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Master Thesis

聚氯乙烯管釋出塑膠微粒潛勢之研究：以臭氧、自由餘氯以及熱進行加速試驗老化

Release of Microplastics from Poly (Vinyl Chloride) Pipes: An Accelerated Aging of Ozonation, Chlorination and Thermal Conditioning

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本論文係紀煜騰君(學號 R09541125)在國立臺灣大學環境工程學研究所完成之碩士學位論文，於民國 112 年 07 月 24 日承下列考試委員審查通過及口試及格，特此證明。

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誌謝

這本碩士論文，雖說篇幅相對其他同學的著作較少，但內容濃縮了兩年多實驗不斷失敗再重鑄的精華，其中我首先感謝的是我的指導老師林逸彬老師，提供實驗室的資源、實驗建議，以及指導學術研究的思維，還有幫我改破英文；再者感謝家人提供金援讓我在台北沒有流落街頭。最後是實驗室的各位，在實驗室三年間，從一個研究經驗幾乎是零的菜鳥，到還算可以看的碩士畢業生，儀秦學姊在實驗參數設計的思考模式幫了我不少，雖然之後實驗方向被魔改了，但依樣畫葫蘆孵出另一組並不是難事。學姊一直是實驗室大家的靠山，下學期畢業後，新入實驗室的各位會有一段很長的陣痛期吧，排除學術研究的話，學姊同時也是一位很好的同儕，熱於分享而且經驗豐富，是讓身為宅宅的我踏出圈最棒的朋友。同屆已經畢業的靖軒，實力強不太愛說話，很暖心、手工技術又好，在學期間幫了我很多忙，也一起講過不少屁話，一起做計畫、揉黏土、採樣雖說辛苦，但都是在學期間重要的回憶，更重要的是還兼任我在學期間的最強靠山，同屆的子軒、葯筑，雖然交流較少，但在學期間互相幫忙做計畫、修課，也擔任了我這菜鳥在課堂間的靠山；而小我一屆的聖翔、文豪、佳洪、明勳，延畢一年的我跟他們就如同學一般的相處，一群男生總是能搞出不少丐一尤事，在延畢這一年不斷學習社交模式、學習與宅宅不同生活圈的事物上幫了我相當多忙，有時可以在學術上交流意見，亦或是聚再一起講屁話都是壓力的排出口。再小一屆的學弟妹們，學術交流上比較少，但偶爾待在實驗室時，一起聊天或是偶爾耍呆都能幫實驗室增添點色彩，總能排解 1-5 月枯燥的重複實驗期間的壓力。

本研究從塑膠微粒的檢測方法建立起，探索塑膠微粒檢測的資源、找不到顆粒、掃描不到有效圖譜、偵測極限不夠等困難，經歷萬難才在生命科學院的螢光顯微鏡扎了根，旋即面臨染劑的調配以及光源設定等困難，終於穩定下來開始進行研究也已過了將近半年的碰壁，但這正是實驗令人著迷的地方嗎？不斷碰壁，發現突破口，時而喪志，時而興奮，每次汲取失敗來優化實驗，正是做研究的醍醐味，正在閱讀這段的學弟/妹們準備好品嚐看看了嗎？

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摘要

塑膠微粒（microplastics）已被確認存在於大多數水體，包括海洋、河水以及自來水等等, 其中自來水與人類的生活最相關。淨水場內部之塑膠元件及配水系統中之塑膠管被認為是自來水中塑膠微粒的潛在來源，而在台灣塑膠管中又以聚氯乙烯（PVC）管為最大宗，幾乎可在所有建築物中見到。本研究透過以淨水程序中常出現的臭氧、氯消毒程序以及熱水進行 PVC 塑膠管的老化，並研究 PVC 管釋放塑膠微粒的潛在風險。實驗結果發現 PVC 管之塑膠微粒釋出量隨著臭氧、自由餘氯以及加熱暴露的條件提升而增加，各參數對應之最大釋出量可達 1,058、1,256 以及 1,303 # L^{-1}。在臭氧以及高溫暴露量提升下，雖說塑膠微粒釋出量提升，但並不影響所釋出塑膠微粒的尺寸組成比例，相對於自由餘氯的暴露，所釋出的塑膠微粒隨著自由餘氯曝露量提升而有變大的趨勢，代表著在餘氯暴露下，大尺寸的塑膠微粒較小尺寸的塑膠微粒更容易釋出。本研究同時也透過羰基指數（Carbonyl index, CI）估算羰基產物在 PVC 管表面上的生成量，配合掃描電子顯微鏡在微觀的尺度下觀察表面，發現到羰基指數在各條件下隨著臭氧、自由餘氯以及熱的暴露提升而變高，與此同時，也發現到孔洞大量生成在 PVC 管的表面，這些孔洞的生成可能與塑膠微粒的脫落有關。孔洞特性在不同條件老化亦有所不同。臭氧傾向於在表面生成孔洞後，持續攻擊孔洞內部使得孔洞尺徑比起較低濃度的臭氧老化更大；餘氯老化傾向於持續生成孔洞，孔洞數量隨著曝露量提升而提升，且表面有明顯受損；而 PVC 管在 80°C 高溫的老化下，表面粗糙度明顯提升，而且相較於臭氧、餘氯老化所生成的孔洞，高溫老化所生成的孔洞更小。儘管各機制對於孔洞生成條件不同，在 CI 隨著老化程度提升而提升的狀況下，可以推斷羰基產物（Carbonyl products）的生成可能與塑膠微粒的掉落有關。

關鍵字：塑膠微粒、聚氯乙烯管、老化、臭氧、餘氯、高溫

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ABSTRACT

Microplastics have been detected in most aquatic systems, including ocean, river and even drinking water. In the drinking water system, plastics pipes used in the water treatment facility and distribution system are potential sources of microplastics. In Taiwan, polyvinyl chloride (PVC) pipe is the most widely used plastic pipe. The potential hazard of microplastics release due to aging should be investigated. In this study, the effects of ozonation, chlorination and heating on the aging and release of microplastics from PVC pipes are investigated. The highest release of microplastics was found to be 1,058, 1,256 and 1,303 # L^{-1} after aging in 30 mg O_3 L^{-1}, 260 mg Cl_2 L^{-1} and 80^{o}C, respectively. The release of microplastics with a size in the range of 10-50 and >50 μm increased with increasing exposure of chlorine while those in size of 1-10 μm was not significantly changed. On the other hand, the size composition of released microplastics due to exposure of ozone and heat tended to maintain constant. The carbonyl index (CI) of PVC pipes generally increased with enhanced aging with ozone, chlorine and heating. Meanwhile, scanning electron microscope (SEM) images showed that hole structures developed on the surfaces of PVC pipes after aging. After the initial hole structures appeared, ozone tended to continuously attack the same sites resulting in bigger hole structures after enhanced ozone exposure. The exposure of chlorine tended to increase the hole structures in their abundance and damage the surface. For thermal aging, smaller

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hole structures and rougher surface were observed after aging at an elevated temperature. Although different surface morphologies were observed under different aging conditions, the formation of carbonyl functional groups on the surfaces may result in the surface roughness and ultimately lead to the detachments of microplastics from aged PVC pipes.

Keywords: microplastics, PVC pipes, accelerated aging, ozone, chlorine, heat

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Chapter 1 Introduction

1.1 Background

Low cost and high durability have led to the excess use of plastics over the past century, resulting in the proliferation of plastic products and plastic waste worldwide. Plastic pipes have been extensively used in water supply. According to the statistics of Taiwan Water Corporation, currently plastic pipes account for 45% of pipes used in water distribution systems in Taiwan (Taiwan Water Corporation, 2023). Plastic pipes may also be used in water treatment plants. Among the different types of plastic pipes, polyvinyl chloride (PVC) pipe dominates. PVC pipes may encounter highly reactive or aggressive substances, such as chlorine and ozone in the water treatment plant as well as in the distribution system. In the premise plumbing, PVC pipes may also be subjected to high temperature after the water is heated. The exposure to these strong oxidants or high temperature may degrade PVC pipes over time and make them a possible source of microplastics in drinking water. This research aims to evaluate the release of microplastic from PVC pipes under these conditions.

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1.2 Research objectives

The objectives of this research are to:

1. Investigate the effects of chlorination, ozonation and thermal conditioning on the release of microplastics from PVC pipes.

2. To explore the mechanisms causing the release of microplastics from PVC pipes.

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Chapter 2 Literature review

2.1 Introduction to Microplastics and their concerns

Plastics are synthetic polymers typically non-degradable in the nature. They tend to fragmentate into small debris and eventually become persistent in the environment (Geyer et al., 2017; Zhang et al., 2021). Plastic particles with a size ranging from 1 μm to 5 mm are termed as microplastics and those with a size less than 1 μm are termed as nanoplastic (Li et al., 2018; Vethaak and Legler, 2021). Microplastics can be further categorized as primary microplastics and secondary microplastics. Primary microplastics are those originally manufactured in micro-size, such as plastic powder and microbeads. In the contrast, secondary microplastics are tiny plastic debris less than 5 mm resulting from the break-down of the original plastic products (Li et al., 2018). Microplastics have been widely detected in seawater, surface runoff, river water, drinking water and even beer (Pivokonsky et al., 2018; Liu et al., 2019; Diaz-Basantes et al., 2020; Johnson et al., 2020; Tong et al., 2020; Wang et al., 2020; Bäuerlein et al., 2022).

The presence of microplastics has been documented in the potable water and drinking water (Johnson et al., 2020; Bäuerlein et al., 2022), which are prone to be ingested by human. The plastic pipes and plastic components could be the sources of microplastics in the water treatment plants (Mintenig et al., 2019). In Taiwan, many

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plastic pipes have been in service for a long time, especially in the premise piping system, and PVC pipe has been the dominant plastic pipe used in old buildings due to its low cost. Previous studies have demonstrated that the plastic pipes and plastic components used in the water treatment plant and distribution system could be the sources of microplastics under UV radiation (Zhang et al., 2022a), ozonation (Zhang et al., 2022b), and chlorination (Whelton and Dietrich, 2009).

Microplastics has become a growing concern for water quality, ecological and human health. It has been documented that microplastics can induce intestinal damage of aquatic life, release unbound monomer, and facilitate the transport of hazardous substances such as heavy metals and biofilm due to their adsorption on the microplastics (Brennecke et al., 2016; Lei et al., 2018; Marsden et al., 2019). Lei et al. (2018) further reported the size of microplastics plays a crucial role in their toxicological effects.

2.2 Detection of microplastics

The Fourier Transform infrared spectroscopy (FTIR) and Raman spectroscopy are common instruments used to qualify and quantify microplastics (Mintenig et al., 2019; Johnson et al., 2020). FTIR is a technique that utilizes a broad range of wavelength of infrared radiation to amplify the vibrational energy of molecules in the functional groups. By performing Fourier Transform on the obtained signal, an infrared spectrum is

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generated. Each functional group exhibits characteristic peaks at specific frequency in the infrared spectrum, allowing for identification and characterization of functional groups such as carbonyl and hydroxyl groups in plastics. By comparing the sample spectra with a reference database, the identification of plastics can be achieved. μFTIR (micro-FTIR) is specifically designed for analyzing small particles, including microplastics, with sizes in μm scale. Raman spectroscopy can be used to characterize the functional groups by measuring the Raman shift, which is the change in frequency of scattered light when it interacts with the functional groups in a molecule. Each functional group has a specific Raman shift, which can be used to identify the functional groups in a macromolecule. Although both FTIR and Raman spectroscopy can be used to detect microplastics, they typically require a long time to obtain reliable spectra. In addition, some particles are too small to obtain reliable spectra.

Stereo microscopy and fluorescent microscopy assisted with dye are also used to detect microplastics. The time required is shorter compared to those of μFTIR and μRaman. Typically, the microplastics to be analyzed are first labeled by a specific dye. Nile red is the most common dye that is used to label microplastics. The performance of Nile red can be affected by the types of the solvent used. Common solvents used include methanol, ethanol, acetone, and chloroform (Erni-Cassola et al., 2017; Tamminga et al., 2018; Konde et al., 2020). The labeled microplastics can be excited by a light-emitting

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diode (LED) with a specific range of wavelength and emit the fluorescent with a longer one. In general, the blue and green LED are frequently used. Since stereo microscopy and fluorescent microscopy lack the precision in detection because dye can be adsorbed onto most hydrophobic substances, these two methods are typically used as complementary methods to aid μFTIR and μRaman detection.

In terms of size determination, it has been proposed that one can calculate the diameter of various shapes of microplastics by assuming that the microplastics possess the same shape (e.g., circle or square) (Erni-Cassola et al., 2017), or use the Feret diameter, which defines the size of a particle based on the distance between two parallel lines that are tangential to the boundaries of the object (Tokai et al., 2021).

2.3 Surface characterization of aged plastics

The aging of plastics is typically assumed to be a process following the thermal-oxidative pathway. This process is a cascade of interaction between the surface structure of plastics and oxygen from the atmosphere (Ober and Müllen, 2012). The FTIR and Raman spectroscopy are two suitable tools to characterize the surface properties of degraded plastics. Kelkar et al. (2019) used Raman spectroscopy to characterize the chemical bonding on the surfaces of high-density polyethylene (HDPE), polypropylene (PP), and polystyrene (PS) after chlorination. It was found that the chlorine-carbon bonding at a Raman shift of 678 cm^{-1} appeared after the plastics exposed to a 25 g L^{-1} of

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free chlorine for 1 day. In another study, the aging of PVC by solar irradiation was found to generate surface carbonyl groups in the IR spectrum between 1700-1800 cm^{-1} by using the attenuated total reflection–Fourier Transform infrared (ATR-FTIR) (Jakubowicz and Möller, 1992). The formation of carbonyl groups on the surfaces is an indication of aging. To quantify the formation of carbonyl groups on the surface, it has been proposed that the carbonyl index (CI), which is defined as the ratio of peak integration of carbonyl groups to that of a reference functional group (typically methyl) on the IR spectrum, can be used to indicate the degree of aging (Ouyang et al., 2022; Zhang et al., 2022a; Zhang et al., 2022b). However, the range of IR spectrum used for the integration for carbonyl groups and the methyl group slightly varied across different studies, such as 1650-1850 cm^{-1} and 1420-1500 cm^{-1}(Celik et al., 2023), 1670-1750 cm^{-1} and 1410-1510 cm^{-1}(Ma et al., 2022), and 1779-1680 cm^{-1} and 1420-1490 cm^{-1} (ter Halle et al., 2016; ter Halle et al., 2017), respectively. The carbonyl groups are typically contained in the range of 1550-1810 cm^{-1} (Socrates, 2004) and the methyl group is typically selected in the range of 1400-1500 cm^{-1}. To cover the whole possible carbonyl band and methyl bands in the IR spectrum, the CI was calculated as Equation (1).

$$CI = \frac{I_{1550-1810}}{I_{1400-1500}} \quad (1)$$

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2.4 Effect of chlorination and ozonation on PVC

Chlorine and ozone are commonly used for disinfection or oxidation in water treatment. Chlorine is typically introduced to inactivate pathogens in water treatment. Chlorine is reactive and is able to provide disinfectant residual in water during it transport in the distribution system. The effectiveness of free chlorine disinfection can be described by the CT value, in which C and T represent the chlorine concentration (mg L^{-1} as Cl_2) and the contact time, respectively(Watson, 1908; Kelkar et al., 2019). It has been shown that free chlorine can degrade high-density polyethylene (HDPE) pipes and cause the change of the surface chemical bonding and release of small plastic particles if the CT value is high (Whelton and Dietrich, 2009; Kelkar et al., 2019).

Ozone is an oxidant/disinfectant commonly used in water treatment. Hydroxyl radicals can be generated by the chain reactions of ozone in water. (Staehelin and Hoigne, 1985). Both ozone and hydroxyl radicals can degrade plastics. For example, Zhang et al. (2022b) showed that ozonation damaged LDPE, HDPE, PP, and PVC pellets resulting in the release of microplastics. Wang et al. (2020) investigated the change of microplastics concentration in different treatment units in an advanced water treatment and found that the concentration of microplastics increased after the ozone process.

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Chapter 3 Material and Methods

3.1 Research framework

The research flowchart is shown in Figure1. Overall, this study aims to evaluate the release of microplastics from PVC pipes in chlorination, ozonation, and high temperature conditions and to explore the associated mechanisms.

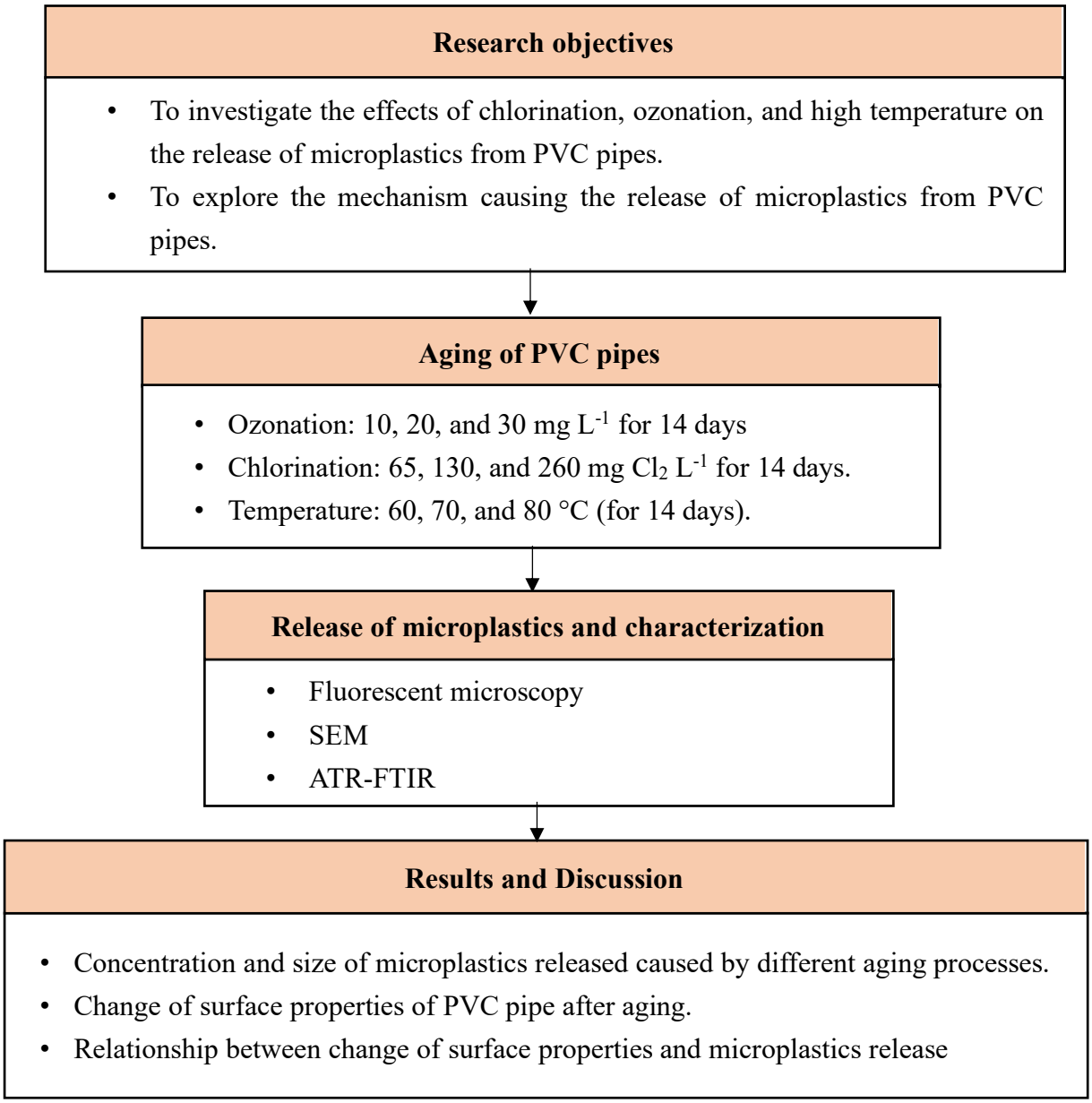

Figure 1. Research flowchart.

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3.2 Materials and chemicals

The PVC pipes (3/4 inches in diameter and 4 meters in length) used in this study were purchased from a local store. All sample pipes were prepared by cutting the pipes into 30-cm-length for experiment. PVC specimens (LxWxH = 10 mm x10 mm x1 mm) were cut from the PVC pipes and used for the characterization of changes in physical and chemical properties after the aging processes. Acetone (≥99.5%), potassium iodide (≥99.5%), and ethanol (≥99.8%) were purchased from Honeywell-Fluka, USA. Nile red powder, Potassium indigo trisulfonate, and high-molecular-weight PVC powder were purchased from Sigma-Aldrich, USA. Ferrous ammoniums sulfate 6-hydrate (98.5-101.5%), sodium hypochlorite solution (5% available chlorine), phosphoric acid (85.0%-87.0%), and Sodium hydroxide pellets (98.2%) were obtained from JT Baker, USA. Sodium dihydrogen phosphate dihydrate (98.0-102.0%) was brought from Nacalai-tesque, JP. N,N-diethyl-1,4-phenylenediammonium sulfate (DPD, ≥99.5%) was purchased from Merck-kGaA, Germany. The deionized water (18.2 MΩ ·cm) used in this experiment were prepared from a PURELAB Classical system (ELGA, UK). All solutions were pre-filtered using a 0.5 μm pore size filter membrane (ADVANTEC GC-50, Japan) to avoid foreign particles. The microplastics released from the aged PVC pipes were collected using a 0.7 μm pore size filter membrane (Whatman, UK).

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3.3 Stock solutions

Ozone stock solution was prepared using the following steps. 1 L DI water was acidified using 0.1 N HCl in the iced bath until pH < 4 prior to purging N_2 gas for at least an hour to remove CO_2 and maximize O_3 dissolution capacity. The O_3 gas were generated by feeding pure O_2 gas to an ozone generator (COM-AD-02, Anseros, Germany), then directed to the water in a gas washing bottle with a constant flowrate of 30 NL h^{-1} for at least 3 hours, which resulted in a saturated concentration in the range of 38~45 mg L^{-1}. The residual O_3 in the effluent of gas washing bottle was quenched by concentrated KI solutions (Figure 2.).

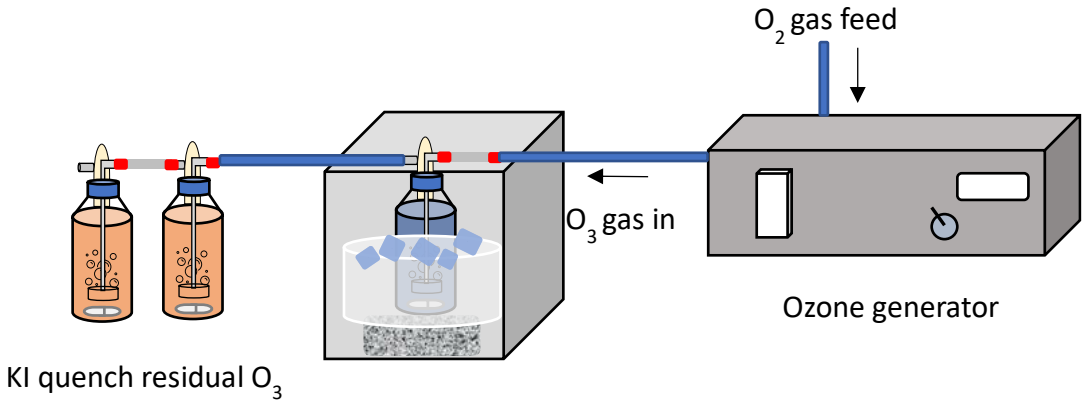

Figure 2. Schematic of preparation of ozone stock solution.

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Nile red stock solution was prepared by dissolving 20 mg of Nile red powder in 10 mL solvent consisting of acetone and ethanol at a 1:1 ratio. The stock solution was stored in 4°C. The stock solution was prepared every 3 months.

Indigo stock solution was prepared following the procedures described in the Standard Method (4500-O_3). 1 mL of phosphoric acid was added into DI water in an 1 L volumetric flask prior to dissolving 770 mg of potassium indigo trisulfonate, followed by the replenish of DI water for a total volume of 1 L. This indigo stock solution was stored in the dark condition at room temperature and remained stable for 4 months. Indigo reagent II for the determination of ozone concentration greater than 0.3 mg L^{-1} was prepared by the addition of 13 g of sodium dihydrogen phosphate dihydrate, 7 mL of concentrated phosphoric acid, and 100 mL of indigo trisulfonate stock solution in a 1 L volumetric flask, then filled DI water until 1 L mark.

3.4 Ageing of PVC pipes

The influences of three aging processes including chlorine aging, ozone aging and thermal aging on the release of microplastics from PVC pipes were investigated in this study.

For chlorine aging, the dosage of chlorine was estimated by the CT values. Based on the data from the Taipei Water Department, the average concentration of residual chlorine

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in the distribution system was 0.5 mg L^{-1} as Cl_2 in 2022. Here, 5, 10, and 20 years of service life were considered. To accelerate the chlorine aging in 14-day exposure, the required chlorine concentration was determined to be 65, 130, and 260 mg L^{-1}, which corresponded to the CT values of 910, 1,820, and 3,640 mg-day L^{-1}, respectively.

For ozone aging, 75 mL of ozone solution with a concentration of 10, 20, or 30 mg O_3 L^{-1} was used to fill the PVC pipes, and both ends of the pipe were be sealed with PVC hat. After one day, the ozone solution was collected, and the pipes were refilled with fresh O_3 solution. The procedures were repeated for 14 days. The microplastics released during the 14-day ozone incubation period were analyzed.

For thermal aging, the PVC pipes were filled with DI water and incubated in a container inside the water bath with a temperature of 60, 70, or 80°C as shown in Figure 3. Each pipe is covered by aluminum foil and PVC hat on the top and bottom, respectively. The DI water was collected and replenished with new DI water everyday. The procedures were repeated for 14 days.

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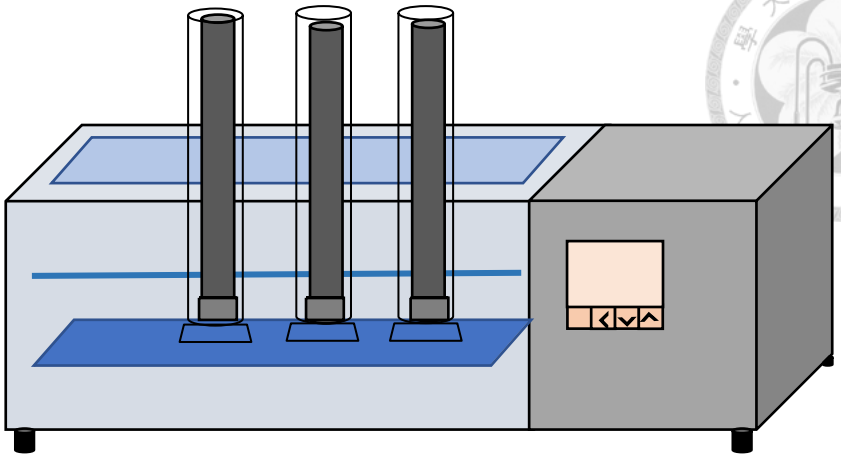

Figure 3. Schematic of thermal conditioning.

3.5 Analytical methods

For microplastic detection, the microplastics released during the aging process were collected using a 47 mm diameter glass fiber filter membrane with a 0.7 μm pore size. The filter was dried at 60°C for 30 minutes. Nile red with a concentration of 2 μg mL^{-1} was introduced to label the microplastics collected on the filter membrane, followed by the incubation at 50°C in the oven for 10 mins as shown in Figure 5. Nile red could be excited by certain wavelengths of LED and emit the fluorescence with a longer wavelength. To determine the suitable excitation wavelength of the LED for PVC, the confocal microscopy (AxioObserver Z1, Zeiss, Germany) was introduced to scan the emission wavelength. Two LED sources of 488 nm (blue) and 561 nm (green) were selected as they have been introduced as the excitation source for PVC microplastics (Erni-Cassola et al., 2017).

The emitted fluorescence intensity of purchased PVC powder and fragment of PVC

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pipes for every 5 nm was measured as shown in Figure 4. The maximum fluorescence intensities occurred at 620 and 635 nm for both PVC powder and PVC pipe samples and the green LED (561 nm) showed a more consistent excitation for the two samples. Thus, the excitation using green LED was employed for the fluorescent microscope.

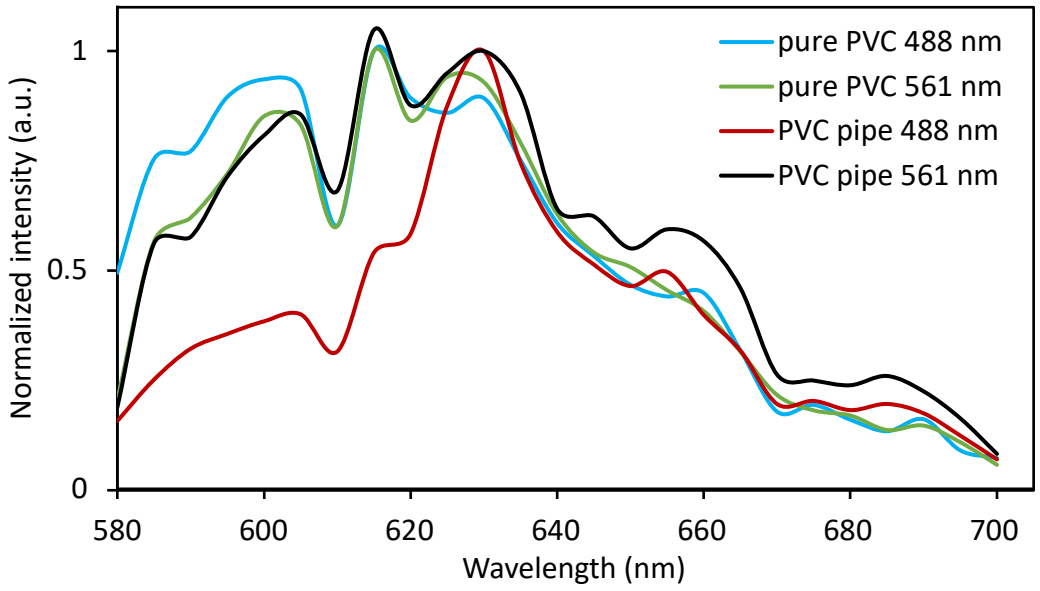

Figure 4. Emitted fluorescent of pure PVC powder and fragment of PVC pipes excited by the Blue (488 nm) and green (561 nm) LED.

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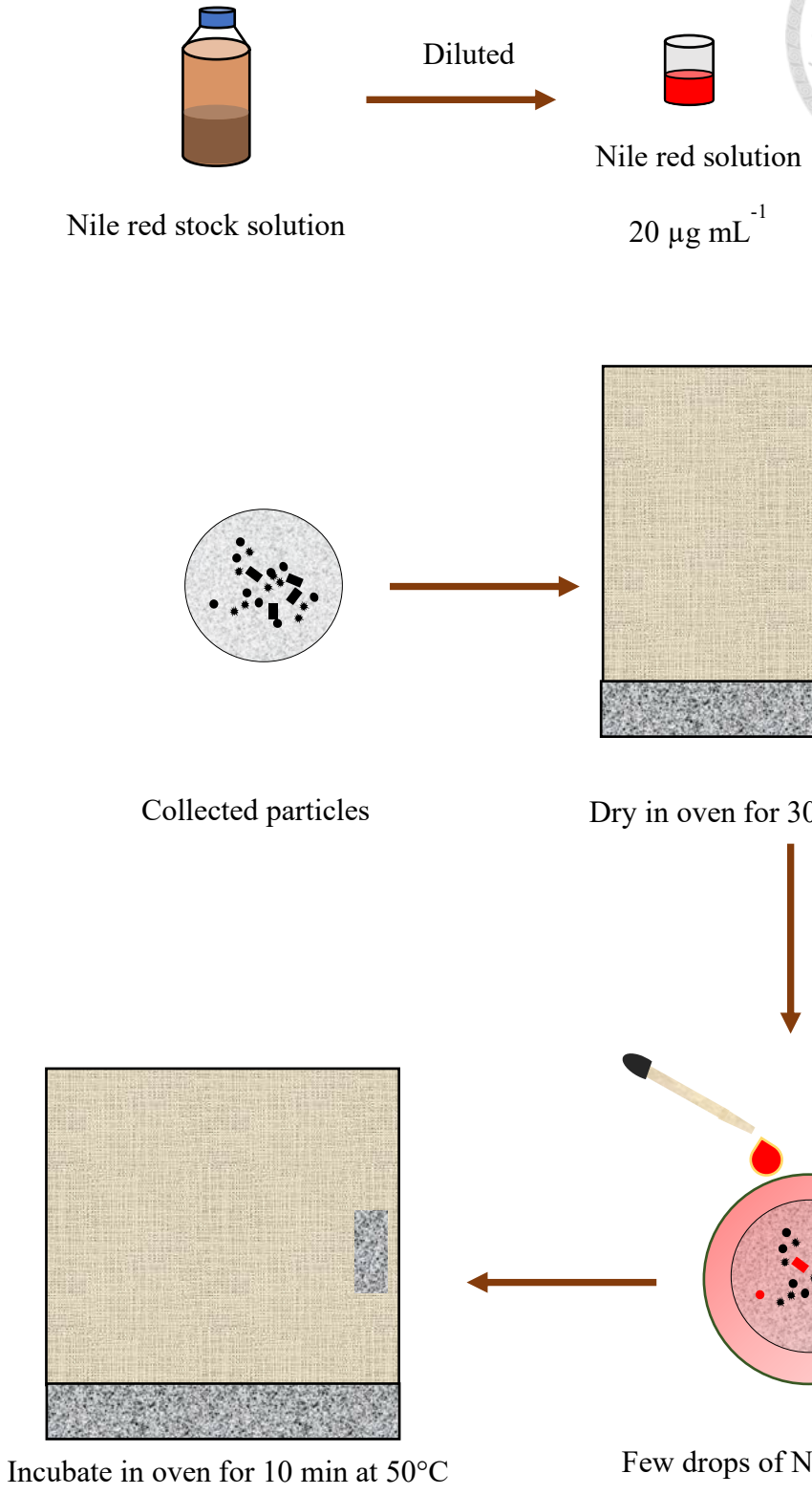

Figure 5. Procedure of Nile red labeling

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Scanning electron microscopy (SEM; JEOL JSM 6000F, Japan) was used to investigate surface degradation caused by the aging processes and magnification was set 500x. Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR, PerkinElmer, Frontier, USA) was used to analyze the chemical composition on the surfaces to determine the CI for different aging processes. The IR spectrum was at 4 cm^{-1} resolution and determined using 16 scans from 4000-650 cm^{-1}. The IR spectrum was processed using Origin Pro, including the baseline removal, smoothing, and normalization. The integration of IR spectrum was carried out by excel using Trapezoidal rule as Equation (2).

$$\int_a^b f(x)dx \approx \sum_{i=1}^{N} \frac{f(x_i)+f(x_{i+1})}{2} \Delta x \quad (2)$$

Solution pH was measured using the pH meter (SP2100, SUNTEX, Taiwan) with an electrode pre-calibrated using pH 4.0, 7.0, and 10.0 standard solutions. The concentration of free chlorine was determined by the Standard Method 4500-Cl G. DPD colorimetric method (Rice et al., 2012). 10 mL of sample was mixed with 0.5 mL of N,N-Diethyl-p-phenylenediamine (DPD) indicator solution and 0.5 mL phosphate buffer solution, and measure the absorbance with UV spectrophotometer (UV-1800, Shimadzu, Japan) in 515 nm, then convert the absorbance to equivalent Cl_2 concentration.

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The absorbance of ozone stock solution was measured by the UV spectrophotometer at 258 nm using a 1:1 diluted stock solution and the concentration of stock solution was calculated by Beer-Lambert's law as shown in Equation (3).

$$[O_3] = \frac{(MW)(ABS)}{(b)(\varepsilon)} \times 2 \times 1000 \frac{mg}{g} \quad (3)$$

where the $[O_3]$ represents the concentration of ozone (mgL^{-1}), MW represents the molecular weight of ozone (48 $g\,mol^{-1}$), ABS represents the absorbance at 258 nm of the 1:1 diluted ozone stock solution, b and ε represent the length of the cell (1 cm) and extinction coefficient for ozone (3100 $M^{-1}cm^{-1}$), respectively.

The ozone concentration of the experimental solution was determined by the Standard Method 4500-O_3 B. Indigo Colorimetric Method (Rice et al., 2012). 1 mL of ozone experimental solution was mixed with 9 mL of indigo reagent II and the absorbance at 600 nm was measured by the UV spectrophotometer. The concentration of ozone was calculated by Equation (4).

$$[O_3] = \frac{(\Delta ABS)(V_T)}{(f)(b)(V_S)} \quad (4)$$

where ΔABS represents difference of absorbance between blank (9 mL indigo reagent II

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and 1 mL deionized water) and the diluted ozone solution; Vt and Vs represent total volume (10 mL) and sample volume (1 mL), respectively; f and b represent the sensitivity factor (0.42 L (mg O_3) $^{-1}$ cm^{-1}) and the length of cell (1 cm), respectively.

Fluorescent microscopy (AxioImager.Z2, Zeiss, Germany) was used to quantify microplastics. To minimize the bias, the entire filter membrane was analyzed instead of selecting random cells for analysis. The cells were separately scanned and then merged. A total of 1,521 divided cells (1,320 μm * 1,320 μm each) were scanned using an excitation source of 555±25 nm. To avoid photobleaching, the power of the LED and exposure time were kept to a minimum. The merged image was then analyzed using ImageJ, with the image being adjusted to 8 bits. A threshold with a lower limit ranging from 25-30 and an upper limit of 255 were set to mark the microplastics. All PVC particles with a projected area greater than 1 μm^2 could be detected by this method.

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Chapter 4 Result and Discussion

4.1 Effect of pH on the release of microplastics

The influences of pH on the release of microplastics from PVC pipe segments are shown in Figure 6. The average concentrations of microplastics released at pH=10, 7, and pH=4 were determined to be 234, 266, and 342 # L^{-1}, respectively. Statistically, solution pH does not affect significantly the release of microplastics from PVC pipe based on these results ($p>0.05$).

It should be noted that when evaluating the influences of ozone exposure, chlorine exposure and temperature on the release of microplastics from PVC pipe, the solution pH was not fixed at a constant value for all experiments. For example, the pH values for 10-30 mg/L ozone solutions were around pH 4 and those for 65-260 mg/L as Cl_2 chlorine solutions were around pH 10, respectively. For the influences of temperature, the solution pH was maintained at around pH 7.

Despite the results showed that the influence of pH on the release of microplastics was not significant, a slight increase of microplastics release the increasing pH was observed, which might be attributed to sample variations or experimental errors. Nevertheless, the influence of pH on the detachment of microplastics was assumed to be minor.

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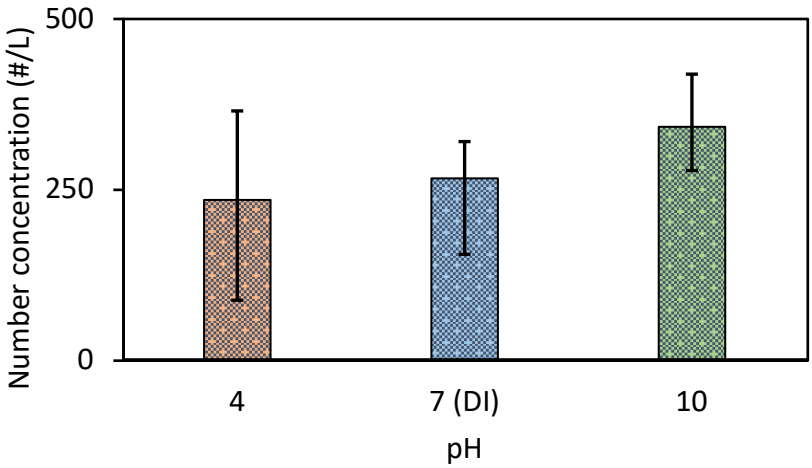

Figure 6. Release of microplastics after pH=4, DI (pH≈7), and pH=10 solution aging.

4.2 Effect of ozonation on the release of microplastics

The influences of ozone aging on the release of microplastics from PVC pipes are shown in Figure 7. In general, the release of microplastics increased with the increasing ozone exposure ($p<0.05$), with the maximum release of 1,058 # L^{-1} when PVC pipes were incubated in an ozone concentration of 30 mg L^{-1}. It should note that the pH in each ozone concentration ranged from pH 4 to pH 5 and the control experiment was conducted using pH 7 DI water. As shown previously, the pH played a minor role in the release of microplastics. Zhang et al. (2022b) used ozone with a constant mass flowrate of 8 mg min^{-1} to age PVC pellets at 85°C, then the aged PVC pellets were taken out and added to 1 L of finished water and placed in a shaker rotating at 400 rpm for 12 h to investigate the potential to release microplastics. The concentration of PVC microplastics released in this particular study was only about 63±13 # L^{-1}. The relative low concentration of PVC

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microplastics, compared to this study, could be due to the faster decay of ozone at a higher temperature, the solution used did not decarbonated to maximize the capacity of ozone dissolution, or the maximum release of microplastics was occurred while PVC pellets was aging, hence the effect of ozone on release of microplastics could be underestimated.

The size distributions of microplastics released after different ozone exposure are shown in Figure 8. It was found that the microplastics with a size of <10 μm and 10-50 μm increased with the increasing ozone concentration while those with a size >50 μm did not show notable changes in their abundance. The distribution of microplastics sizes for each ozone exposure did not show significant differences as shown in Figure 9.

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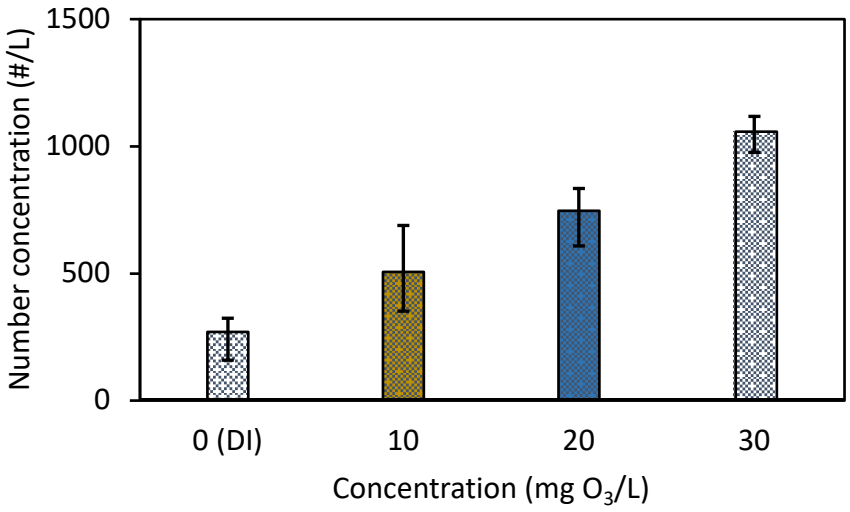

Figure 7. Release of microplastics from PVC pipes after ozone aging.

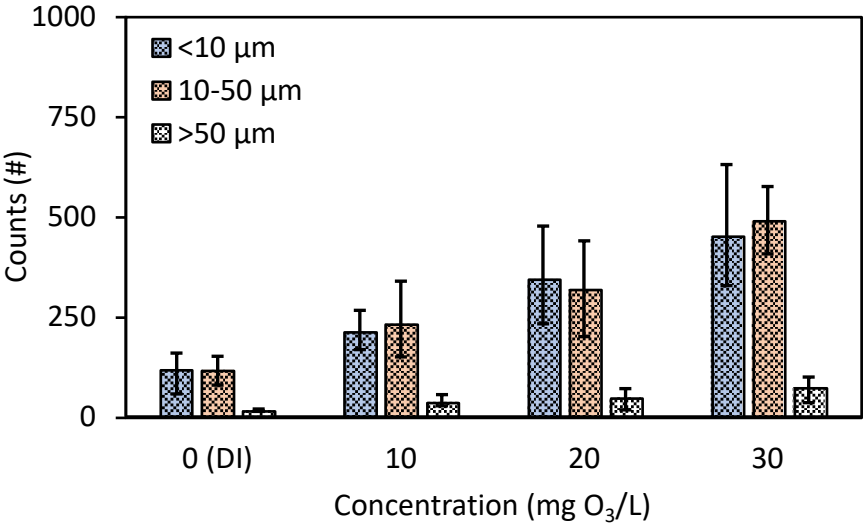

Figure 8. Size distribution of released microplastics after ozone aging.

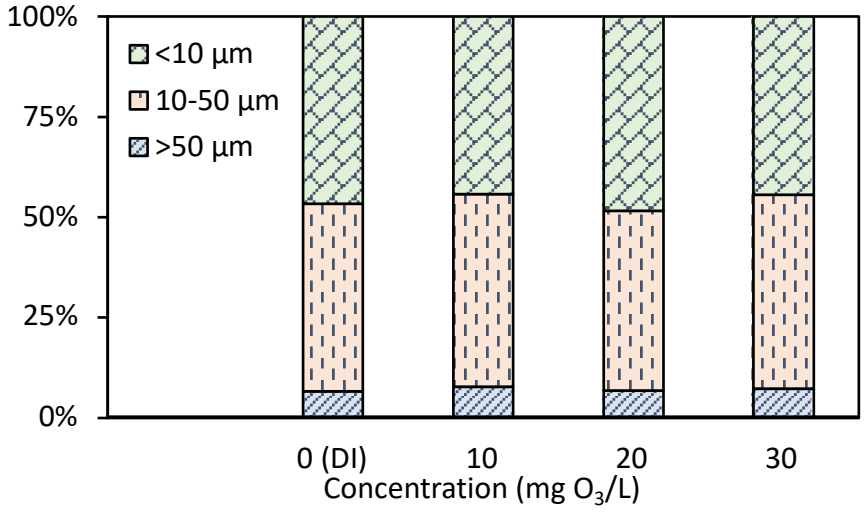

Figure 9. Percentage of different size of microplastics after ozone aging.

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4.3 Effect of chlorine on the release of microplastics

The influences of chlorine aging on the release of microplastics from PVC pipes are shown in Figure 10. In general, the release of microplastics increased with the increasing chlorine exposure ($p<0.05$), with the maximum release of 1,256 # L^{-1} when PVC pipes were incubated with a concentration of 260 mg Cl_2 L^{-1}. It should be noted that the chlorine solution was prepared using sodium hypochlorite, which is a weak base. The pH in different chlorine concentrations ranged from pH 9 to pH 10.

The size distributions of microplastics released after aging in different dose of chlorine are shown in Figure 11. It was found that the microplastics with a size of 10-50 and >50 μm increased with the increasing chlorine exposure while those with a size <10 μm did not show notable changes in their abundance. The size distributions of microplastics released after different chlorine exposure are shown in Figure 12. The percentage of >50 μm microplastics increased with the increasing chlorine exposure while those <10 μm showed the opposite trend, indicating that a higher exposure of chlorine tended to enhance the release of larger microplastics.

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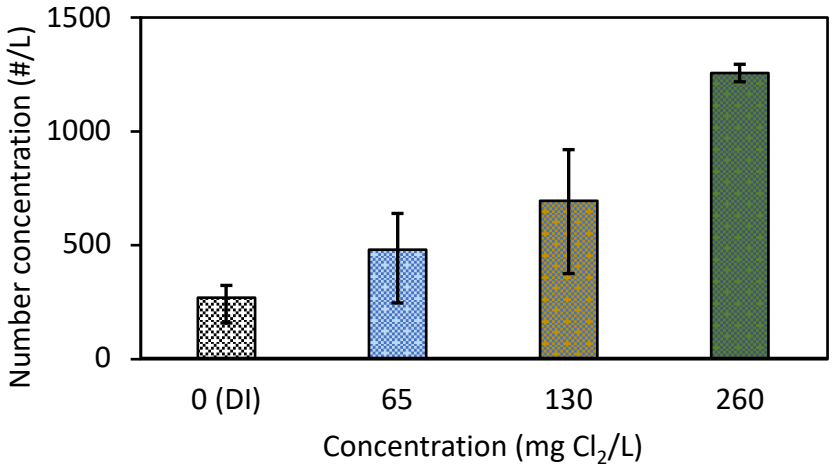

Figure 10. Release of microplastics after chlorine aging.

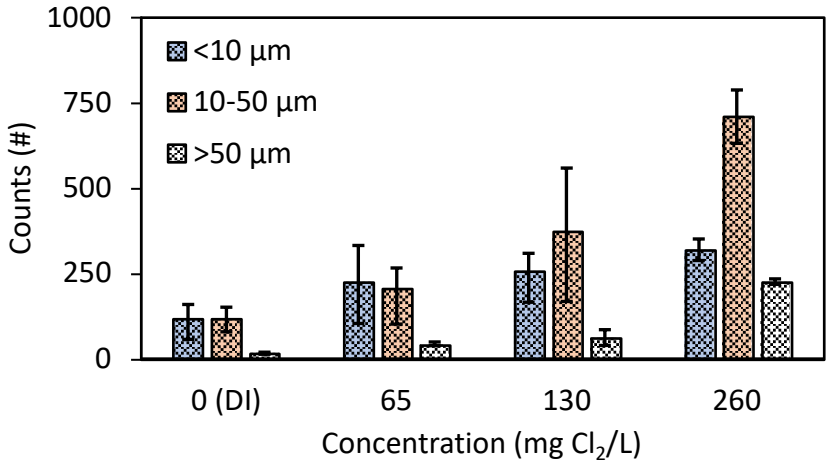

Figure 11. Size distribution of released microplastics after chlorine aging.

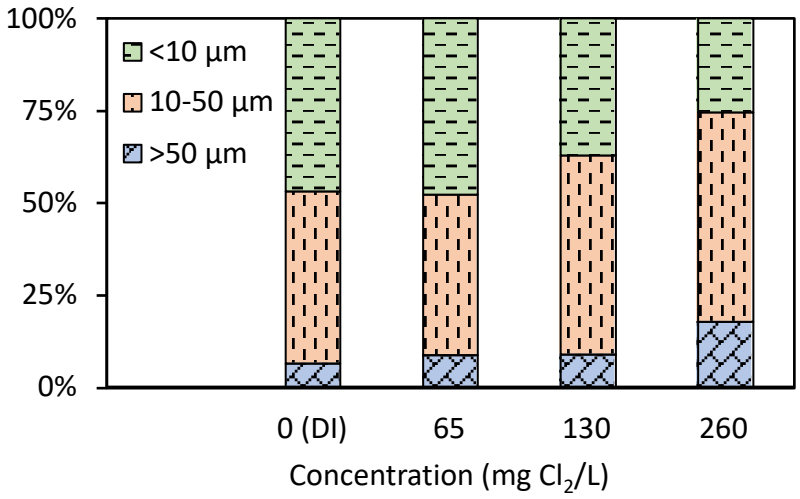

Figure 12. Percentage of different size of microplastics after chlorine aging.

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4.4 Effect of heat on the release of microplastics

The influences of temperature on the release of microplastics from PVC pipes are shown in Figure 13. The release of microplastics increased with the increasing temperature ($p<0.05$), with the maximum release of 1,303 # L^{-1} when PVC pipes were incubated at 80°C.

The size distributions of microplastics released after aging at different temperatures are shown in Figure 14. It was found that the microplastics with a size of <10 and 10-50, and >50 μm all increased with the increasing temperature. The percentage of microplastics sizes for different temperature is shown Figure 15. The percentage of microplastics did not change significantly with temperature despite the concentration increased with the increasing temperature.

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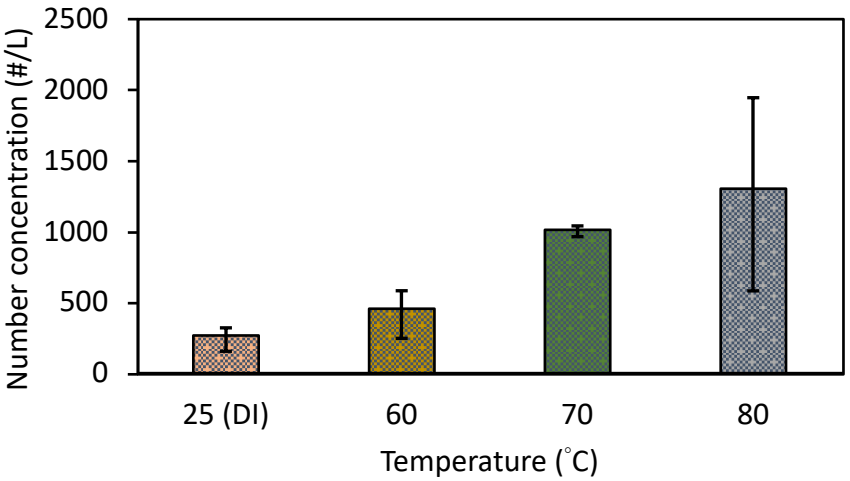

Figure 13. Release of microplastics from PVC pipes after aging at different temperatures.

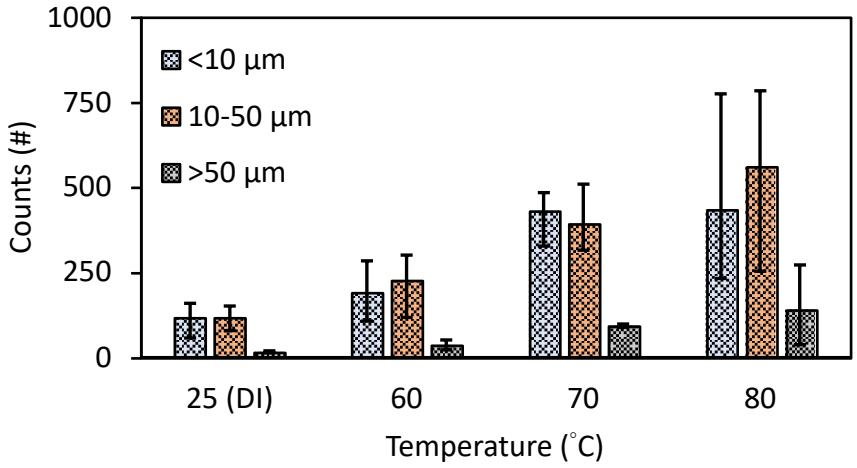

Figure 14. Size distribution of released microplastics after aging at different temperatures.

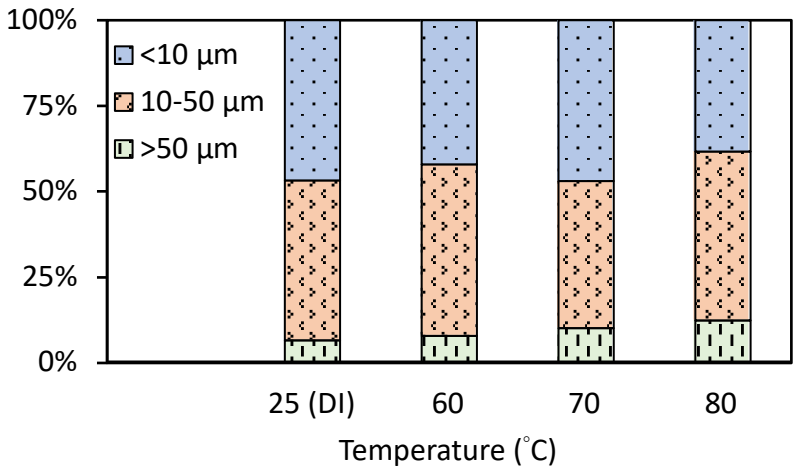

Figure 15. Percentage of different size of microplastics after aging at different temperatures.

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4.5 Changes of carbonyl bonding and surface morphology on the surface of PVC pipes in the aging process

The normalized IR spectrums and calculated CI of PVC after different aging processes are shown in Figure 16. The signal of CH_2 bonding (1500-1400 cm^{-1}) did not change significantly with the increasing ozone exposure, chlorine exposure and temperature. On the other hand, the signal of carbonyl groups (1810-1550 cm^{-1}) slightly increased with the increasing ozone exposure, chlorine exposure and temperature. The highest CI in each aging process were 1.138 at 30 mg O_3 L^{-1}, 0.471 at 260 mg Cl_2 L^{-1} and 0.364 at 80°C, respectively. A similar phenomena was observed in the study by Zhang et al. (2022a), who used UV to age PVC plastic specimen and found that the release of microplastics was associated with the increasing CI. The change in CI indicated that the aging processes could generate more carbonyl functional groups on the surfaces as PVC aged. Interestingly, Zhang et al. (2022b) used ozone to age PVC pellets. They found an increase in CI after ozonation but the release of microplastics was not significantly enhanced. It is likely that a threshold increases in CI existed to initiate the release of microplastics from PVC products.

The SEM images of virgin PVC before aging and those aged under different conditions are shown in Figure 17. The virgin PVC possessed smooth surfaces with little amounts of hole structures (Figure 6(a)). The hole structure developed, and the numbers

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of holes generally increased as the PVC aged by ozonation, chlorination, and high temperature. Two exceptions were found: 1. For PVC pipes aged by ozone, the hole structures found after aging by 30 mg L^{-1} ozone decreased in number but their sizes became bigger than those aged by 10 and 20 mg O_3 L^{-1}. 2. For PVC pipes aged at different temperatures, the pipes aged at 80°C exhibited smaller hole structures but the surfaces became rougher compared to those aged at 60 and 70°C. The bigger hole structures found when aging by 30 mg L^{-1} ozone PVC could be contributed to the continuous attack of ozone toward the hole structures developed previously, in turn, microplastics tended to detach more easily from these hole structures and make them become bigger but less in numbers. As for the smaller hole structures found at 80°C, the exact reason was not clear, but the rougher surfaces caused by a higher temperature could be responsible for the more abundant detachments of microplastics.

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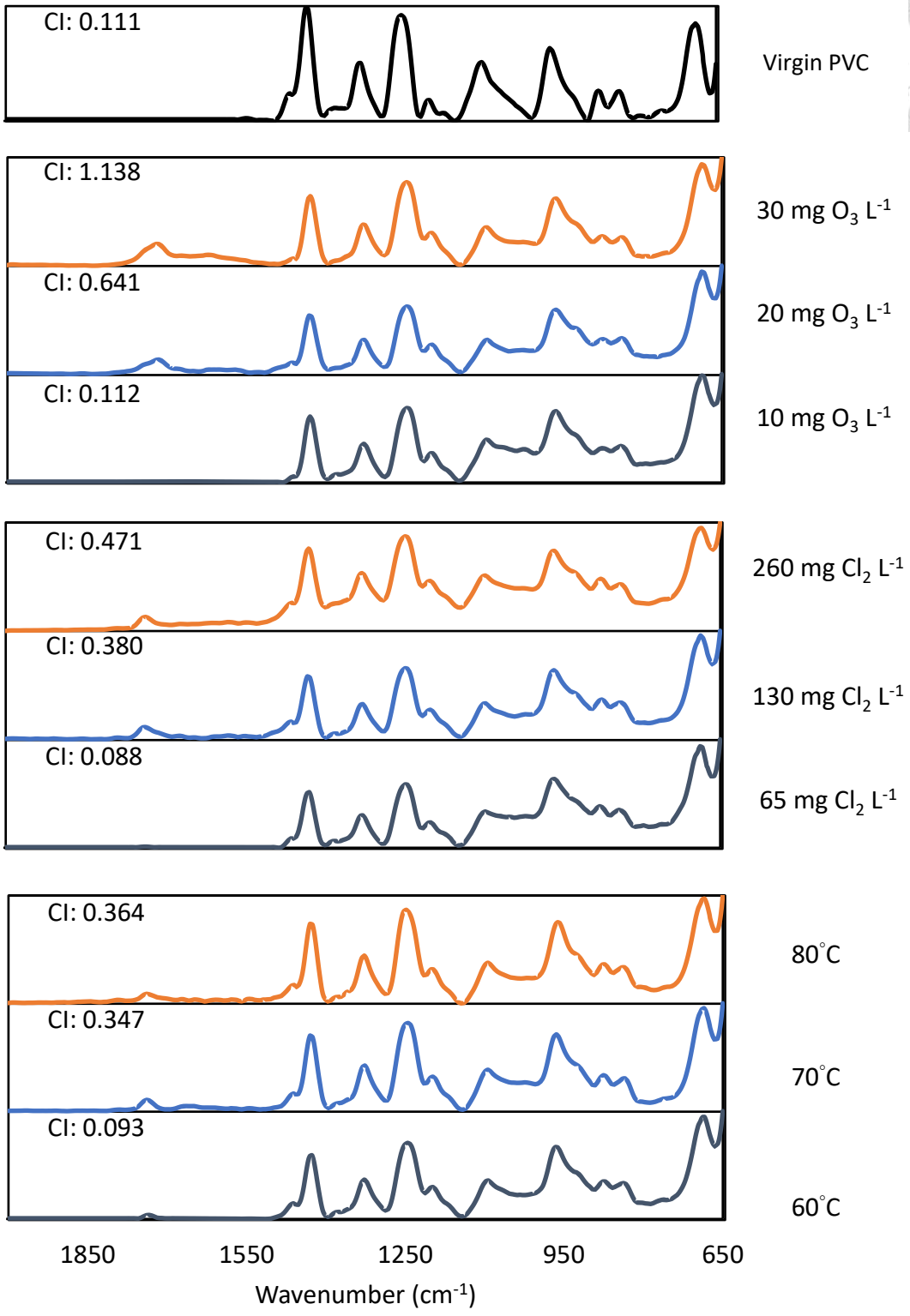

Figure 16. The normalized IR spectrum and calculated CI of PVC pellets after different aging processes.

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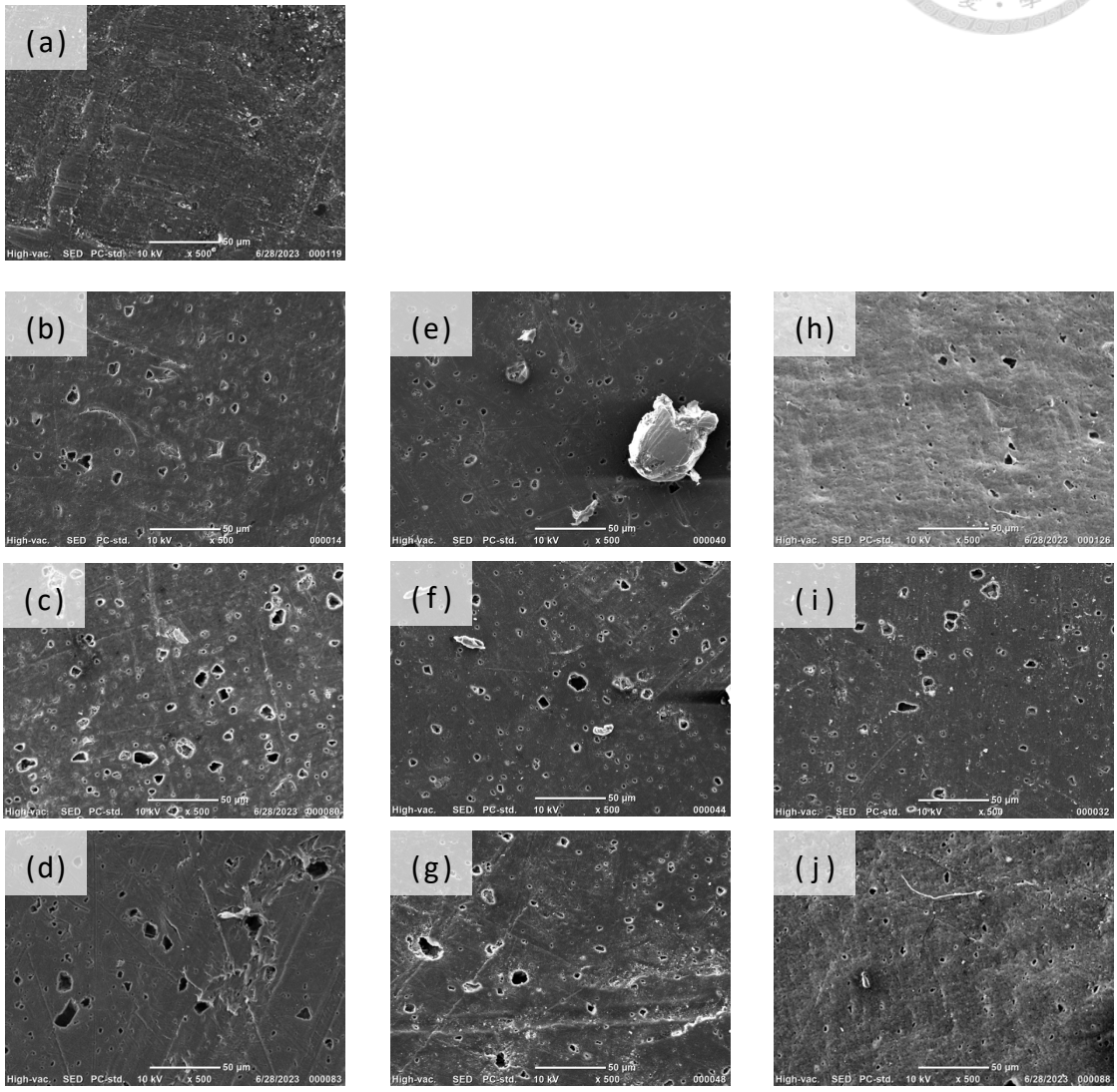

Figure 17. The SEM image of (a) un aged PVC, (b)-(d) aged at 10, 20 and 30 mg O_3 L^{-1}, (e)-(g) aged at 65, 130, and 260 mg Cl_2 L^{-1}; (h)-(j) aged at 60, 70, and 80°C.

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Chapter 5 Conclusions and Recommendations

5.1 Conclusions

The effects of pH, ozonation, chlorination, and temperature on the release of microplastics from PVC pipes was investigated in this study. The changes of surface bonding and surface morphology were also investigated. The conclusions are summarized as follows:

1. The influence of solution pH on the release of microplastics was not significant.
2. The release of microplastics from PVC pipes increased with the increasing exposure of ozone, chlorine, and temperature. The highest release for each aging process was found to be 1,058 # L^{-1} at 30 mg O_3 L^{-1}, 1,256 # L^{-1} at 260 mg Cl_2 L^{-1}, and 1,303 # L^{-1} at 80°C, respectively.
3. The size distribution (1-10 μm, 10-50 μm, and >50 μm) of released microplastics was investigated. The 10-50 μm and >50 μm fractions tended to increase with the increasing exposure of chlorine. The proportions of each size did not change significantly with the increasing ozone exposure and temperature although the concentration of microplastics increased.
4. The CI generally increased with the increasing exposure of ozone, exposure of chlorine, and temperature. The maximum CI for each aging process were 1.138, 0.471, and 0.364 when PVC pipes aged at 30 mg O_3 L^{-1}, 260 mg Cl_2 L^{-1}, and 80°C,

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respectively.

5. The number and size of hole structures on the PVC surfaces, in general, tended to increase with the enhanced aging conditions although exceptions at high ozone concentration and high temperature were found.

5.2 Recommendations

Despite this research has demonstrated the potential of microplastics release from PVC pipes when aging in ozonation, chlorination, and thermal conditioning, all experiments were conducted under stagnant conditions. The release under flowing water was not investigated. In addition, other aging process such as UV radiation that could be encountered in the distribution system and premise plumbing was not studied. Following recommendations are provided.

1. The effects of hydraulic abrasion caused by flowing water on the release of microplastics from aged PVC pipes should be investigated.
2. The UV radiation can cause the degradation of PVC outer surfaces. Whether this could lead to the release of microplastics from the inner wall should be further explored.
3. The aged PVC pipes after a long service time in the distribution system or household piping system can be collected and used to investigate the release of microplastics.
4. The release of microplastics from plastic pipes made by other materials such as HDPE

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(High-Density Polyethylene), PP (Polypropylene) and ABS (Acrylonitrile butadiene styrene) should be investigated.

5. This research was carried out by accelerated aging conditions. Whether these can represent the potentials of microplastics release from PVC pipes under real conditions should be further investigated.
6. The kinetics of microplastics release can be further investigated to determine whether the released microplastics could be broken down to smaller fragments.

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