



Surface Modification of Polyethylene Microplastic Particles during the Aqueous-phase Ozonation Process

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Abstract

Microplastics coexist with the chemical reactive oxygen species in natural waters, however, there is still a lack to elucidate the effect of these radicals on the microplastic surficial oxidation. In this study, the ozonation of polyethylene microplastics was carried out under varying ozone dosages ranging from 4 to 7 mg/min for 60, 120 and 180 min, where its ozone uptake was iodometrically compared and surficial modification was spectroscopically analyzed using FTIR and XPS. For that, the lowest ozone uptake was 16% at 4 mg/min ozone supplied for 60 min whereas the highest was observed of 44% at 7 mg/min ozone added for 180 min. Moreover, in the FTIR analysis, carbonyl (1,600-1,800 cm^{-1}) and hydroxyl (3,200-3,600 cm^{-1}) indices were improved more than 20% and 13% when they were ozonized at 7 mg/min for 180 min compared to 4 mg/min for 60 min, respectively. XPS also revealed that 7 mg/min of ozone supplied for 180 min provided the highest of oxygen functionalities, but while there was no significant change in C-C bond. It can be concluded that the surficial modification of PE including formation of oxygen functionalities could be more preferably influenced by the reaction time than ozone dosages.

Keywords: FTIR, Microplastic, Ozonation, Polyethylene, X-ray photon spectroscopy



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1 **1. Introduction**

2 The prevalence of microplastics (MPs) has been recently recognized as a threat to the biosphere
3 owing to their infinitesimal size responsible for highly stable nature towards natural degradation
4 processes [1, 2], thereby related adverse effects have been reported across all over ecosystems
5 from low to high trophic levels of food chain: microorganisms [3–5], plants [6, 7], animals [8–
6 11], and even human beings [12]. These significant ecological impacts persuade the researchers
7 to investigate the aging behavior of these tiny particles in an environment. Till date, several
8 studies have been conducted to determine the changes in physicochemical properties occurred as
9 a result of physical, chemical [13, 14] and biological processes [14], moreover the requirement
10 for the detailed research is obligatory.

11 In line with this, the advanced oxidation processes (AOPs) have been widely
12 implemented and proven to be effective for the oxidation of plastics owing to the presence of
13 reactive oxygen species including hydroxyl radicals, superoxide, peroxide, and atomic oxygen
14 formed under a variety of chemical processes including ozonation [15, 16], persulfates activation
15 [17], UV/O₃ [18], UV/H₂O₂ [19] and etc. Recently, the application of these technologies in the
16 field MPs oxidation has gained attention for which several studies can be found in this regard.
17 Briefly, Liu *et al.* studied the alteration properties of polystyrene (PS) and polyethylene (PE)
18 MPs particles using chemical reagents such as potassium persulfate and Fenton reagent and
19 observed the formation of oxygen functionalities on their surface [17]. Similarly, Mao *et al.*
20 investigated the aging behavior of PS exposed to ultraviolet-A (UV-A) irradiation having an
21 absorbance at 340 nm in the different environmental matrix (*i.e.*, air, water, and sea water) [20],
22 implying that the highest oxidation of the PS was detected in air matrix. In addition to, Tajkia et

1 al. [21] observed an increase of 30% in carbonyl indices of low density polyethylene (LDPE)
2 MPs treated under UV irradiation using zinc oxide (ZnO) nanorods as a photocatalyst. These
3 studies provide a clear evidence of applicability and effectiveness of AOPs for the alterations of
4 MPs. Moreover, it eventually contributed to similar resultant owing to the involvement of
5 conspecific radicals, although there are differences in their oxidation initiators [22]. Hence, the
6 ozonation can be also one of the potential candidates for simulating the effect of reactive oxygen
7 species on the surficial oxidation of MPs in the natural waters. Molecular ozone is a powerful
8 oxidant with the oxidation potential of 2.07 V in a gaseous phase [23], making it turning into the
9 hydroxyl radicals and other reactive oxygen species in an aqueous phase [24] and its polymeric
10 oxidation have been investigated a lot [23, 25, 26].

11 This is the first attempt to explore the effect of ozonation of PE MPs particles through an
12 aqueous phase ozonation at 4 different ozone dosages (*i.e.*, 4, 5, 6, and 7 mg/min) for three
13 different time durations of 60, 120, and 180 min. Herein, PE MP particles used was consisting of
14 5 different particle size range distribution: (i) $< 75 \mu\text{m}$ constitute 3.4% of sampled MPs; (ii) 75-
15 $125 \mu\text{m}$, 7.2%; (iii) 125-250 μm , 43.0%; (iv) 250-500 μm , 43.1%; and (v) $> 500 \mu\text{m}$, 3.3%,
16 respectively, which were determined by multi-phase sieving. After that, the degree of oxidation
17 of PE MPs was determined by Fourier transform infrared (FTIR) spectroscopy and X-ray
18 photoelectron spectroscopy (XPS). This study should be helpful to elucidate the effect of the
19 reactive oxygen species to MPs distributed in natural waters along with their surficial alteration.

20

21 **2. Materials and Methods**

22 **2.1. Ozonation of PE MP Particles**

1 The ozone treatment system was composed of ozone generation system and reaction chamber as
2 presented in Fig. 1. Reaction chamber was equipped with two 300 mL Erlenmeyer flasks, which
3 were served as the main ozonation chamber followed by ozone trapping equipment, respectively.
4 Prior to the ozonation, the reaction mixture (pH 6.59 at 25°C) was made of 1% (w/v) PE MP
5 particles (medium density of 0.94 g/mL; melting point of 109-111°C, Aldrich Chemical Co.,
6 USA) in distilled water and then infused into the main flask. It was continuously agitated on a
7 magnetic stirrer set with a stirring speed of 100 rpm under the ambient temperature to uniformly
8 disperse PE MP particles during the treatment. Secondary flask was prepared by adding 100 mL
9 of 1.2 M potassium iodide (KI, Samchun Chemicals, Korea) solution to capture off-gas ozone
10 which was released to be unreacted from the ozonation chamber. These two flasks were
11 thoroughly capped by using a silicon stoppers and connected each other with the Pyrex tube
12 (6.34 mm diameter, Koreel, Korea) to prevent ozone undesirably escaping. And thereafter, ozone
13 was generated through dielectric barrier discharge (DBD) plasma [27] from the dry oxygen
14 (Purity; 99.5-99.9%) fed at a pressure of 1 MPa into the ozone generator (Ozonetech, Korea).
15 The ozone dosage was then adjusted to variably keep at 4, 5, 6 and 7 mg/min referring to the
16 readings of ozone gas analyzer (H1 Series Ozone Analyzers, INUSATM, USA). They were
17 immediately entered into the reaction chamber where PE MP particles were oxidized for varying
18 times of 60, 120 and 180 min. After the termination of each experiment, the treated PE MPs were
19 separated using 0.45 µm cellulose acetate membrane filter (ADVANTEC[®], Tokyo Roshi Kaisha
20 Ltd., Japan) to analyze the possible surficial modification followed by being dried for 24 h in a
21 drying oven (50°C, Vision Scientific Co., Ltd., Korea), which were then stored in vacuum
22 desiccator at room temperature for further surface analysis of FTIR and XPS.

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2.2. Measurement of Ozone Uptake by PE MP Particles

The off-gas of ozone released during the oxidation of PE MP particles was captured by KI solution in the off-gas ozone trap, which were used to measure the extent of the flow rates of ozone gassed out and ozone uptake by PE MP particles. First, the flow rate was determined by modified iodometric titration method [17, 28], where the residual ozone reacted with iodide ion (I⁻) to form iodine (I₂). Briefly, 10 mL of KI solution captured off-gas ozone was mixed with 5 mL of 2% (w/v) of sulfuric acid (95%, Samchun Chemicals, Korea) solution and the mixture was then titrated with standardized sodium thiosulfate solution (0.001 N, Na₂S₂O₃·5H₂O, Daejung Chemical, Korea) till pale yellow color appeared. After that, 1 mL of 1% (w/v) of starch ((C₆H₁₀O₅)_n, Duksan Chemicals, Korea) indicator was added, which were then secondary titrated till color changed from blue to colorless. From that, the total volume of sodium thiosulfate solution consumed for titration was recorded, from which the flow rate (O_{3, off-gas}) was calculated by using the Equation (1), presented by Chtourou et al. [15]:

$$O_{3, \text{ off-gas}} \text{ (mg/min)} = \frac{(A \times N \times B \times 24)}{(t \times V)} \quad (1)$$

Where, A is the volume of sodium thiosulfate solution used for titration (mL), B is the total volume of KI solution used to capture ozone (100 mL), V is the volume of KI used for titration (10 mL), N is the normality of sodium thiosulfate solution (0.001 N), and t is the ozonation time (min). It was converted to the flow rate of off-gas ozone by multiplying the conversion factor of 24. After that, the percentage ozone uptake by PE MP particles was also determined by Equation (2), with the off-gas ozone flow rate obtained under the presence (O_{3, PE}) over absence (O_{3, Blank}) of PE particles in the reaction chamber, respectively.

$$\text{Ozone uptake (\%)} = \frac{[O_{3,Blank}] - [O_{3,PE}]}{O_{3,Blank}} \times 100 \quad (2)$$

2.3. Fourier Transform Infrared (FTIR) Spectroscopy

For the first time, a pellet was made by grinding a mixture of 100 mg of potassium bromide (KBr, FTIR grade, Merck, Germany) and 5 mg of oxidized PE MP particles in an agate mortar followed by pelletizing with AltasTM manual hydraulic press (SPECAC Inc., USA). The surface modification of those pellets of PE MP particles after ozonation at 4 different ozone dosages for three different time reactions was analyzed by FTIR (VERTEX 80V, Bruker, Germany) in the wavenumber ranging from 4,000 cm⁻¹ to 400 cm⁻¹ with a resolution of 4 cm⁻¹. The obtained numbers of FTIR spectra were corrected by baseline method [29] and then normalized to the band at the wavenumber of 1,472 cm⁻¹ (C=C, double bond stretching) because it was to be unchangeably sustained as of that of virgin PE peak even though PE particle has been oxidized, otherwise rest of those peaks having been changed after the oxidation. From these normalized spectra, the degree of carbonyl and hydroxyl indices were determined by integrating the peak areas in between 1,600-1,800 cm⁻¹ and 3,200-3,600 cm⁻¹, respectively, using a linear end-to-end baseline approach.

In the meantime, the crystallinity of PE MPs was estimated as suggested by Zerbi et al. [30]. Namely, comparing peak height at 730 cm⁻¹ (corresponding to crystalline content) versus 719 cm⁻¹ (amorphous content) can obtain the percentage of crystalline phase content as calculated by the following Eq. (3):

$$\text{Crystalline phase content (\%)} = \left[1 - \frac{\{1 - (I_{730}/I_{719})/1.233\}}{(1 + I_{730}/I_{719})} \right] \times 100 \quad (3)$$

1 Where, I_{730} and I_{719} are the respective absorbance intensity of peak at 730 cm^{-1} and 719 cm^{-1} in
2 the normalized FTIR spectra, and 1.233 is the theoretical intensity ratio of $\frac{I_{(730)}}{I_{(719)}}$ at the settling
3 angle of 42° .

5 **2.4. X-ray Photoelectron Spectroscopy (XPS)**

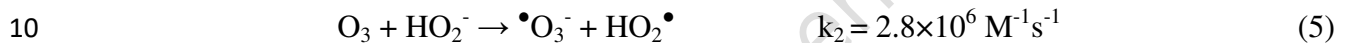
6 X-ray photoelectron spectra of PE MP samples were determined using XPS (K-Alpha, Thermo
7 scientific, USA) equipped with monochromatic Al-K α source. From this, low resolution
8 spectrum (0 to 1,200 eV of binding energy) was used to monitor possible changes of elemental
9 concentrations such as sodium (Na), silicone (Si), and nitrogen (N), along with the determination
10 of ratio of oxygen to carbon (O/C), while high-resolution spectra for C1s region (280 to 293 eV)
11 and O1s region (526-538 eV) were deconvoluted into subpeaks by Origin software (OriginPro
12 9.0, Electronic Arts, USA) to distinct the type of carbon-oxygen functionalities newly appeared
13 on the PE surface since after the ozonation.

15 **3. Results and Discussion**

16 **3.1. Ozone Uptake by PE MPs**

17 The flow rate of off-gas ozone released during ozonation was determined using Eq. (1) and
18 thereafter, compared in the presence (the test) over the absence (*i.e.*, the control) of PE MP
19 particles under the given experimental conditions of 4 different ozone dosages and 3 different
20 reaction times, as presented in Fig. 2. It showed that the flow rate was continuously declined in
21 both control and test samples as the inlet ozone dosages was increased from 4 to 7 mg/min for
22 each reaction time: for the control samples, it was decreased from 3.5 to 1.2 mg/min just since

1 after 60 min, from 2.9 to 1.0 mg/min immediately after 120 min, and from 2.5 to 0.8 mg/min
 2 after 180 min, respectively. It was also confirmed that the prolonged treatment duration made
 3 off-gas ozone flow rate much furtherly decreased. It can be attributed to ozone decomposition by
 4 OH^- , HO_2^- , O_2^- radical ($\bullet\text{O}_2^-$) and ozone itself (pH 6.59 at 25°C), as suggested in Eq. (4)-(7) [25,
 5 26, 28]. These reactions depicted that ozone decomposition could be accelerated as the ozone
 6 dosage and the reaction time increased, more promoting the generation of superoxide anion ($\bullet\text{O}_2^-$)
 7 with a much higher reaction rate of $1.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (Eq. (6)) involved in ozone decomposition,
 8 consequently leading to decrease of the off-gas ozone flow rate.



13 In the meantime, Fig. 3 showed that as higher as ozone dosage and as long as the reaction time
 14 could make the higher percentage of ozone uptake to be evident by comparing the control over
 15 the test of off-gas ozone flow rate: the ozone uptake by PE MP particles has been increased at the
 16 lowest to be 16% (injected ozone of 4 mg/min for 60 min), while at the highest to be 44% (7
 17 mg/min; 180 min). Moreover, it was presumed that the MP oxidation could be triggered as of a
 18 result of ozone uptake by PE MP particles. In other words, relatively lower dosage for shorter
 19 reaction time could be served as initiating oxidation of PE MP particles, which could be slightly
 20 enhanced by increasing the amount of ozone dosage at the same reaction time (*i.e.*, 60 min). On
 21 the contrary, extending the reaction time longer than 60 min at the same dosage could more
 22 increase the extent of oxidation of those of particles. It therefore implied that the reaction time

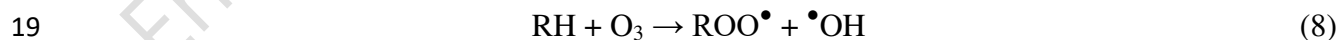
1 can be considered as the key factor in the uptake of ozone by PE MP particles, whereas the
2 ozone dosage might be served as a potential factor contributing in ozonation of them.

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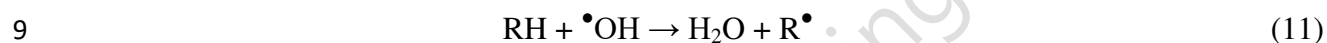
4 **3.2. FTIR Analysis of Ozonized PE MP Particles**

5 3.2.1. FTIR Spectra of treated PE MP particles

6 FTIR spectra (Fig. S1) showed that ozonation has generated new functionalities on the surface of
7 PE MP particles at the wavenumber of 1,030 cm^{-1} (C-O), 1,652 cm^{-1} (R-CHO with
8 intermolecular H-bond), 1,683 cm^{-1} (R-CO-OR'), 1,718 and 1,720 cm^{-1} (RC(=O)R') irrespective
9 of varying dosages and reaction times, whereas the peaks for vinyl group (900-1,000 cm^{-1}) was
10 not observed. In particular, the absorption band at 1,720 cm^{-1} (>C=O, stretching ketonic group)
11 reflects to the strong probability of aliphatic aldehydes, carboxylic acid and aliphatic ketones
12 being occurred [31] as well as smaller amount of carboxyl groups as of intermediates [32]. In
13 addition to, Kefeli et al. [33] reported that the ozonation of such saturated hydrocarbon chains
14 forms peroxy-radicals, which is then converted into peroxides, ketones, and aldehydes [34–36].
15 In other words, the appearance of these functionalities suggested by the fact that peroxy radicals
16 formed on the polymeric chain of PE MP particles due to the attack of ozone and its derivatives
17 (*i.e.*, reactive oxygen species) [28], furtherly generates hydroperoxides, ketones and alcohols
18 [37], as presented in following Eq. (8)-(10):



1 Besides, a broad absorption band between 1,100 to 1,200 cm^{-1} could be resulted from the
2 overlapping of different absorption groups including such as alcohols, esters, ethers and acids
3 [38], which were also attributed to the attack of OH^- , HO_2^- and O_2^- on the surface of the PE MP
4 particles. The generated OH^- played a role of initiator in the oxidation process by abstracting
5 hydrogen atoms from the polymeric chain, leading to the formation of alkyl radicals (Equation
6 (11)) which can eventually result in the generation of oxygenated functionalities. In addition to,
7 they are responsible for the formation of O_2^- under the presence of promoters (*e.g.*, ozone and
8 primary alcohol) inducing the surficial oxidation of PE MP particles [26].



10 In line with, the appearance of these carbon-oxygen functionalities is served as the major
11 indicator of changes taken place from oxidatively deformed polymers [39] which can in turn
12 provide the evident clue for their possible oxidative modifications occurred referring to the
13 Norrish type I and II reactions. The Norrish type I reaction (Fig. S2 (a)) produces acyl and alkyl
14 radicals. The acyl radicals further react with oxygen to produce polymer peracid radicals and
15 followed by polymer peracids abstracting hydrogen. These polymer peracids can breakdown into
16 hydroxyl radicals and polymer carboxyl radicals eventually converting into carbonyls together
17 with other functional groups. This reaction may be terminated via crosslinking. Whereas, in
18 Norrish type II reaction (Fig. S2 (b)), the hydrogen is abstracted from a γ carbon or polymeric
19 chain-end is decomposed to generate carbonyl and vinyl groups [29].

20 In the meantime, the broad absorption peaks observed between 3,400-3,600 cm^{-1} or at
21 1,377 cm^{-1} commonly assigned to the O-H bond of the alcohol groups. They might be arisen due
22 to the reaction with another alkyl radicals which can produce double bond/crosslink, or reaction

1 with the other reactive oxygen species leading to the formation of OH-containing functionalities
2 such as alcohols and hydroperoxide on the surface of PE [38]. In particular, the peak height
3 corresponded at the wavenumber of $3,555\text{ cm}^{-1}$ was appeared to be formed by the presence of
4 hydroperoxides [40], ultimately contributing to the generation of various functional groups such
5 as ketones [41] and concomitantly providing the active sites for the further oxidation process of
6 PE [34].

7 8 3.2.2. Carbonyl index (CI)

9 As aforementioned, carbonyl groups, in this study, were likely to be occurred on the surface of
10 PE MP particles through Norrish Type I reaction, since the newly appearance of vinyl groups
11 was not found in the FTIR spectra. They were significantly increased once ozone injected in
12 comparison with those of control, clearly implying that these oxidized functionalities (*i.e.*,
13 ketones and esters) were generated by the attack of radicals. For this reason, the carbonyl indices
14 (CIs) of each treated PE MP particles were compared by calculating based on the suggested
15 methodology in section of 2.3. As can be seen in Fig. 4, CI value for 180th min was tended to be
16 remarkably increased as the ozonation has been initiated, which was then furtherly escalated to
17 the highest value of 20% at the ozone dosed at 7 mg/min, even though their degrees of increment
18 were relatively small in the comparison with those of other literatures to be observed [32, 42].
19 Nevertheless, it was comparably implied that shorter reaction time may not effectively facilitate
20 in deriving that much of increase in the CIs comparing to that of the longer reaction time. It
21 might be ascribed to the fact that tight molecular arrangement still firmly resisted against those

1 of given shorter time of reaction, which in turn could make the longer treatment duration to be
2 needed to furtherly oxidize.

3

4 3.2.3. Hydroxyl index (HI)

5 Fig. 5 presented the changes in hydroxyl index (HI) of PE MP particles after the ozonation
6 treatment under 4 different dosages and three different reaction times, and it showed an overall
7 increasing trend of HIs (approx. 13%) for a relatively longer treatment duration (*i.e.*, 120 and
8 180 min), while shorter reaction for 60 min rather led to decreasing the HI values, even though
9 ozone has been increasingly injected as high as 7 mg/min into the reaction. It simply meant that
10 the higher increase of those of index for longer reaction time could be obviously justified by the
11 fact that there have been more extent of generation of hydroperoxides resulting from such
12 escalating ozone dosages and longer reaction time, which can be consequently subject to more
13 conversion of carbonyl groups, as previously described. However, in the case of 60 min, HI had
14 a decreasing trend despite of the increment of ozone dosages, because there might be not given
15 enough reaction time to be consumed to form the amount of hydroperoxides demanded in
16 modifying that of PE surfaces, even at 7 mg/min of inlet ozone dosage. Therefore, longer time
17 duration could be more predominant controlling factor rather than that of ozone dosage in more
18 significantly breaking down the surficial chemical structure of PE MP particles.

19

20 3.2.4. Crystallinity

21 Owing to their semi-crystalline structure [43], the crystallinity of PE MP particles has been
22 changed during the surficial modification to be progressed. Chain scission resulting from Norrish

1 I or II reactions reduces the entanglement density in amorphous phase, which allows for the
2 shorter chained molecules to be more freely loosened and to recrystallize each of the loosened
3 again to be attracted [39], consequently contributing to increase of crystallinity. On the contrary,
4 the crosslinking mainly occurred by Norrish type I reaction decrease the crystallinity of polymer
5 materials. In this study, the crystallinity has been declined all experimental conditions, in terms
6 of 4 different dosages and three different reaction times, compared to that of unmodified (Fig. 6),
7 implying that the Norrish type I reaction accompanied by crosslinking has been involved in the
8 surface modification of PE MP particles, as aforementioned. Moreover, the relatively more
9 prolonged reaction time could induce to the more inconsistent decrease of crystallinity in
10 comparison with the shorter of 60 min. It is presumably supposed that the crosslinking between
11 the PE molecules has been correspondingly broken down as a result of ozone uptake being
12 increased to agreeably attack PE MP particles for relatively longer time.

13

14 **3.3. X-ray Photoelectron Spectroscopy**

15 In order to get the clear information for variation of the carbon-oxygen functionalities on PE MP
16 surface after the ozone treatment for 180 min under the given 4 different ozone dosages, XPS
17 spectra of them were comparatively analyzed with low- (Fig. S3) and high-resolution scan modes
18 (Fig. 7), respectively. First, low-resolution scan modes for the control as of the unmodified and
19 the treated PE particles were compared to each other with respect to their elemental composition
20 and O/C ratio, which could distinguish to examine their possible surface oxidation to be occurred
21 (Table 1). From this, carbon (C) and oxygen (O) were majorly detected along with a relatively
22 small quantities of sodium (Na), nitrogen (N), and silicon (Si), which can be possibly derived

1 from the plastic additives used in the manufacturing process. The O/C ratio of ozonated PE MP
2 particles was gradually increased as higher as ozone dosage was applied, evidently indicating
3 that the surface oxidation of PE has been associated into instigating more hydrophilic nature.
4 Second, to further explain the changes occurring on the PE surface, high resolution scans of the
5 O1s and C1s region were obtained under four different ozone dosages as aforementioned, which
6 were then deconvoluted into three sub-peaks of at the binding energy of 531 eV (O-H), 533 eV
7 (C-O/C=O) and 534.5 eV (O-C=O) in the case of O1s region (Fig. 7 (a)-(e)), and 285 eV (C-
8 C/C-H), 286.5 eV (C-OH), and 288 eV (C=O) for C1s region (Fig. 7 (f)-(j)), respectively. In
9 regard to the O1s region, O-H and C-O bonds were initially formed in all PE MP particles
10 ozonated, readily changed into C=O, which were further converted into O-C=O groups,
11 depending on the inlet ozone dosages. For instance, it was observed that O-H groups are more
12 dominantly formed on the surface of PE particles along with little amount of C=O/C-O even at 4
13 mg/min (Fig. 7 (b)). Further increasing ozone dosage initiated to convert O-H groups into
14 carbonyl groups (Fig. 7 (c)) and consequently generated O-C=O groups at 7 mg/min (Fig. 7 (e)),
15 being in agreement with the result of ozone uptake and FTIR analysis. Likewise, the
16 deconvoluted C1s region (Fig. 7 (g)-(j)) showed the increase in the degree of intensity of C-OH
17 groups, whereas that of C-C bond was not significantly changed during ozonation process. It
18 implied that surficial change occurs only in the amorphous region, not crystalline region where
19 ozone hardly to penetrate, which has been verified from previous scientific publications [32].

20 On the other hand, the overall experimental data delineates that as greater as ozone dosage
21 and as longer as treatment time can more favor the extent of oxidation process to be more taken
22 place on the MP particles. However, in XPS result, it was observed that the relatively lower

1 ozone dosage supplied to the reaction chamber, 4 and 5 mg/min, clearly favors the more
2 increased formation of hydroxyl radicals [23], from which more than those of dosages further
3 added were still kept in increasing to the level of the radicals although the ozone uptake was
4 much higher increased. It was also demonstrated that ozonation of PE has a slow initiation stage
5 due to tight packing of its polymer molecules, which require a longer treatment time (at least 6 to
6 8 h) for the penetrating into the crystalline region to break down the polymeric chain. In this
7 aspect, the treatment duration of 180 min could be also still insufficient to effectively breaking
8 down the polymeric chains or innovatively change the surface morphology of those.

10 **4. Conclusion**

11 In this study, PE MP particles were ozonated under the given ozone injection conditions in terms
12 of varying ozone dosages and reaction time along with taking consideration for the quantification
13 of ozone uptake to investigate any possible surface chemical modifications on PE MP particles
14 as examined by the FTIR and XPS analyses. To sum up, it was concluded that shorter treatment
15 duration was insufficient to support the higher ozone uptake by PE MPs, while increasing
16 reaction time can enhance the level of ozone uptake rate and the degree of oxidation as having
17 been verified with the CI, HI and crystallinity together with the variation in carbon-oxygen
18 functionalities. These parameters overall indicated that the surface oxidation in the aqueous
19 phase was mainly attributed to the attack of reactive oxygen species generated from ozone
20 decomposition, which can make various functional groups on PE MP particles via Norrish type I
21 reaction accompanied by crosslinking. In line with this, the optimum dosage and duration time
22 were determined with 7 mg/min and 180 min, having a highest value of CI and HI while a lowest

1 crystallinity after the surface modification of PE MP particles. Nevertheless, further research will
2 be necessarily conducted to enhance the level of oxidation performance which can lead to more
3 increasingly breaking down MP in natural waters.

4 5 **Acknowledgement**

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10

11 **Author Contributions**

12 R.Z. (M.S. student) designed and conducted the experiment along with data analysis and writing
13 of the manuscript. S.Y.P (Ph.D. student) edited the manuscript and provided the critical feedback
14 and contributed to shape the research study. C.G.K (Professor, INHA University) approved all
15 the experimental results and modified the manuscript.

16

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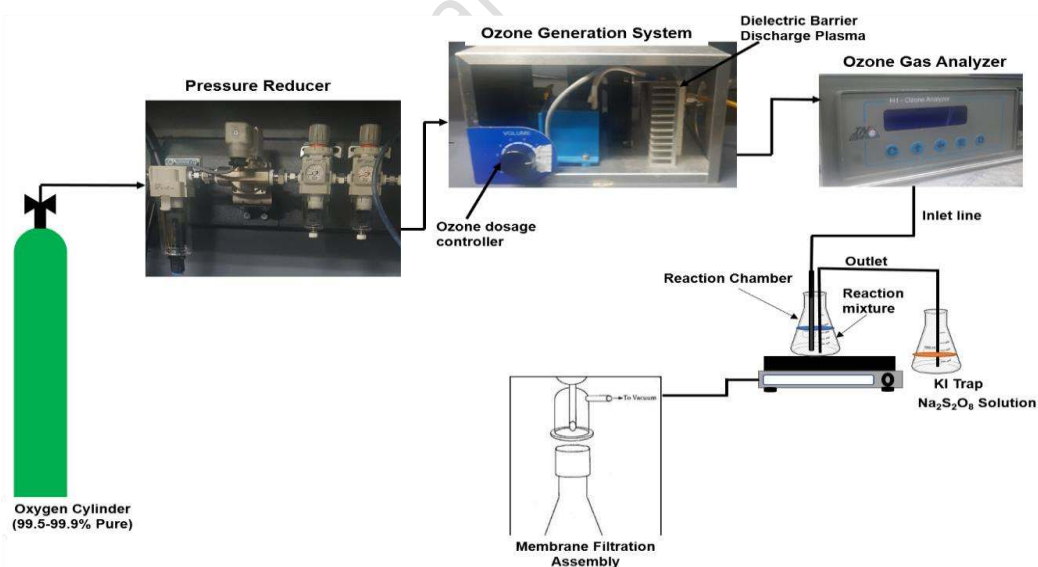
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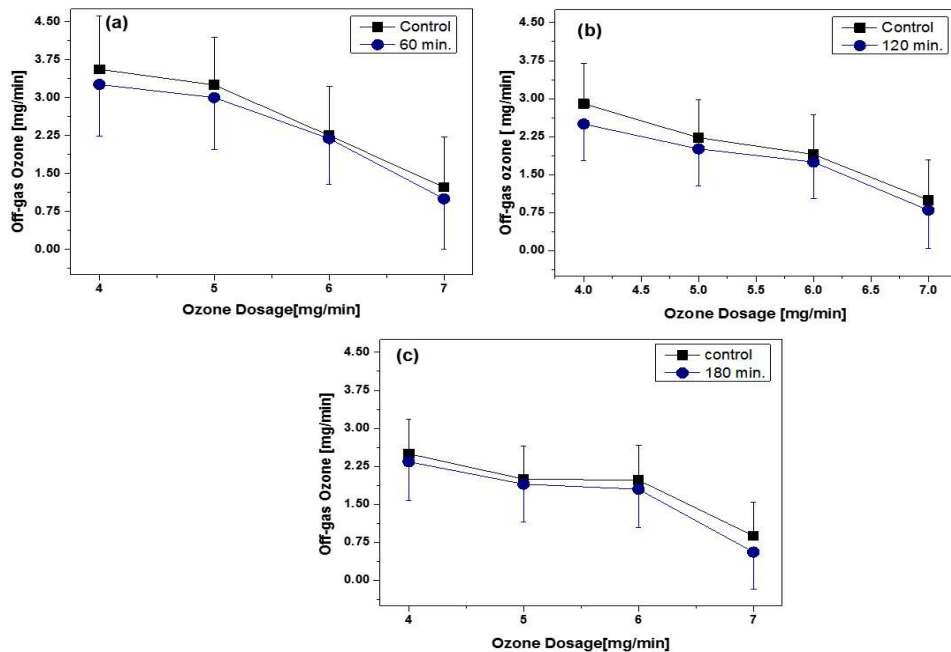
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14
 15 **Fig. 1.** Schematic diagram of ozone oxidation process on PE MP particles constituting of ozone
 16 generation system and reaction chamber.

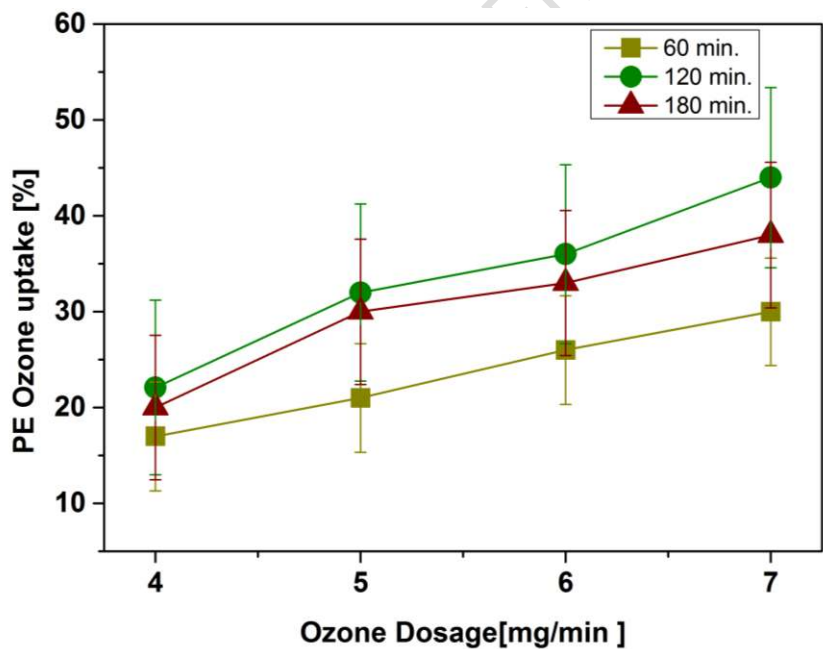
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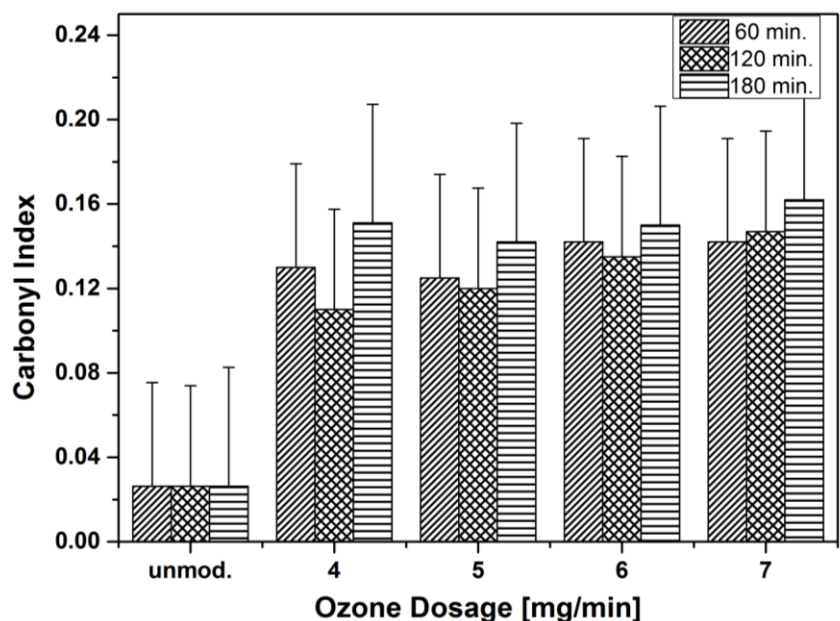
3 **Fig. 2.** The comparison of off-gas ozone flow rate in the presence/absence of PE MP particles
4 under the given inlet ozone dosages of 4, 5, 6, and 7 mg/min for (a) 60 min, (b) 120 min, and (c)
5 180 min, respectively.

6

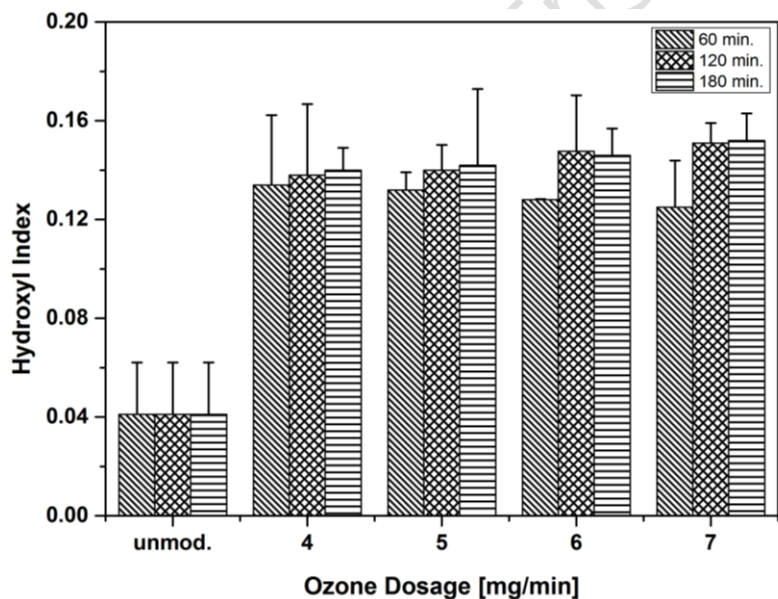


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8 **Fig. 3.** Percentage ozone uptake by PE MP particles during the ozonation at the ozone dosage of
9 4, 5, 6, and 7 mg/min for 60, 120, and 180 min.

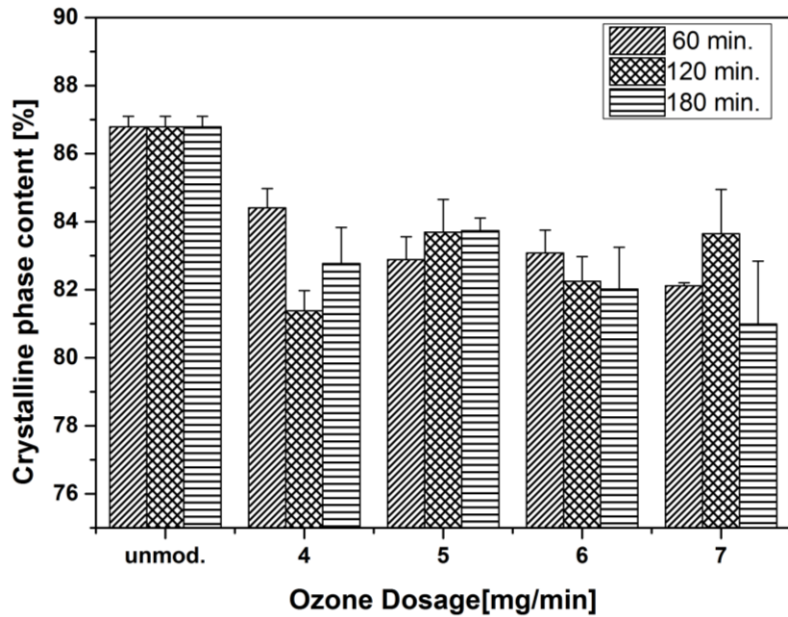


1
 2 **Fig. 4.** The variation of carbonyl index (CI, 1,600-1,800 cm^{-1}) estimated from the FTIR spectra
 3 for various ozone dosages and different treatment times in terms of 4, 5, 6, and 7 mg/min for 60,
 4 120, and 180 min normalized to the reference absorption band at 1,472 cm^{-1} .



6
 7 **Fig. 5.** The variation of hydroxyl index (HI, 3,200-3,600 cm^{-1}) for various ozone dosages and
 8 different treatment times in terms of 4, 5, 6, and 7 mg/min for 60, 120, and 180 min estimated
 9 from normalization with reference band of 1,472 cm^{-1} .

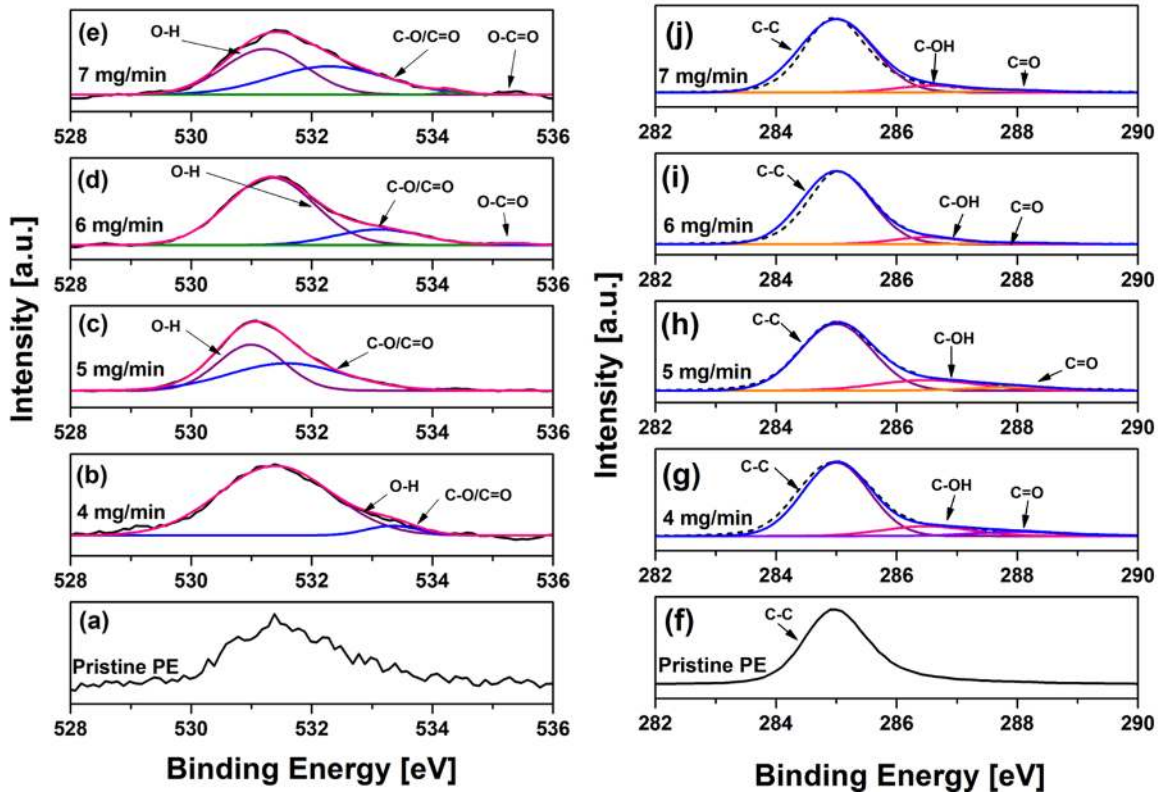
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1

2 **Fig. 6.** The variation of crystallinity for various ozone dosages and different treatment times in
 3 terms of 4, 5, 6, and 7 mg/min for 60, 120, and 180 min comparing to that of unmodified PE MP
 4 particles.

5



6

1 **Fig. 7.** The comparative study of deconvoluted peaks for the control and the tested by high
 2 resolution spectra of O1s into O-H, C-O/C=O (a-e) and C1s into C-C, C-OH and C=O (f-j),
 3 respectively.
 4

5 **Table 1.** The percentage of element composition of PE particles and their O/C ratio from the
 6 low-resolution spectra of XPS after the ozonation for 180 min.

Element	Unmodified PE	Ozone Dosages			
		4 mg/min	5 mg/min	6 mg/min	7 mg/min
Na	0.12	0.18	0.13	0.11	0.22
N	0.11	0.23	0.62	0.82	1.88
Si	0.10	0.22	0.39	1.09	1.67
O	2.5	2.9	3.3	3.6	3.9
C	96.7	96.28	94.68	94.66	92.21
O/C	0.025	0.030	0.034	0.038	0.042

7