.

XPS results indicated that the O/C ratio increased significantly (SI Table S3). Intensities of C—O and C = O bonds increased, suggesting that the long chain was shortened (Figs. S8 and S9). Meanwhile, the intensities of the peaks related to C—H remarkably increased. These results collectively confirmed that oxygen containing groups were introduced in the process of aged PET-MP.

Additionally, the ATR-FTIR spectra (Figs. S11 and S12) and 2D-COS (Figs. S13 and S14) showed that, the dynamic aging mechanism of PETand PVC-MP is not affected by pH (Tables S4 and S5). Notably, the intensities of the autopeaks at pH 3.0 and 7.0 were stronger than at pH 10.0, which was in line with the photodegradation characterization results (Figs. S13 and S14).

3.4.3. Intermediates and degradation pathway

The intermediates products of MPs were identified using HPLC-MS (Figs. S15 and S16). The identified substances include alkenes, ketones, alcohols, aldehydes, lactones, ketoacids, and esters (Tables S6 and S7). Based on previous studies and the above results, the degradation process of PVC- and PET-MPs are proposed in Scheme S2.

Scheme S2 A displayed the possible degradation pathway of PVC and PET. In the first step, the PVC-MP attack the C-Cl bond and trigger dichlorination under UV light (Miao et al., 2020b). The dehydrochlorination readily took place with the production of carbo-cations, which were subsequently transformed into alkene and polyene (C = C) structures, respectively (Scheme S2 A, Step 1) (Gardette and Lemaire 1991; Jian et al., 1991). In the second step, PVC-MP was oxidized by O₂ and H₂O to form oxygen containing groups (e.g., alcohols and ketones) into solution (Liu et al., 2019; Wang et al., 2020). In the third step, the hydrocarbon-based substances were further attacked by $O_2^{\bullet-}$ radicals to form smaller substances with low molecular weight such as alcohols, carboxylic acids and esters, which were eventually degraded into CO2 and H₂O (Miao et al., 2020a). For PET, the active substance •OH attacked the C-O bond (Scheme S2 B, Step 1) (Wang et al., 2019c), leading to its break, and formation of short-chain intermediates, which were further attacked to generate PET monomers (Sun et al., 2018; Wang et al., 2019c). Subsequently, the oxidation reaction is mainly divided into two types (Wang et al., 2019b), which involves the formation of radicals during ester bond cleavage and carboxylic acid of polymer chains terminating (Day and Wiles 1971; Sang et al., 2020). Finally, the degradation process of PET was in agreement with PVC, forming low molecular weight (Day and Wiles 1971, 1972).

4. Conclusions

Clay minerals are widely present in the environment and play important roles on the fate of heavy metals and organic molecular pollutants. For the first time, we demonstrate that the clay minerals (kaolinite and montmorillonite) accelerated the MPs photodegradation. Under UV light irradiation, both minerals, particularly kaolinite, facilitated the production of •OH and $O_2^{\bullet-}$ in the reaction systems, which actively participated in the degradation of MPs. Compared with previous studies, this study shows a more detailed degradation process of MPs. More importantly, our research results show that in aqueous system, clay minerals obviously promoted the MP degradation. Therefore, the conversion of MPs in mineral-rich topsoil may have different manifestations, and more investigations are warranted in future researches.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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Supplementary materials

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