

Study on Photodegradable Water-Soluble Compounds of Expanded Polystyrene

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Abstract : Many previous studies have focused on revealing the harmfulness of microplastic particles, whereas very few studies have focused on the effects of chemicals, particularly photooxidation product. In this study, products of photodegradation from expanded polystyrene (EPS), compounds produced by photolysis by ultraviolet (UV) light, were investigated. EPS was directly irradiated and photolyzed using a UV lamp, and then the extracted sample was analyzed using high-resolution mass spectrometry (HRMS). Multiple ionization techniques, including electrospray ionization, atmospheric pressure chemical ionization, and atmospheric pressure photoionization, were used. In total, >300 compounds were observed, among which polystyrene monomer, dimer, and oxidized products were observed. In this work, the data presented clearly demonstrate that it is necessary to identify and monitor oxidized plastic compounds and assess their effect on the environment.

Keywords : plastics, photodegradation, expanded polystyrene, water-soluble

Introduction

Currently, >300 million tons of plastics used in various forms in all fields are annually produced.¹ Only ~10% of this plastic is recycled, and ~8 million tons of plastic are dumped in the sea every year.^{2,3} This plastic waste that is dumped into the sea gets collected and has led to the formation of a huge island of plastic waste in the Pacific Ocean.⁴ For a long time, environmental degradation and pollution-related problems caused by plastics have been predicted; however, only recently has this issue attracted attention from the public.^{5,6} Plastics exist on the coast, in the sea, in rivers, in the soil, and even in the air.⁷⁻¹¹ Based on autopsies of the corpses of multiple marine animals washed up on the beach, plastic fragments have been identified in the stomach in all corpses examined.¹² Furthermore, microplastics have been reported in the

intestines of deep-sea shrimp living in the Peru–Chile Trench and Mariana Trench, both of which are the deepest locations in the world.¹³ Moreover, microplastics have been identified in the water we drink.¹⁴ Governments around the world are now implementing various regulatory policies and campaigns in an effort to reduce plastic usage.^{15,16}

In 2019, expanded polystyrene (EPS), one of the most used plastics (for use in construction, packaging and food containers), has a global market value of US\$9.7 billion.¹⁷ This share is expected to grow by 4.6% per year.¹⁷ In particular, it is the most representative plastic waste that can be easily identified on the coast.¹¹ EPS is reported most frequently per unit area among microplastics with sizes of 1–5 mm on Korean beaches.¹⁸ EPS is both useful for transporting and packaging chilled or frozen food and is extensively used as aquaculture buoys, which can be easily identified on beaches because aquaculture buoys are often lost or dumped in the sea.^{17,19} To summarize, EPS is extremely light among plastics such that it can be easily blown away by the wind, broken into smaller pieces by wind and waves, and it serves to transport various pollutants to move long distances.^{18,20-24} Chemical additives are used to make commercial plastics such as EPS.²⁵ Although the chemical identity of this additive is unclear, hazardous chemicals such as hexabromocyclododecane and phthalates are used as additives.^{7,19,22,26} Persistent organic pollutants when absorbed by the body disrupt the hormonal system.^{27,28} Under the influence of sunlight, plastic is degraded via a photocatalytic

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oxidation process.²⁹⁻³¹ It has ultraviolet (UV)-absorbing functional groups such as an aromatic ring or tertiary carbon of chain structure, therefore, it absorbs strong UV energy to form free radicals, which reacts with oxygen in the atmosphere.^{25,32} Because free radicals can break polymer bonds in plastics, the bonds in EPS can be broken down by photocatalytic oxidation by sunlight.³³ EPS counteracts the effects of microorganisms because of its aromatic backbone, favors a photochemical oxidation pathway that absorbs sunlight, and breaks down in smaller particles when exposed to UV light.³⁴ Fragmentation increases the surface area of EPS and accelerates this process. Photolysis of EPS produces dissolved organic carbon via a complex degradation pathway.^{25,35,36} Therefore, EPS can become a chemical contaminant.^{7,19,23,27} In particular, water-soluble chemicals can affect marine life.³⁷

Although there have been many studies on the effects of microplastics and leachate produced by EPS decomposition,^{38,39} very few of them have comprehensively identified chemical substances produced by photolysis.^{40,41} Because high-resolution mass spectrometry (HRMS) is extensively used to study environmental pollutants, it is helpful for identifying unknown compounds.⁴²⁻⁴⁴ In particular, electrospray ionization (ESI) is most extensively used for environmental analysis because it is suitable for polar molecular analysis.^{43,45} However, all ionization methods used in MS are inherently selective; therefore, use multiple ionization methods to comprehensively identify a wide range of chemicals present in a sample.⁴⁶ For example, both atmospheric pressure chemical ionization (APCI) and atmospheric pressure photoionization (APPI) are useful for analyzing non-polar molecules (not suitable for ESI). This study used HRMS and ESI, APCI, and APPI methods to identify water-soluble compounds produced from EPS degraded by UV light irradiation.

Experimental

Sample Preparation

The EPS was cut in a cube shape with a side length of ~0.5 cm, and the total weight was prepared to be ~0.5 g and placed in a transparent quartz crucible with 100 ml of purified water.²⁹ The UV output value of the experimental lamp (Newport 6258 Xenon lamp, CT, USA) was 300 W. In Korea, based on data published by the Korea Meteorological Administration (National Institute of Meteorological Sciences, 2018), the sum of the annual cumulative amount of UV A and B is 267.27 MJ/m². Therefore, 5 days and 6 h of exposure with the lamp corresponds to the sum of the annual cumulative amount of UV A and B in Korea. Thus, in this study, the samples were exposed for 5 days and 6 h. When EPS is irradiated using UV light, fine particles are generated, and the water color becomes yellowish and cloudy. The turbid water was filtered and extracted using solid-phase extraction (SPE) to

separate dissolved organic compounds. An Oasis PRiME HLB extraction cartridge from Waters Corporation (MA, USA) was used for extraction. All cartridges were washed with purified water and activated with methanol before sample extraction. Purified water and methanol used in the experiment were purified by J.T. A solvent from Baker-Fisher Scientific (NH, USA) was used. Moreover, two blank samples were prepared. One blank is purified water that has been exposed to UV light but does not contain EPS, and the other blank is EPS stored in purified water but without exposure to UV light. The UV exposure or storage time in purified water, and the SPE method is the same for both blanks and samples. They were prepared to compare EPS photodegradation because chemicals in EPS, such as additive compounds in EPS, can be extracted and dissolved in water.

MS Instrumentation

Samples extracted by SPE were analyzed using negative mode ESI and positive mode APCI and APPI MS. Three different ionization methods were used to treat a diverse range of compounds with different polarities. A direct injection Q-Exactive ion trap mass spectrometer (Thermo Scientific) was used for the analysis. The extracted sample was introduced in the mass spectrometer using a syringe pump (Hamilton Co., NV, USA). The capillary temperature was set to 300°C, the automatic gain control (AGC) value was set to 1×10^5 , the scan range was set to 90–460 *m/z*, and the S-lens value was set to 50.

Data Processing for MS.

MS data collection and processing were performed using a Thermo Fisher Scientific Xcalibur 4.0. A peak with a sample signal-to-noise (*S/N*) ratio higher than 30 and signal intensity higher than 1×10^5 was selected and processed. The background signal was removed using FunRich⁴⁷ (version 3.1.3). Chemical formulae were specified from the list observed within ($C_cH_hO_o$) 10 ppm error using conditions of C (0–200), H (0–400), and O (0–10). The molecular composition was determined using Composer64 (version 1.5.6) (Sierra Analytics Inc., Modesto, CA, USA) and our own program,^{48,49} and the double bond equivalence (DBE, double bond equivalence) was calculated as the chemical formula of $C_cH_hO_o$ using the following equation:

$$DBE = c - \frac{h}{2} + 1$$

Results and Discussion

To examine chemicals produced by UV exposure to EPS, samples obtained from SPE elution were analyzed with (-) ESI, (+) APCI, and (+)APPI MS. For (+) ESI, (-) APCI, and (-)APPI, the spectra obtained did not show any significant results compared to the background signal. Hence, the ionization techniques were not used in this study; rather, a

chemical formula was assigned to each signal value based on the mass accuracy. The ppm error between the theoretical mass value of the observed signal and the measured mass value was calculated using the following formula:

$$\text{ppm} = \frac{(\text{Observed mass} - \text{Theoretical mass})}{\text{Theoretical mass}} \times 10^6$$

Table 1 shows the examples of chemical formulas and ppm error values assigned for each m/z value. Furthermore, the assigned formulae identified in the spectrum of (-) ESI, (+) APCI, and (+) APPI are presented in the table. Most previous studies on plastics decomposition has been reported using ESI. However, the data presented in Table 1 show that using various ionization sources is necessary. For example, the chemicals not detected in ESI are detected in APCI and APPI and vice versa. Thus, depending on the ionization method used, different types of compounds are detected.

Figure 1 shows the number of compounds detected by each ionization techniques is presented as a Venn diagram. Overall, 152, 225, and 268 compounds were detected by (-) ESI, (+) APCI, and (+) APPI. APCI and APPI detected more number of compounds compared to ESI. Comparing results obtained from (+) APCI and (+) APPI, a larger number of the peaks (e.g., 196) were commonly observed; moreover, the most abundant peaks were commonly observed by (+) APCI and (+) APPI.

Figures 2a and b show the van Krevelen diagrams (VKD) of compounds observed only by each (-) ESI and

(+) APPI, respectively. VKD is frequently used to display HRMS data from complex mixtures. The structures of the major peaks were assigned based on polystyrene structures and are shown in the figures. Chemicals with a relatively high carbon-to-oxygen ratio (O/C ratio) were detected by ESI, according to the VKD. However, with APPI, compounds having a relatively low O/C ratio were detected.

Figures 2c and d show the VKD of the common compounds between (-) ESI and (+) APPI respectively

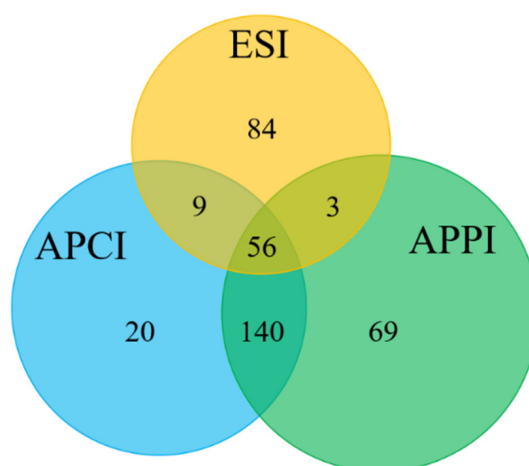


Figure 1. Venn diagram demonstrating the number of compounds identified by analyzing EPS photodegradation products using (-) ESI, (+) APCI and (+) APPI MS.

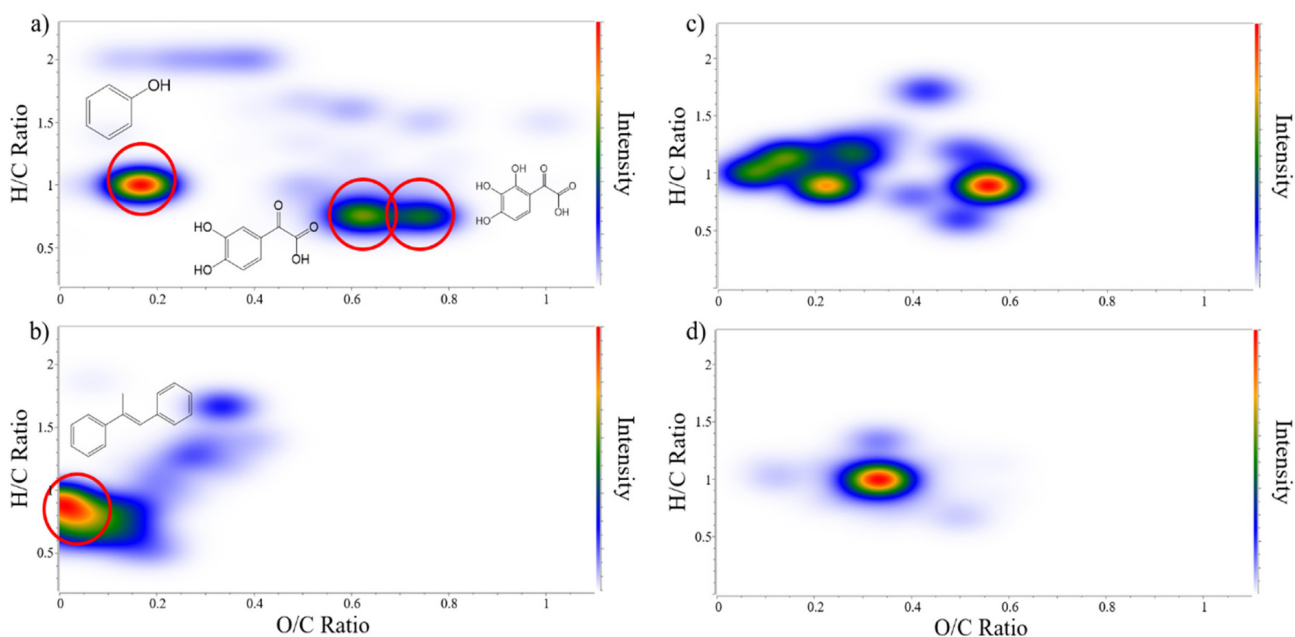


Figure 2. Ven Krevelen diagrams based on the compounds detected a) only with (-) ESI MS, b) only with (+) APPI, common between c) (-) ESI and d) (+) APPI.

Table 1. List of photodegradation products generated from EPS detected by (-)ESI, (+)APPI, and (+)APCI MS.

Assigned formula	Ionization method	Theoretical m/z	Observed ion m/z	Mass error
C ₆ H ₆ O	ESI	93.0346	93.0346	0.0
C ₈ H ₈	APCI	105.0699	105.0702	2.9
	APPI	105.0699	105.0702	2.9
C ₇ H ₆ O	APCI	107.0491	107.0494	2.8
	APPI	107.0491	107.0494	2.8
C ₇ H ₈ O	APPI	108.057	108.0572	1.9
C ₆ H ₆ O ₂	ESI	109.0295	109.0295	0.0
C ₉ H ₈	APCI	117.0699	117.0700	0.9
	APPI	121.0648	121.0649	0.8
C ₈ H ₈ O	APPI	121.0648	121.0649	0.8
	ESI	121.0295	121.0295	0.0
C ₇ H ₆ O ₂	APCI	123.0441	123.0441	0.0
C ₈ H ₆ O ₂	APCI	135.0441	135.0439	-1.5
	ESI	135.0452	135.0452	0.0
C ₈ H ₈ O ₂	APPI	137.0597	137.0596	-0.7
	ESI	137.0244	137.0244	0.0
C ₇ H ₆ O ₃	APCI	139.039	139.0388	-1.4
C ₉ H ₆ O ₂	APCI	147.0441	147.0438	-2.0
	APPI	149.0597	149.0595	-1.3
C ₉ H ₈ O ₂	APPI	149.0597	149.0596	-0.7
	ESI	151.0401	151.0401	0.0
C ₈ H ₈ O ₃	APCI	153.0546	153.0544	-1.3
	APPI	153.0546	153.0544	-1.3
C ₇ H ₆ O ₄	ESI	153.0193	153.0193	0.0
C ₈ H ₆ O ₄	ESI	165.0193	165.0194	0.6
C ₁₀ H ₁₀ O ₃	APPI	179.0703	179.0700	-1.7
C ₈ H ₆ O ₅	ESI	181.0143	181.0142	-0.6
	APCI	193.1012	193.1008	-2.1
C ₁₅ H ₁₂	APPI	193.1012	193.1009	-1.6
	ESI	197.0092	197.0083	-4.6
C ₈ H ₆ O ₆	APCI	209.0961	209.0957	-1.9
	APPI	209.0961	209.0957	-1.9
C ₁₅ H ₁₂ O	APCI	225.091	225.0905	-2.2
	APPI	225.091	225.0905	-2.2

(same m/z values, but different abundances). The data clearly show that the sensitivity of detection varies depending on the structure and composition of the chemical for each ionization technique. This agrees with the previous study's ionization preference results, which showed that ESI is suitable for ionizing more polar molecules, and APCI and APPI are suitable for ionizing less and non-polar molecules. To summarize, the results shown in Figure 2 show that different compounds can be observed depending on the ionization method used.

Figure 3 shows carbon number vs. DBE plots for the

HC, O₁, O₂, O₃ class compounds observed by (-) ESI and (+) APPI. The HC class compound is composed of only carbon and hydrogen without oxygen. The O_x class compound is composed of an unlimited number of carbon and hydrogen atoms and x number of the oxygen atom(s). For example, C₈H₈ belongs to the HC class and C₇H₆O to O₁ class. For ESI, results of O₁, O₂, and O₃ class compounds are obtained and presented. APCI shows the results of HC, O₁, and O₂ class compounds. The structure shown in each area is the structure predicted and proposed based on polystyrene structure. A styrene monomer

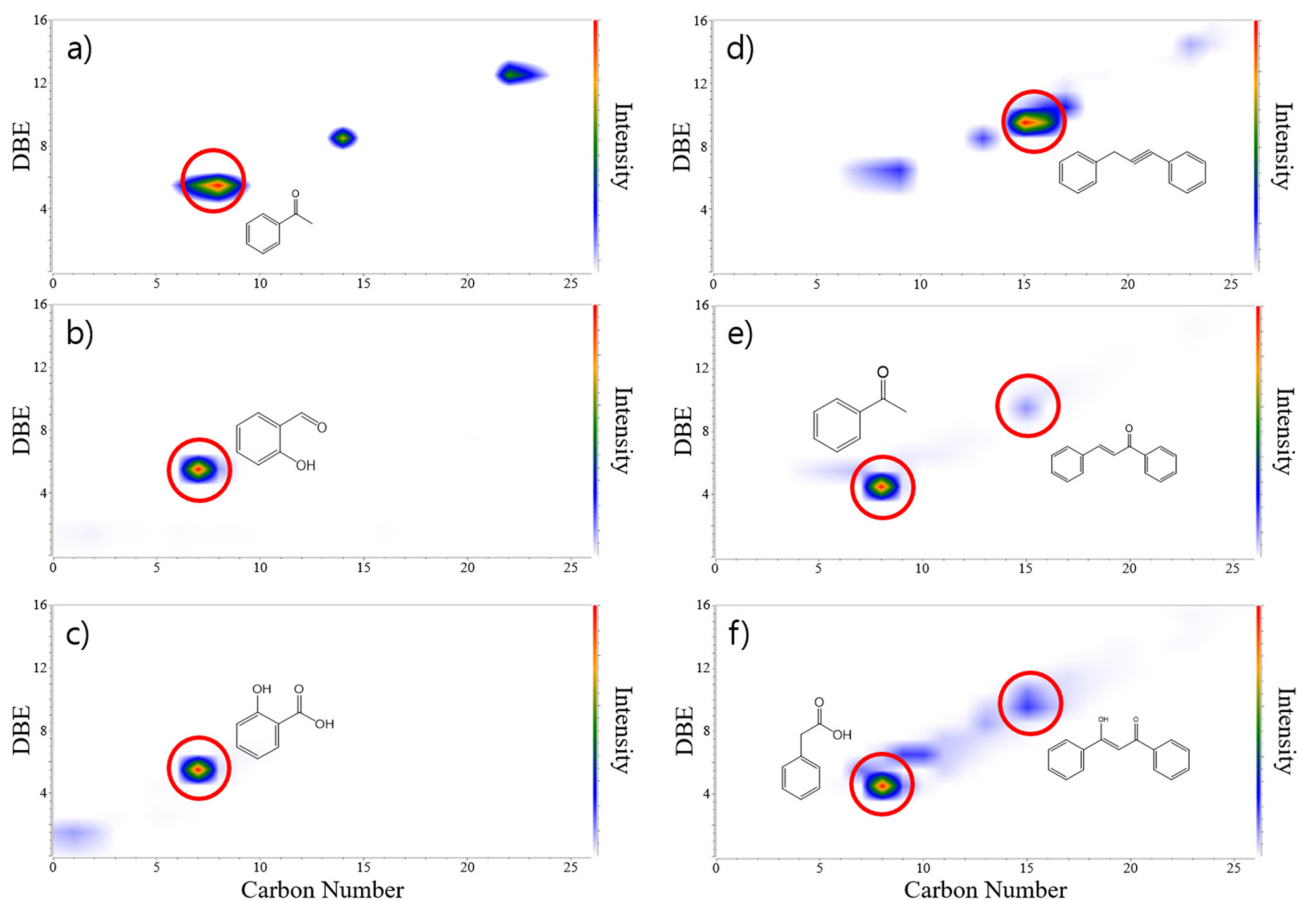


Figure 3. Carbon number vs DBE plots constructed from a) O₁, b) O₂, and c) O₃ class compounds observed with (-) ESI and d) HC, e) O₁, and f) O₂ class compounds detected with (+) APPI.

(C₈H₈), a dimer (C₁₆H₁₆), and a trimer (C₂₄H₂₄) are identified among decomposition products obtained by decomposing EPS using UV irradiation. Furthermore, the oxidation products of styrene such as benzaldehyde (C₇H₆O), hydroxybenzaldehyde (C₇H₆O₂), hydroxybenzoic acid (C₇H₆O₃), and phenylethanol (C₈H₁₀O) were observed. When EPS is oxidized and decomposed through UV energy, it is degraded and produced into multiple main structures.^{35,50-52} If these compounds can be separated and identified, the degradation mechanism can be revealed. Based on the MS data obtained from UV irradiation of EPS, a series of oxidation, beta cleavage, rearrangement, and isomerization reactions are expected to occur.

Conclusions

ESI, APCI, and APPI with HRMS were used to examine the polar and non-polar compounds produced by the photolysis of EPS. MS data show the presence of a variety of water-soluble chemicals, including hydrocarbon molecules and oxidative degradation products of styrene monomers and dimers. These results indicate that EPS is

photolyzed by UV light to produce various degradation products. This indicates that not only fine-grained EPS and various additives but also photodegradation products must be considered. Therefore, the information described in this study can provide a fundamental basis for evaluating the photodegradation consequences and effects of EPS.

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