

Analysis of Chlorination & UV Effects on Microplastics Using Raman

Spectroscopy

by

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ABSTRACT

Microplastics are emerging to be major problem when it comes to water pollution and they pose a great threat to marine life. These materials have the potential to affect a wide range of human population since humans are the major consumers of marine organisms. Microplastics are less than 5 mm in diameter, and can escape from traditional wastewater treatment plant (WWTP) processes and end up in our water sources. Due to their small size, they have a large surface area and can react with chlorine, which it encounters in the final stages of WWTP. After the microplastics accumulate in various bodies of water, they are exposed to sunlight, which contains oxidative ultraviolet (UV) light. Since the microplastics are exposed to oxidants during and after the treatment, there is a strong chance that they will undergo chemical and/or physical changes. The WWTP conditions were replicated in the lab by varying the concentrations of chlorine from 70 to 100 mg/L in increments of 10 mg/L and incubating the samples in chlorine baths for 1–9 days. The chlorinated samples were tested for any structural changes using Raman spectroscopy. High density polyethylene (HDPE), polystyrene (PS), and polypropylene (PP) were treated in chlorine baths and observed for Raman intensity variations, Raman peak shifts, and the formation of new peaks over different exposure times. HDPE responded with a lot of oxidation peaks and shifts of peaks after just one day. For the degradation of semi-crystalline polymers, there was a reduction in crystallinity, as verified by thermal analysis. There was a decrease in the enthalpy of melting as well as the melting temperature with an increase in the exposure time or chlorine concentration, which pointed at the degradation of plastics and bond cleavages. To test the plastic response to

UV, the samples were exposed to sunlight for up to 210 days and analyzed under Raman spectroscopy. Overall the physical and chemical changes with the polymers are evident and makes a way for the wastewater treatment plant to take necessary steps to capture the microplastics to avoid the release of any kind of degraded microplastics that could affect marine life and the environment.

DEDICATION

To my parents,

Smita Kelkar

Pushkaraj Kelkar

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CHAPTER 1

1. INTRODUCTION

1.1 Motivation

As of 2013, more than 300 million tons per year of plastic are being generated by 192 coastal countries around the world [1]. In 2010 alone, it was estimated that 275 million tons of plastic were generated and around 12.5 million tons ended up in the oceans or freshwaters [1]. Recent research by Santa Barbara's National Center for Ecological Analysis and Synthesis (NCEAS) indicated that 8 million metric tons of plastic ends up in our oceans. If current production and consumption continues, it is estimated that by 2025 there will be 160 million tons of plastic in the oceans [2]. The predominate plastics found in the environment are high density polyethylene (HDPE), low density polyethylene (LDPE), poly(ethylene terephthalate) (PETE), polystyrene (PS), polypropylene (PP) and poly(lactic acid) (PL).

The microplastics with a reduced size and a greater surface area are the real danger to the environment. Any plastic particle less than 5 mm in diameter is considered as a microplastic [3]. Microplastics are generated by three major sources. First, the plastic industry produces pellets that are used in the production of the products like water bottles, boxes, jar, lids, etc. A secondary source are the microbeads used by the personal care industry in the production of shampoos, face scrubs, toothpastes, etc. These pellets and microbeads already fit in the definition of microplastics as they are smaller than 5 mm in size. The third source is the degradation of plastics that accumulate in the environment. The plastics that aggregate to form ocean floats are located at the surface of the sea and are exposed to harsh conditions, including sunlight, erosion, and varying

temperatures. The ultraviolet (UV) rays play a leading role in the degradation of the plastics by photolysis, photo-oxidative and thermo-oxidative degradation. Additionally, exposure to saltwater enhances the degradation as well as physical erosion of the particles by the waves and the friction with the sand and the rocks [1]. These degradation pathways cause the plastics to become brittle and fragmented, which can cause the physical breakdown of large particles and debris into microplastics. Each of these pathways lead to the accumulation of microparticles in the environment, and, subsequently, on the shore, on the sea bed, and inside the digestive tract of aquatic organisms.

The microbeads and pellets that are produced by the plastic and personal care industry are in the same size ranges and those that find their way directly into the freshwaters and oceans by escaping filtration in the wastewater treatment plants (WWTP). Many of the WWTPs in the USA and Canada are not set up to filter out the microplastics. There are a few WWTPs in Europe that can remove up to 97% of the total volume of microplastics. They utilize microfiltration to remove microplastics and organics from the wastewater. This technology requires high quality membranes and a lot of infrastructural changes to be made in the facility that may not be economically feasible for all treatment plants. A standard waste water treatment plant usually contains 1) a traditional grit removal chamber, 2) a primary and perhaps a secondary clarifier, 3) an activated sludge system, 4) aeration tanks to remove the organics, and 5) finally a disinfection chamber that uses chlorination, UV treatment, or ozone [4]. A WWTP that implements membrane technology could use combinations of membrane bioreactors (MBR), ultrafiltration membranes, and nanofiltration membranes with an external pressure system to push the

wastewater through the membrane pores leaving behind the colloids. These series of membrane technologies perform the flocculation, clarification, and filtration processes. If a traditional WWTP were to be retrofitted with a membrane-based system, then the clarification and filtration process equipment would become redundant. A similar scenario in La Center, a small city in the state of Washington, occurred when the sequencing batch reactor (SBR) was replaced by MBR and the cost for installation of all the phases was approximately \$25M [5].

Pipes used nowadays in the construction of home and commercial building’s sewage systems are often made of plastic. This is primarily because unlike metal pipes, plastic pipes are cheaper, do not corrode, and have a longer lifetime. These pipes are sturdy and convenient as they are lighter in weight but they also have problems associated with them. A recent study investigated pipes made from HDPE and found that chemicals like 4-chloro-2-methylbutan-2-ol and 2,3-dichloro-2-methylbutane in effluent water, which were the products of oxidative degradation of the HDPE pipe wall by chlorine [6].

Table 1.1: Contaminants found on Microplastics and their health effects

Contaminants	Health effects in humans and animals
Polycyclic Aromatic hydrocarbons (PAHs)	Can cause skin, lung, bladder cancer, inflammation of skin [7]
Excess chlorine	Lung damage, bloody nose, fluid buildup in lungs [8]
Organochlorine Pesticides	testicular cancer, poor sperm count [9]

Poly-brominated diphenyl ethers	Thyroid dysfunction, developmental problems in children [10]
Bisphenol A	Lowers sexual function, impairing human reproduction, sperm defects, hyperactivity etc. [11]

Chlorine will oxidize the polymers and form new bonds with carbon atoms on the polymer as well as break other bonds. The byproducts of the oxidation, which have been found to form in chlorinated water [1], can pose a threat to humans. Additionally, the consumption of marine animals like fish, shrimp and other shellfish poses a threat to human health, because the organisms could be contaminated with chlorine-containing polymeric byproducts and microplastics. The entry of chlorine into our bodies is not a very harmful situation as our tap water contains around 2-4 mg/L chlorine, but the consumption of chlorine-containing polymeric byproducts could prove harmful and warrants further investigation.

This study herein focuses on developing an understanding of the physical and chemical effects that chlorination and UV treatment have on the polymer particles under the wastewater treatment plant conditions using Raman spectroscopy, differential scanning calorimetry, and size exclusion chromatography. These studies will open pathways to think about the ways in which wastewater treatment plants can be modified to prevent the escape of these chemically and physically changed microplastics.

CHAPTER 2

2. CHLORINATION AND UV TREATMENT ON MICROPLASTICS

2.1 Materials and Methods

A total of 3 different types of polymers were studied for changes. The selection was based on the availability of the microplastic in the oceans and freshwaters. High density polyethylene (HDPE), polypropylene (PP), and polystyrene (PS) represent three of the top seven commodity plastic used by consumers and industry. Since the study involves microplastic derived from daily products, like plastic bottles, coffee cups etc., we decided to use those materials directly. The sources are summarized in Table 2.1 below. The materials obtained were washed with distilled water and dried before use to make sure there were no additional contaminants.

Table 2.1: Sources of microplastics

Polymer	Source
HDPE	Milk jug
PS	Coffee cup lid
PP	Coffee cup lid

2.1.1 Methods

Since any plastic particle under the size of 5 mm is qualified as a microplastic, we cut the products into particles that were 5 mm in size and then lowered the particle diameter to 1-2 mm to provide a greater surface area for the solvent to interact with the plastics. The experiments were done in 25 mL glass scintillation vials after the plastics were washed and cleaned of any external contaminant. Between 10-12 mg of plastic was added to

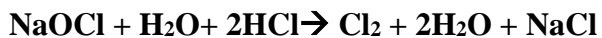
each vial, which ensured that an equal amount of plastic was being treated in the vials. The microplastics were incubated in the solutions with a chlorine concentration of 70, 80, 90 or 100 mg/L. Additional details are provided below.

2.1.2 Chlorination Chemistry

The primary source of chlorine was NaOCl in all the experiments. Wastewater treatment plants require the pH to range between 6-7 throughout the treatment process to facilitate disinfection. When NaOCl is added to water, it reacts to form hypochlorous acid and hypochlorite ions along with NaOH. The formation of the strong base NaOH increases the pH, which is not good for disinfection as it reduces the amount of hypochlorous acid and increases the hypochlorite ions.



Therefore, 12 M HCl was used to lower the pH to 6-7. The volume of HCl required for each chlorine concentration is shown in Figure 2.1. The addition of HCl promotes the formation of hypochlorous acid to form chlorine gas and NaCl.



The chlorine gas formed is not going to directly react with microplastics or degrade them. Chlorine has the tendency to react with the water and form hypochlorous acid and a chlorine anion, the chlorine anion and hypochlorous acid are the species responsible for the microplastic degradation.



All the vials contained stir bars and the lids were closed immediately to retain the chlorine formed due to the reaction above. The following nomenclature was used to identify each polymer sample, 100 65 9d corresponds to CONCENTRATION (mg/L Cl_2), TEMPERATURE ($^\circ\text{C}$), and TIME (min).

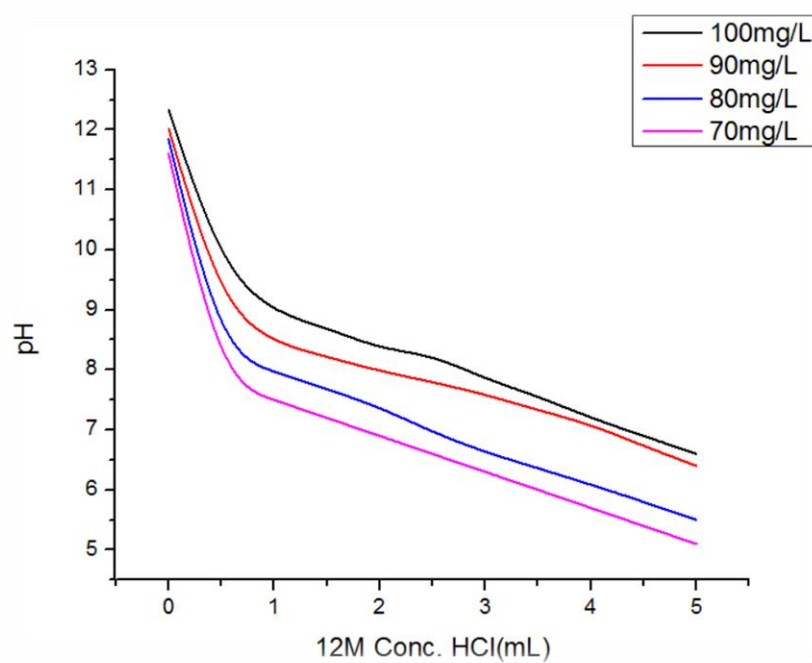


Figure 2.1: Volume of HCl required to maintain a pH in the range 6-7, which replicates WWTP conditions.

2.1.3 Chlorination treatment methodology

First, the plastic samples were cut into equal sizes (1-2mm diameter). Then, the particles were washed with deionized water to remove visible contaminants and dried. The polymers were weighed out and added to a scintillation vial equipped with a stir bar. Next, water was added to the vials followed by the NaOCl solution. The necessary amount of concentrated HCl (Refer to Figure 2.1) was added and then the lids were closed. Next, the solutions were incubated in a temperature controlled oil bath for the desired amount of time. After the predetermined incubation time, the vials were opened

and the plastics collected by filtration. The particles were rinsed with deionized water and dried using Kimwipes.

2.1.4 Raman spectroscopy characterization

The plastic samples were characterized using Raman spectroscopy according to the following protocol. First, the output power was set to 50% to analyze a silicon wafer placed over the glass slide. Next, the exposure time was set to 10 seconds and the laser power to 10% of the maximum intensity (i.e., ~0.75 mW). The sample was loaded using tweezers on top of the silicon wafer. Preliminary focus was achieved using the 5X objective before shifting to the 20X lens. The sample was focused before shifting to the 50X lens and then the sample was focused again. The shutter was opened to expose the sample to the laser and the spectra was collected.

The spectra obtained were exported to the Origin Pro data analysis software for further workup. The baseline was corrected using the baseline correction feature in Origin Pro, and in certain cases peak heights were normalized to 1.0 to study the relative changes in peak height ratios. For absolute intensity plots, an average of 3 readings of Raman intensity was taken and was plotted against the time to study the fall in intensity with respect to time.

2.1.5 UV degradation protocol

The solutions analyzed for degradation by UV light were prepared the same as above (for chlorination treatment). In this case, three solutions were tested: 1) tap water + 4 mg/L chlorine (TWC), 2) 3.5 wt.% NaCl (SW), and 3) 3.5 wt.% NaCl + 4 mg/L chlorine (SWC). The rationale for adding 4 mg/L chlorine to the samples was that the normal water in day to day use has around 2-4 mg/L of chlorine present in it to eliminate germs and infections and these are also the safe values for human exposure. For each sample,

the vials were closed and stored on the roof of the Engineering Research Center building on the Tempe campus.

2.1.6 Differential Scanning Calorimetry analysis

The chlorine treated polymers were subjected to thermal analysis to study changes in the glass transition temperature and polymer crystallinity. A TA Instruments Q2000 DSC was used to test the samples. To have a greater variety and solid trend, four different types of samples, Original, day 1, day 4, and day 9 samples were selected. The HDPE and PP were heated from 23 °C to 200 °C at a rate of 10 °C/min. Then, the instrument was held at 200 °C for 30 min before being cooled from 200 °C to -80 °C at 50 °C/min. The second heating ramp started at 50 °C and ended at 300°C, heating at a rate of 10 °C/min. The enthalpies reported were obtained from the second heat. Polystyrene was heated from 23 °C to 300 °C at the rate of 10 °C/min, held at 300 °C for 30 min, and then cooled from 300 °C to 50 °C at 50 °C/min. Then, the second heating ramp was started at 50 °C and ended at 300 °C, heating at 10 °C/min. The glass transition temperatures reported were obtained from the second heat. The enthalpy of melting and the glass transition temperatures were determined using appropriate analysis features of the Universal Analysis software (TA Instruments).

2.2 Results and Discussion

2.2.1 Chlorination studies

2.2.1.1 HDPE

The wastewater treatment plants operate under conditions that maintain a chlorine concentration between 5-20 mg/L, pH values between 6-7, temperature of 20-35 °C, and a total residence time between 30 to 60 min. The parameters and processes are adjusted

depending upon whether the influent comes from slaughterhouses, chemical industries, textile industries, and/or household waste. In our first experiments, the samples (HDPE, PP, PS) were tested at 20 mg/L chlorine, 35 °C, and pH 6.5 for 60 min. However, no perceptible change was seen in the Raman spectra of the samples.

Therefore, to probe under what conditions the samples would degrade, the chlorine concentration, the incubation time in solution, and the temperature were all elevated to extreme values. The chlorine concentrations were 100, 90, 80, or 70 mg/L, the incubation times were 1 to 9 days, and the temperature was 65 °C. A significant change was observed in the Raman spectra collected for each polymer.

HDPE was incubated in the chlorine solutions for a period of 1-9 days and analyzed using Raman spectroscopy. The spectra showed significant changes in the form of new peaks, diminishing peaks, the complete disappearance of peaks, and, potentially, the shifting of peaks. The peak intensity in Raman spectroscopy is correlated to the degree of crystallinity of the plastic, the laser power intensity, the amount of material (i.e., sample thickness), the internal stresses of the sample [12], and the chemical functionality. As noted in experimental section, sample sizes and sample thicknesses were kept constant and were measured using calipers.

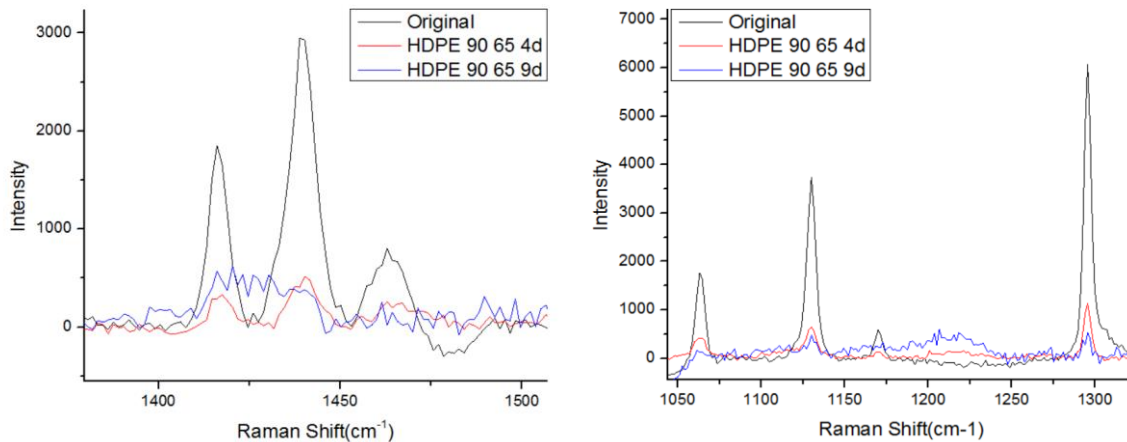


Figure 2.2: Absolute intensities from HDPE Raman spectra at 90 mg/L chlorine concentration showing a decrease in intensity with increased exposure.

A few prominent existing peaks that represented the backbone of HDPE displayed reductions in peak intensities. Figure 2.2 showcases the drastic intensity changes in these peaks over the 4 day and 9 day incubation. The notable peaks in Figure 2.2 are at 1064 cm^{-1} (C-C-C asymmetrical chain), 1130 cm^{-1} (C-C-C symmetrical chain), 1295 cm^{-1} (CH_2 twist), and 1416 cm^{-1} (CH_2 bend) [13] [14].

The absolute Raman intensities for HDPE are dependent on five factors: the functionality of the plastic, crystallinity of the plastic, surface roughness, thickness of the plastic, and laser intensity of the instrument. The laser intensity was kept constant throughout all experiments, and as noted above, the changes in thickness were determined to not influence the Raman intensity. Therefore, for HDPE, three of the five factors can still influence the Raman intensity. Figure 2.3 shows the intensity plots for select peaks in HDPE that showed a decrease over time. Intensity plot for the new peaks forming with HDPE are in figure 2.4. Out of the remaining three factors affecting the absolute intensities, the changes in the spectra show that there is a change in the functionality of HDPE and, as detailed later, the crystallinity of HDPE is decreasing with prolonged

exposure to chlorine treatment. However, surface roughness was not analyzed and it is unknown if spectral reflectance has caused any change in Raman intensity.

Without a doubt, the decrease in Raman intensity in Figure 2.3 can be attributed to either a change in functionality or a decrease in crystallinity. This observation is supported by the formation of bonds attributed to the oxidative degradation of HDPE by chlorine, as

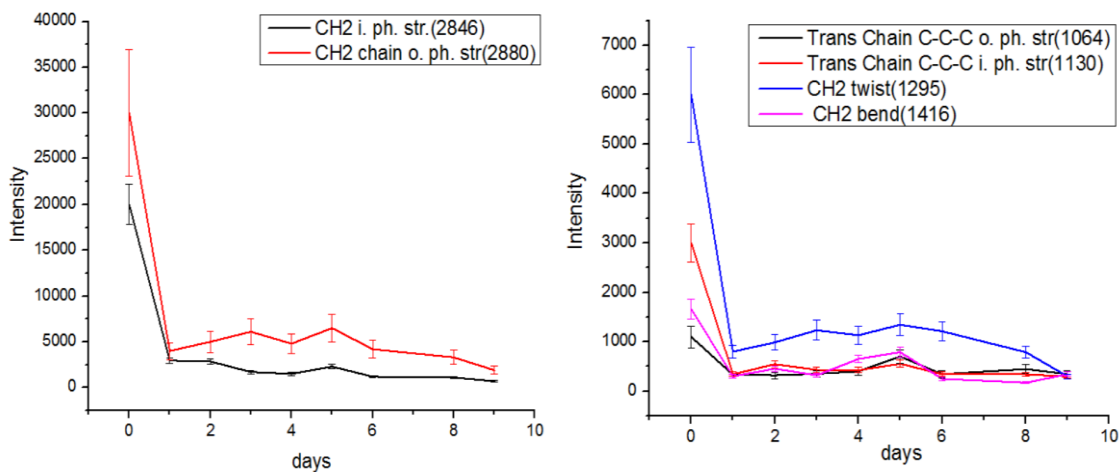


Figure 2.3: Absolute Raman intensities of decreasing peaks for HDPE.

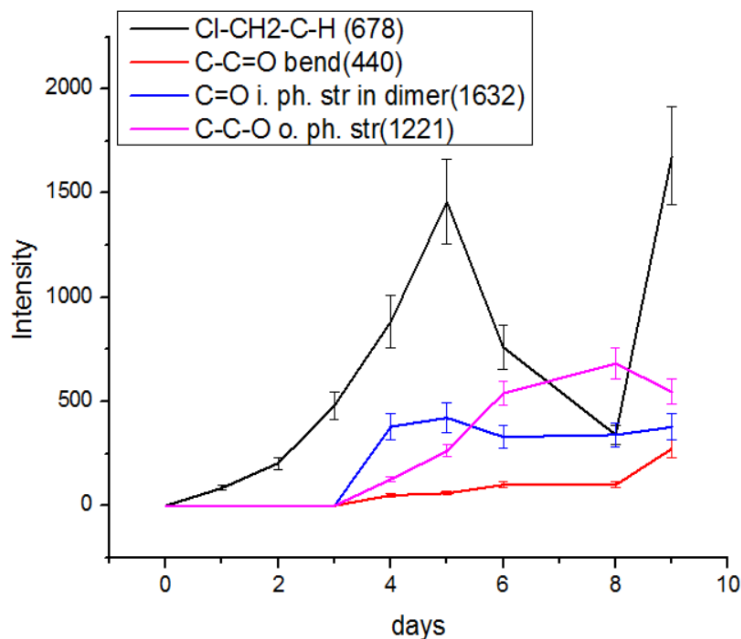


Figure 2.4: Absolute Raman intensities of new peaks for HDPE exposed to 90 mg/mL chlorine solutions.

seen in Figure 2.4. In Figure 2.4 peaks at 678, 440, 842, 1632, and 1221 cm^{-1} are formed. These peaks can only be possible if the chain is ruptured and chlorine and oxygen radicals attack the backbone to form the above bonds. These peak intensities continue to increase over the test period.

Since the surface roughness of the samples is not known, plotting the absolute intensities is inconclusive due to the multiple effects that can contribute to the decrease in Raman intensity. Hence, the spectra were normalized with respect to the peak at 2875 cm^{-1} , which represents the backbone peak of HDPE. Figure 2.5 shows the Raman spectra with the normalized intensities.

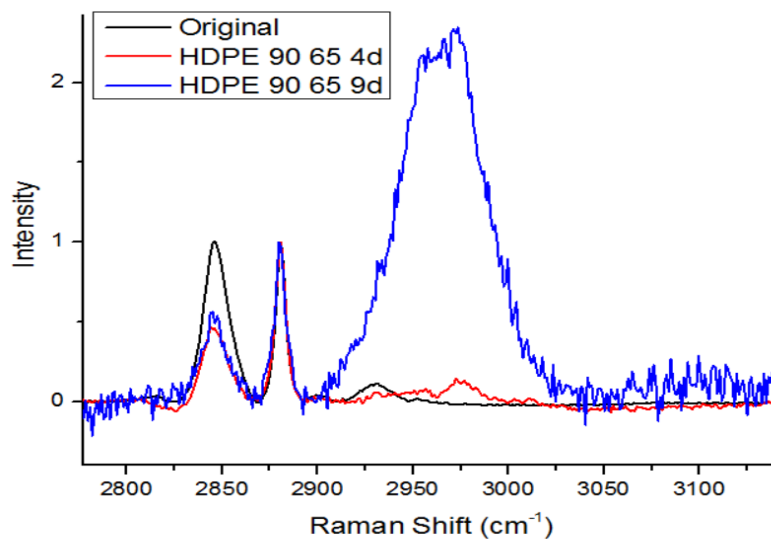


Figure 2.5: Raman spectra for HDPE incubated in 90 mg/L solutions for up to 9 days. The peak intensities have been normalized to the peak at 2875 cm^{-1} .

Figure 2.5 shows the normalized spectra for HDPE without treatment and on day 4 and day 9 of chlorine treatment. The plot clearly shows the formation of a peak at 2970 cm^{-1} with a change in intensity from day 4 to day 9, which represents a $\text{CH}_2\text{-Cl}$ asymmetrical stretch [13]. Meanwhile, the peak at 2846 cm^{-1} in the original spectrum, which corresponds to CH_2 symmetrical stretch, decreases in intensity. This is further confirmation of oxidative degradation caused by incubation in chlorine solutions. Additionally, Figure 2.7 shows a peak at 1295 cm^{-1} that does not display a change with increasing exposure to chlorine. This peak is also attributed to the HDPE backbone, and, thus, accordingly scales relative to the peak at 2875 cm^{-1} .

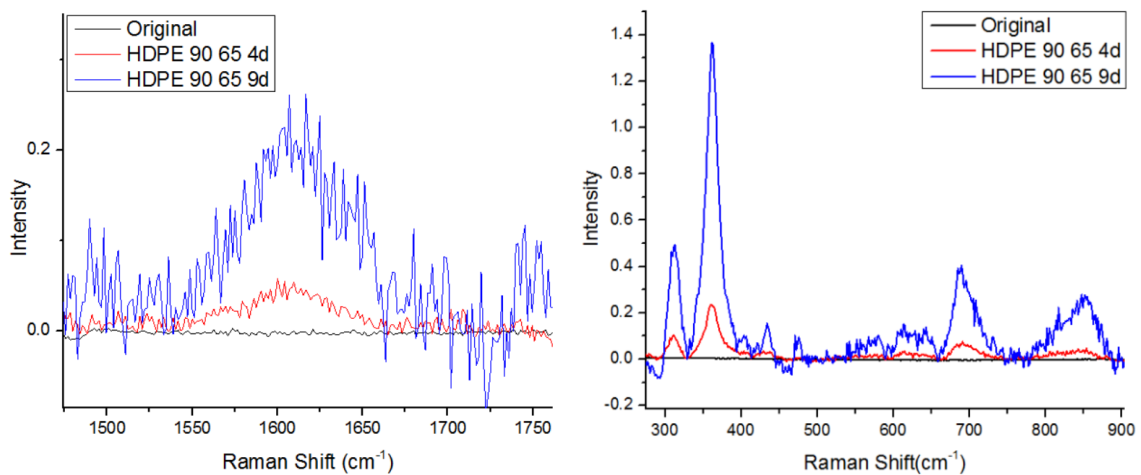


Figure 2.6: Raman Spectra of HDPE normalized to the peak at 2875 cm^{-1} an increase in the relative peak height ratios.

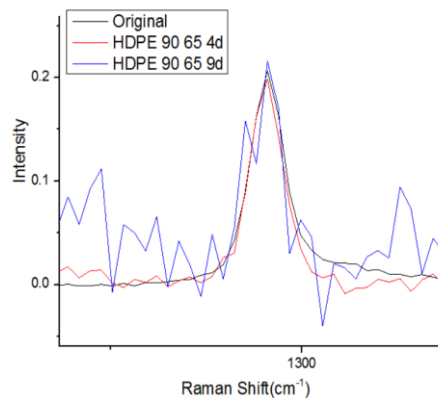


Figure 2.7: Raman plot of HDPE Original (black), 4 days (red) and 9 days (blue) at 90 mg/L

Figure 2.6 shows the spectra of the HDPE, still normalized to the intensity at 2875 cm^{-1} , and the growth of new peaks relative to the normalized peak is clearly visible in the wavenumber ranges of $300\text{--}900\text{ cm}^{-1}$ and at 1600 cm^{-1} . The peak at 440 cm^{-1} corresponds to C-C=O bend, the peak at 678 cm^{-1} corresponds to Cl-CH₂-CH stretch, the peak at 1632 cm^{-1} represents an C=O bond, and the peak at 1221 cm^{-1} is a C-C-O asymmetrical stretch. These changes are further evidence of oxidative degradation of HDPE by chlorine.

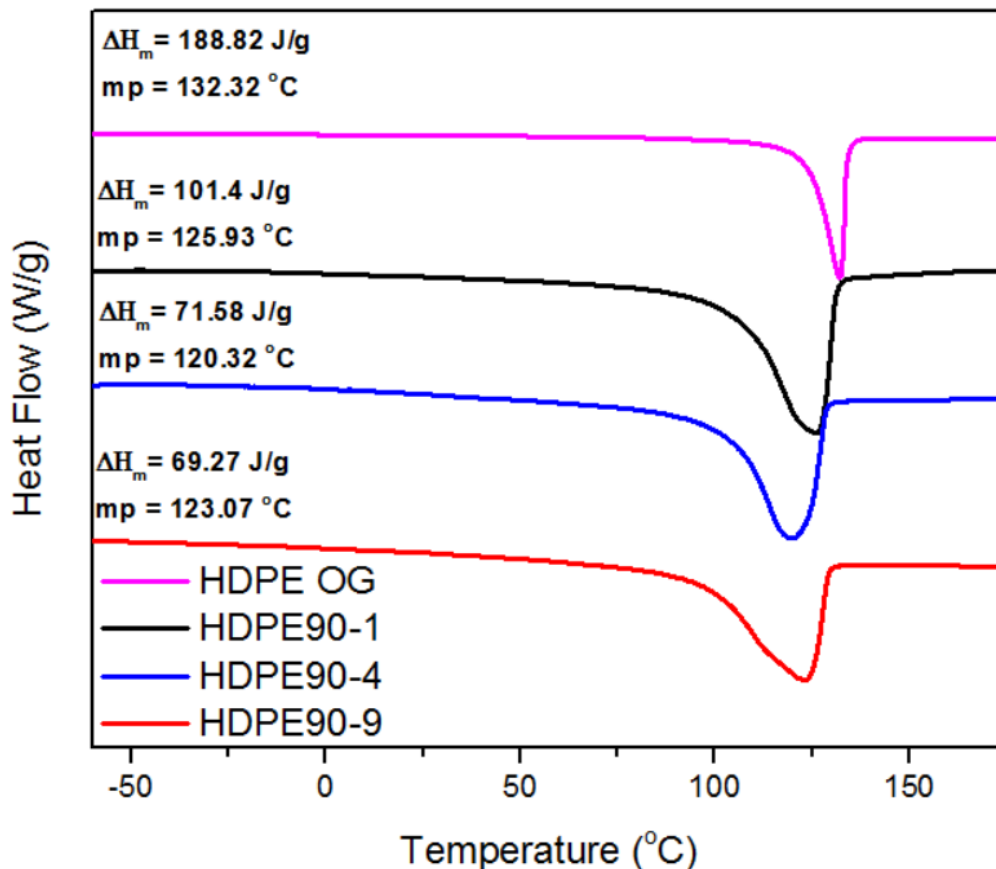


Figure 2.8: DSC traces of HDPE at day 0 (pink), day 1 (black), day 4 (blue), and day 9 (red). Endothermic transitions are pointed downward.

Next, thermal analysis was performed on the incubated HDPE samples (Figure 2.6). The melting point of HDPE day 1 sample is $126.18\text{ }^{\circ}\text{C}$, and it decreases approximately $5\text{ }^{\circ}\text{C}$

over the 9-day experiment to 121.94°C. The enthalpy of melting is gradually decreasing from 80.38 J/g at day 1 to 58.48 J/g at day 4 and eventually reducing to 54.82 J/g at day 9. The enthalpy fall of 26 J/g and 5 °C can be hypothesized as follows. The melting point of any structure is dependent on the enthalpy and entropy, which are associated with the transition of polymers from its crystalline to melt. Since crystallinity refers to the degree of structural order in a solid, a decrease in crystallinity refers to the breaking of that structural order of the molecules and making the samples vulnerable.

$$\Delta H_f/\Delta S_f = T_m$$

Hence, any changes in T_m are directly related to an increase in the enthalpy or a decrease in the entropy. Enthalpy is significant here because the enthalpy for the transition from crystalline to melt is directly related to the intermolecular forces between the polymer chains [2]. Hence, a reduction in the enthalpy required to melt a crystalline polymer directly implies a reduction in the intermolecular forces between the polymeric chains and, thus, demonstrates a weakening of the structure. A decrease in the melting point can also indicate an increase in entropy. A crystalline structure with regular packing is a sign of stable structure and, thus, minimal entropy. An increase in the entropy is a sign of a destabilized polymer structure. Hence, a decrease in T_m is evidence that the polymeric structure is becoming weaker during the test. In summary, the combination of Raman spectroscopy and DSC confirm that HDPE undergoes oxidative degradation and a transition from semi-crystalline to amorphous with increasing exposure to chlorinated solutions.

2.2.1.2 Polystyrene

Polystyrene is widely used in plastic product manufacturing because of its low cost of production and desirable properties. A range of products, such as foams coffee cup lids, restaurant to-go containers, and floatation materials at docks, use polystyrene making it more prone to be found in the form of litter and waste.

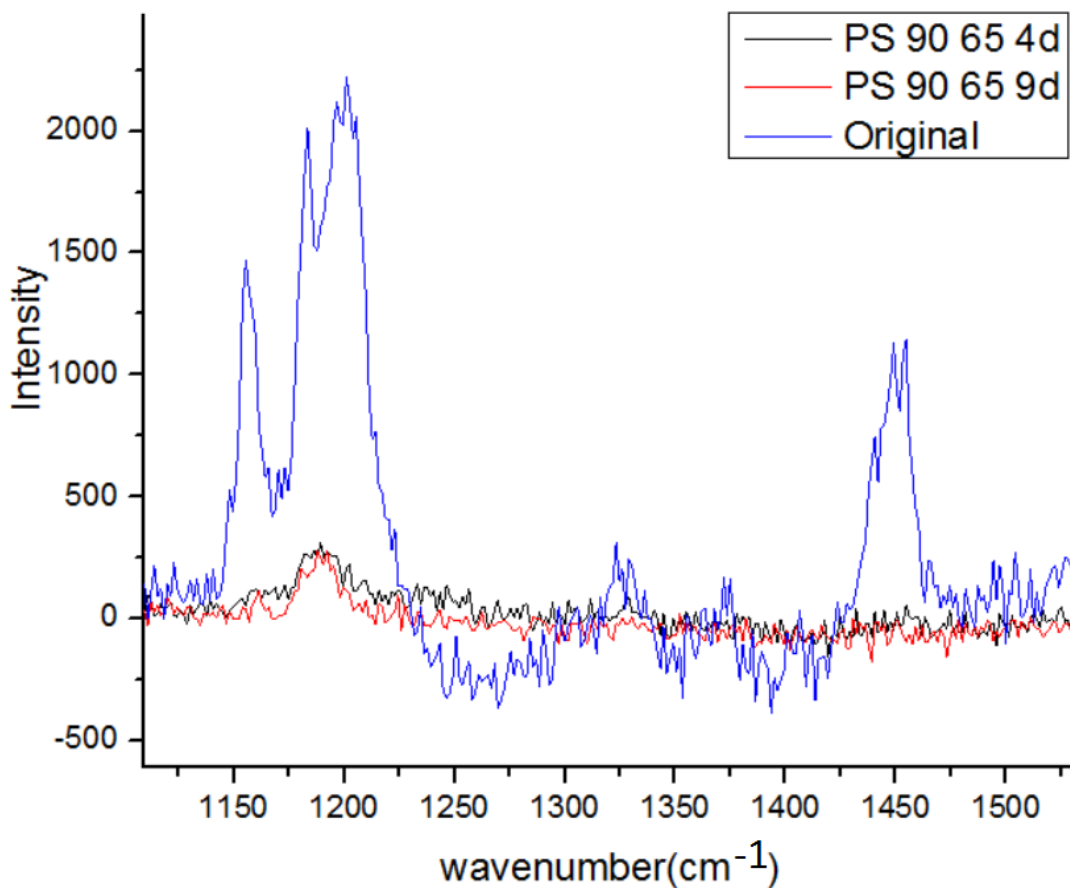


Figure 2.9: Raman spectra of polystyrene incubated in 90 mg/L chlorine solutions showing a decrease in intensity of peaks.

The above plot shows the Raman spectra for PS incubated in chlorine solutions for 0, 4, and 9 days. The spectra were collected on the same day within a 30 min span. There is a fall in absolute intensity with respect to an increase in the number of days exposed to

chlorinated solutions. Of the three factors noted above that can influence the Raman intensity, the crystallinity of the plastic can be eliminated for polystyrene because it is amorphous, as noted below based on the thermal analysis performed. Therefore, for polystyrene, the Raman intensity can be a factor of chemical functionality and surface roughness. Again, surface roughness was not measured, but it is not expected to fluctuate

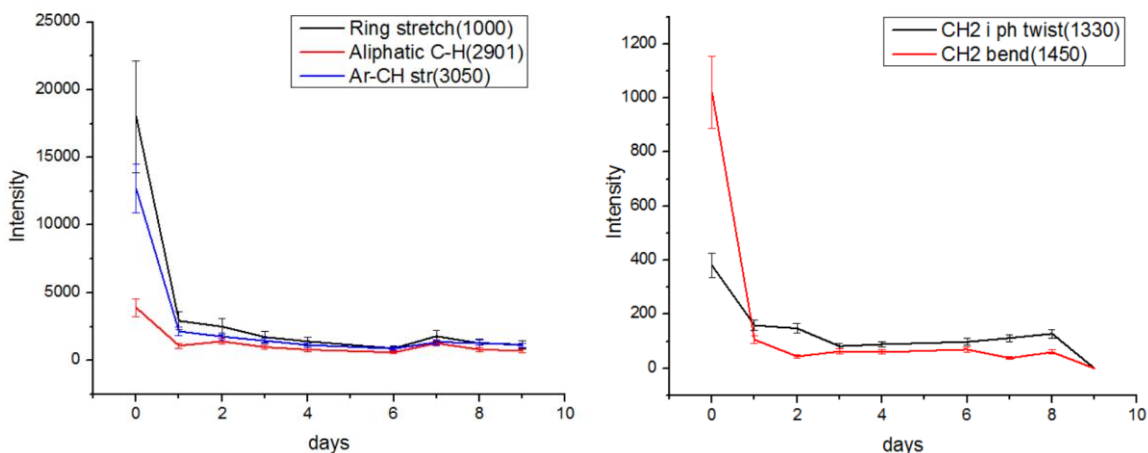


Figure 2.10: Raman intensity plots for PS at 90 mg/L chlorine concentration showing fall in intensity for peaks

extensively. As such, it is predicted that the decreases in absolute Raman intensities are associated with chemical changes to the polymer structure. Figure 2.10 shows the absolute Raman intensities over the entire 9 day exposure to chlorinated solutions.

In greater detail, Figure 2.10 displays the decrease in intensity in peaks at 1000 cm^{-1} (Ring stretch), 1330 cm^{-1} (CH₂ symmetrical twist), and 1450 cm^{-1} (CH₂ bend) [13]. The peak at 1000 cm^{-1} decayed to the baseline intensity after the second day of the treatment. This is supplemented by the degradation of the polystyrene backbone, which contains

aliphatic C-H groups (2901 cm^{-1}) [13]. Also, the peak for the aromatic C-H stretch (3050 cm^{-1}) [13] reduced in intensity from several thousand to several hundred.

There was no evidence of new oxidation or chlorination bonds, but the backbone was weakened. This suggests that there might be complete cleavage of chains and new bonds can form if polystyrene is treated at higher concentrations for longer periods of time. The physical characteristics of the sample changed dramatically because of incubation in the solution, to the point that the fragments were very fragile after 8 and 9 days of treatment.

The Raman spectra for polystyrene were normalized to the peak at 3052 cm^{-1} and the behavior of the neighboring peak relative to this peak was studied. The peak at 2901 cm^{-1}

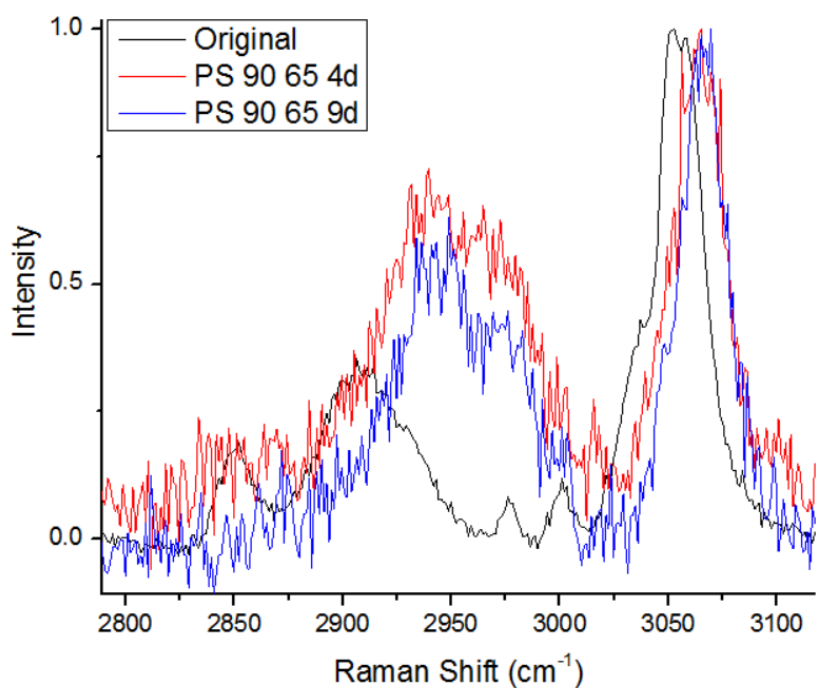


Figure 2.11: Raman spectra for PS incubated in 90 mg/L solutions for 0, 4, and 9 days. The peak intensities have been normalized to the peak at 3052 cm^{-1}

corresponds to the backbone of PS, which clearly changes its behavior relative to the

peak at 3052 cm^{-1} . The peak at 2901 cm^{-1} is sharp in the original sample and shifts to higher frequencies and becomes noisy with increased exposure. The shifting in peak position is potentially caused by the compression of the backbone [15] and could be a sign that the sample is becoming brittle because of the chemical oxidation. Since the bonds are shifting and increasing in relative intensity, there is a possibility that the original sample has soft bonds and bonds at day 4 and day 9 are harder. Figure 2.12 is the representation of the normalized plot that shows constant ratio with which the peaks are changing in intensity for day 4 and day 9.

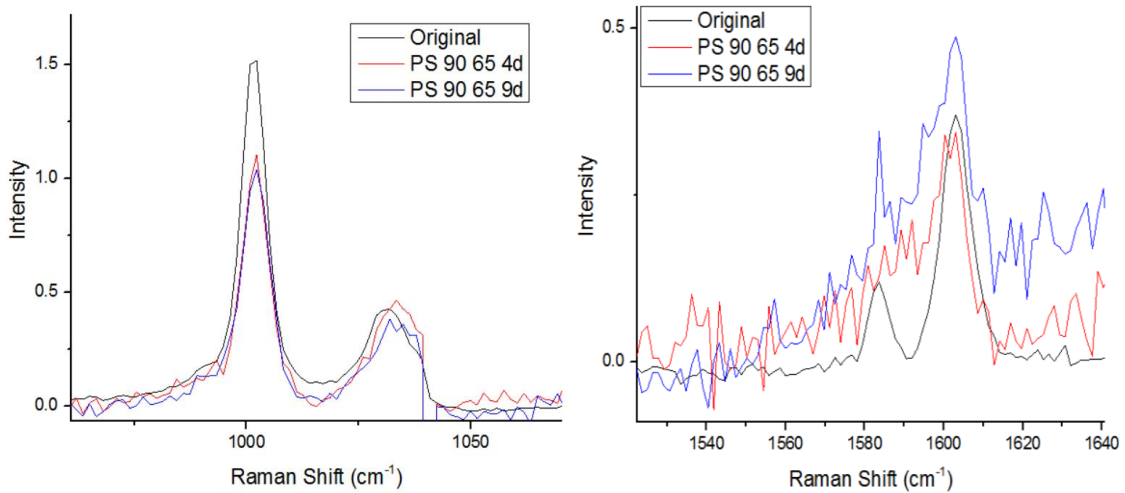


Figure 2.12: Normalized PS spectra showing constant ratio of peak intensity

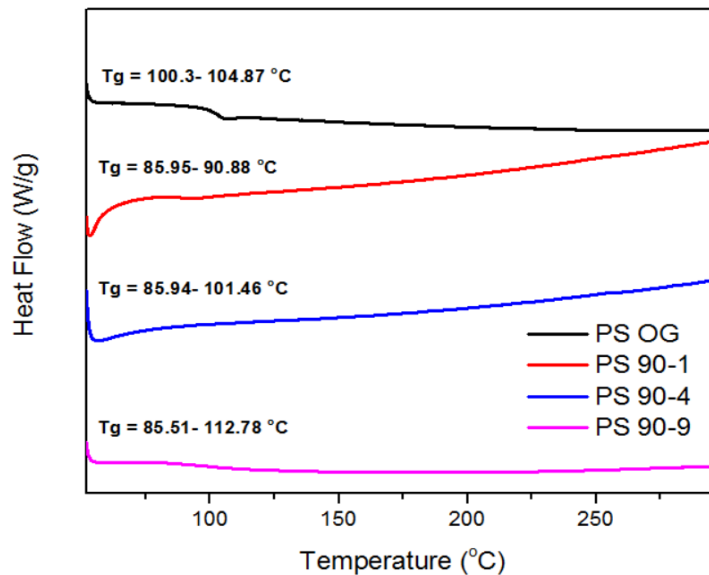


Figure 2.13: DSC traces for polystyrene exposed to 90 mg/L chlorine solutions for 0 days (black), 1 day (red), 4 days (blue), and 9 days (pink). Endothermic transitions are pointed downward.

The glass transition temperature (T_g) of a substance is a thermodynamic transition point that signifies the onset of segmental motion and chain mobility as well as a change in the scaling relationship between free volume and temperature [27]. It is the transition at which plastics transform from hard to rubbery materials. The range for the original PS sample is 100.3–104.87 °C. This range of T_g indicates the temperature at which different length chains of PS will become rubbery. As the PS was incubated in chlorinated solutions, the breadth of the T_g range showed an increasing trend starting from day 1, when the range was 85.95–90.88 °C. It further increased to almost 15 degrees at day 4, when the range was 85.94–101.46 °C. Finally, the range rose to 27 °C on day 9. There is a reduction of the lower limit of the T_g range with respect to time, which implies that the PS chains are being weakened by the chlorine attack and less energy is required to transition to a softened state than for the original sample. In summary, polystyrene was also susceptible to oxidative degradation by chlorinated solutions and displayed peak

intensity decreases, peak shifts, and a change in the lower limit and breadth of the T_g range.

2.2.1.3 Polypropylene

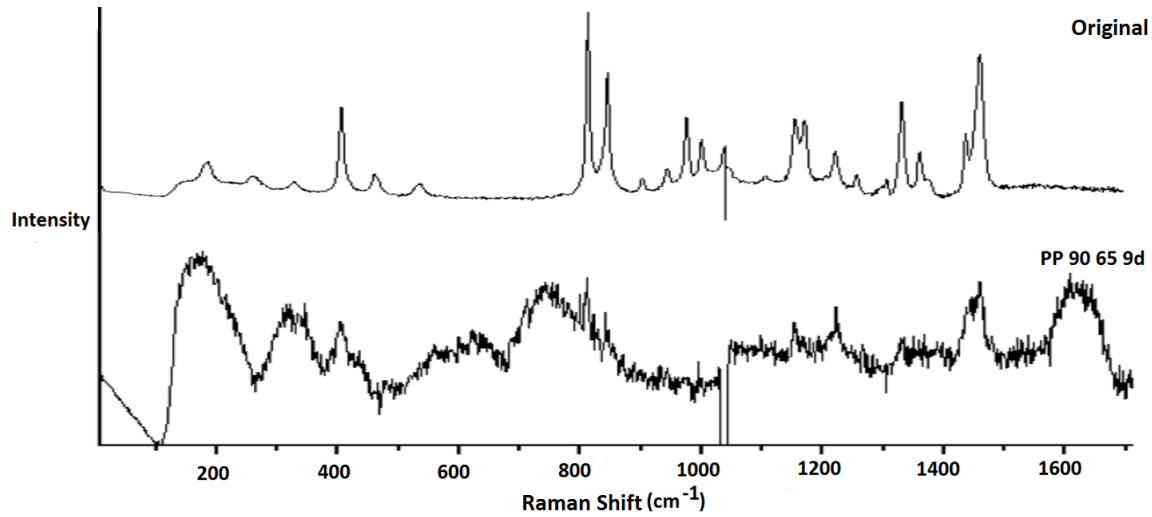


Figure 2.14: Raman spectra of polypropylene before and after 9 days of incubation in a 90 mg/L chlorine solution.

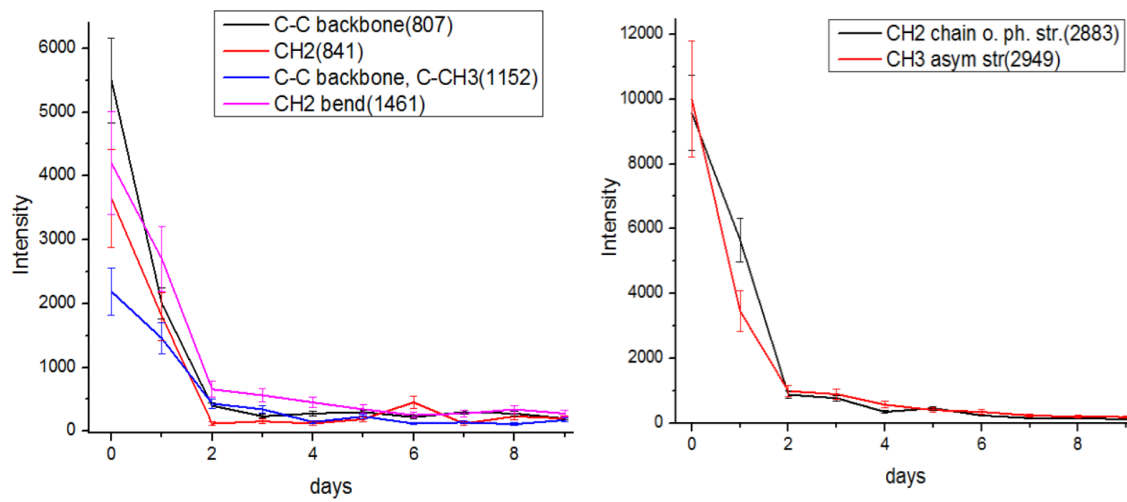


Figure 2.15: Absolute Raman intensity plots for PP in a 90 mg/L chlorine solution over 9 days.

Polypropylene (PP) is used a many commercial, scientific, and industrial applications. The prevalent use of PP motivated its selection for studying the oxidative degradation in chlorinated solutions. As observed and discussed for HDPE, new peaks were observed in the Raman spectra of PP as well as a decrease in crystallinity. The absolute intensity of many peaks decreased as the sample was incubated in the chlorine solution for 9 days. In Figure 2.14, the difference between the 9-day spectrum and original spectrum is portrayed. After 9 days, a noisier spectrum was collected, with very few sharp or well-defined peaks present. Figure 2.15 shows the Raman intensities of peaks attributed to the most prominent bonds of PP, which decrease over time. The intensities are plotted on

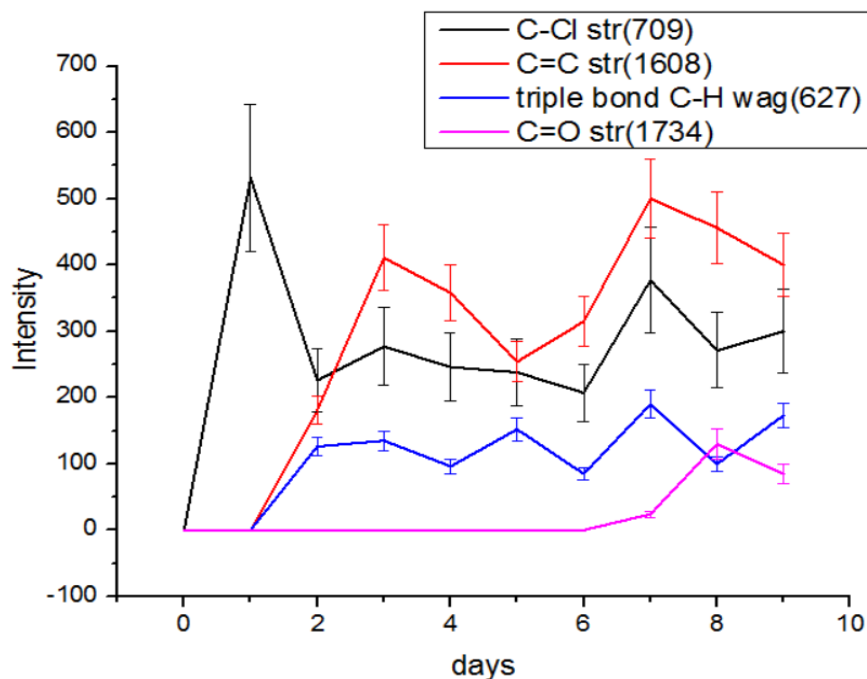


Figure 2.16: Intensity plots of new peaks of PP at 90 mg/L chlorine concentration

two y-axis scales, depending on the magnitude of intensity change. The bonds forming the backbone of PP, such as the peak at 807 cm^{-1} (C-C) and 1152 cm^{-1} (C-CH₃) [13] [16] decrease in intensity from 2000-3000 down to several hundred.

In Figure 2.16, the C-Cl stretch (709 cm^{-1}) [13] [16] is seen forming at day 1 of the treatment. However, the intensity does not increase over time from day 1 to day 9. Additionally, a new peak at 1608 cm^{-1} representing an aliphatic C=C stretch is seen [13] [16]. This is an indication of chain cleavage and the formation of a double bond between carbon atoms that was not in the original PP sample. An oxidation peak attributed to C=O is seen to form at day 7. Finally, a peak associated with the C-H of a C \equiv C bond, which indicates advanced oxidation of the polymer. These observations lead to the conclusion that chain cleavage and the formation of new bonds occurs simultaneously with a reduction in crystallinity. As noted above for HDPE and PS, the Raman intensity is affected by five factors. For PP, three of those factors are potentially influencing the absolute Raman intensity: sample crystallinity, surface roughness, and chemical functionality. As noted above, the chemical functionality of the sample is changing and as noted below, the crystallinity of the sample changes. Similar to the analysis performed for HDPE, the peak heights were normalized to various peaks associated with the PP backbone; however, now meaningful trends were observed for the relative peak height ratios.

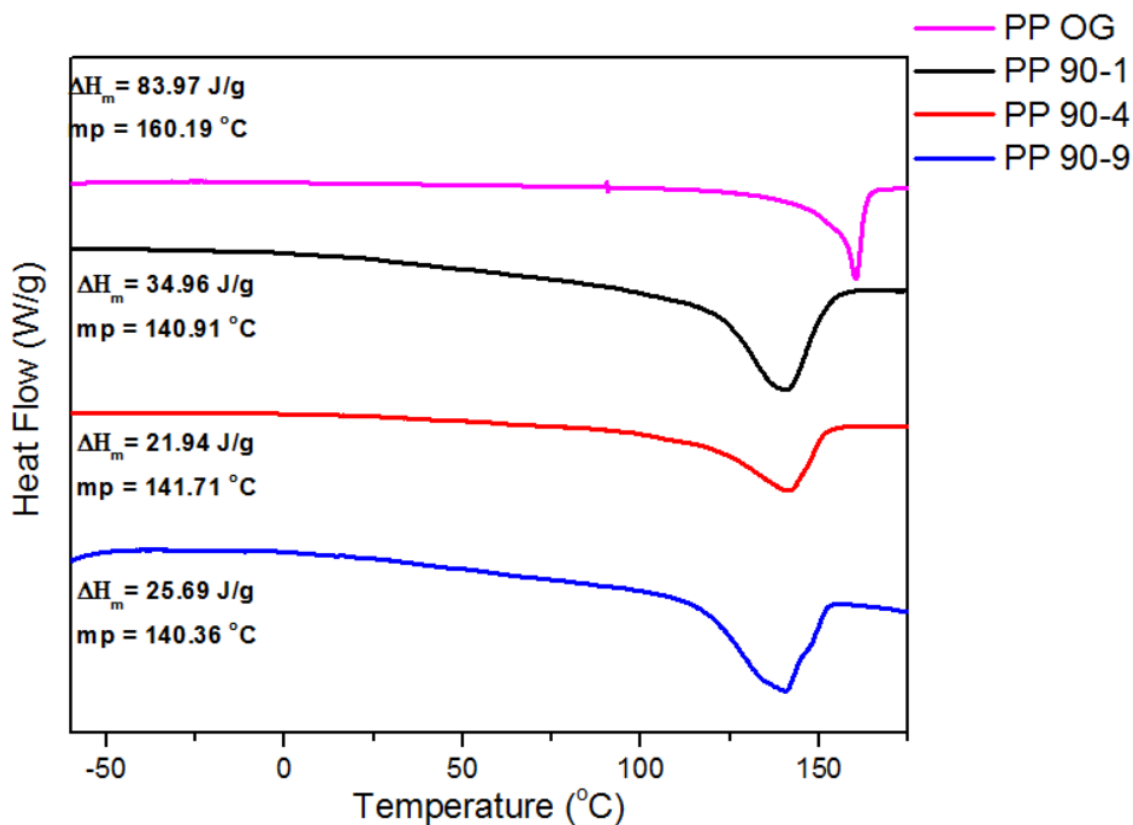


Figure 2.17: DSC traces for PP at day 0 (pink), day 1 (black), day 4 (red), and day 9 (blue). Endothermic transitions are pointed downward.

The chlorine-treated PP samples were also subjected to thermal analysis to analyze the sample crystallinity over time. Figure 2.17 displays the melting point and the enthalpy of melting for the PP samples at various exposure times. The original PP sample displays a very high value for both the melting temperature and the melting enthalpy. The enthalpy of melting was 83.97 J/g at day 0, which decreased to 34.96 J/g at day 1, and eventually to 25.69 J/g at day 9. Meanwhile the melting temperature also decreased by 20 °C from day 0 to day 1, and then remained constant until day 9. The destabilization rate of PP appeared to slow down with time, which is supported by the pattern displayed by ΔH_m

and T_m . Similar to HDPE, PP samples showed a decrease in Raman intensity attributed to both chemical oxidation and decreases in crystallinity.

2.2.2 Effects of UV exposure

2.2.2.1 Introduction

UV studies done on PP, PS, and HDPE by the Toray research center indicated that there was a severe degradation occurring at great depths in all these polymers. Infrared spectroscopy was used to characterize the samples and it was found that the degraded polymers were absorbing UV light very strongly and showing extreme degradation [17]. To understand how microplastics that escape WWTPs are affected by sunlight, the work herein describes the impact of sunlight exposure on the Raman spectra of HDPE, PS, and PP after 1.5 weeks and 29.5 weeks.

2.2.2.2 HDPE

Several peaks were observed and the intensities were plotted as a function of time for samples incubated in salt water with added chlorine (SWC) and for samples incubated in only salt water (SW). A common trend observed in HDPE was that the intensities for samples at 29.5 weeks were far less than the intensities at 1.5 weeks, both of which were less than the untreated samples. The peaks that were analyzed included the backbone carbon chains and CH_2 stretch, twists, and bends. These are the bonds that constitute HDPE and changes in those bonds would represent polymer chain cleavage. Figure 2.18 showcases the changes in the HDPE peaks before and after 29.5 weeks. The peak intensities have significantly reduced and the sample has become disordered. The addition of 4 mg/L chlorine to the SWC caused a significant difference when comparing the Raman spectra for samples incubated in SWC versus SW. Specifically, for samples

in SWC the decrease in the peak intensity from 0 to 1.5 weeks and then from 1.5 weeks to 29.5 weeks was of the same order of magnitude. Conversely, the reduction in the peak intensity for the SW samples was very rapid from 0 to 1.5 weeks and then slower from 1.5 weeks to 29.5 weeks. The addition of chlorine in the vials affected the CH₂ bonds in SWC samples and the intensity reduced to zero after 29.5 weeks. Other prominent peaks for HDPE reduced in intensity by factors of 2-8. The decrease in the intensity could be because the microplastics are becoming more amorphous, the surface is becoming rougher, and/or the chemical composition of the polymer is changing. The CH₂

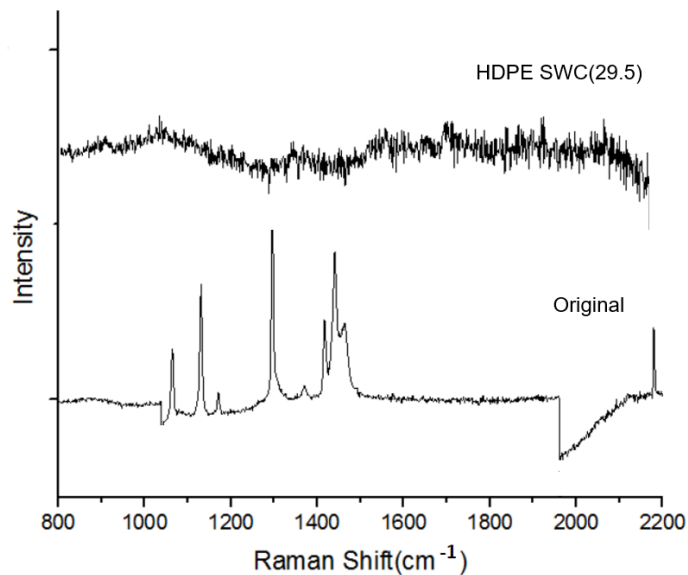


Figure 2.18: Comparative Raman spectra of original HDPE and HDPE at 29.5 weeks

symmetrical stretch (2846 cm⁻¹) and CH₂ chain asymmetrical stretch (2880 cm⁻¹) [13] [14] which both belong to the higher wavenumber region and hence are higher frequency bands, are found to be decreasing by an equal intensity in both solutions.

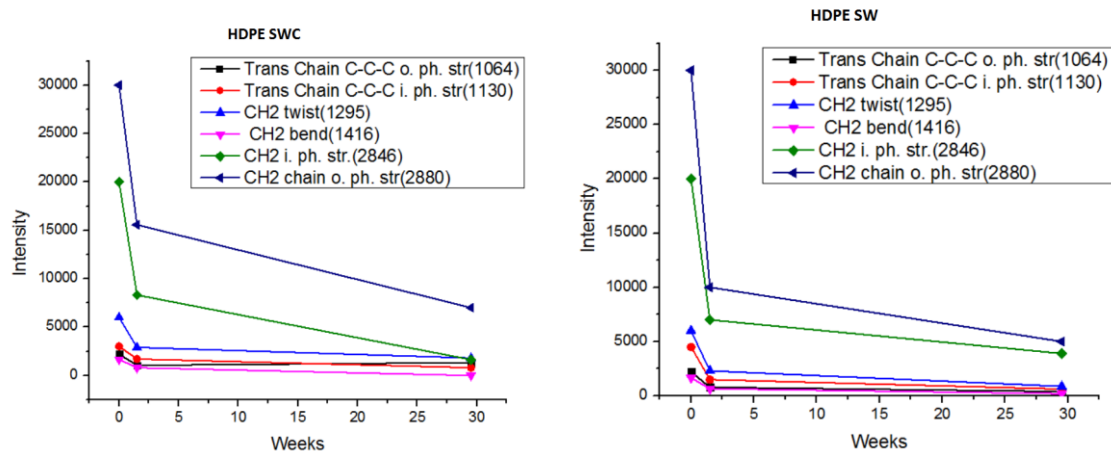


Figure 2.19: HDPE Raman intensity plots for SWC (left) and SW (right)

The spectrum for the HDPE samples in SWC at week 29.5 was mostly flat except for a few peaks. The spectrum had to be obtained using static Raman spectroscopy because it was difficult to obtain a clear spectrum with visible peaks using the full range spectrum acquisition technique.

2.2.2.3 Polypropylene

For polypropylene particles incubated in both the solvents (SWC and SW), the Raman peak intensities reduced significantly (Figure 2.21). Peaks corresponding to the C-C backbone (807 cm^{-1}) and CH_2 (841 cm^{-1}) can be seen decreasing in intensity [13] [16]. In SWC, the peak intensities decreased in steps. The intensity drops by about 33% after 1.5 weeks and then decreases to an intensity of 0 by 29.5 weeks. In SW, on the other hand, a sharp decrease in the intensity could be seen after 1.5 weeks, but the intensity after week 1.5 is seen to be approximately steady with little or no decrease until 29.5 weeks. Overall,

there was a significant decrease in intensity in the main PP peaks, such as the CH₃ asymmetrical stretch (2949 cm⁻¹) and CH₂ symmetrical stretch (2839 cm⁻¹) [13] [16]

Figure 2.20 shows the Raman spectra of PP in SWC at 29.5 weeks and the original spectrum. The figure 2.21 shows the intensity plot for PP at 1.5 weeks and 29.5 weeks.

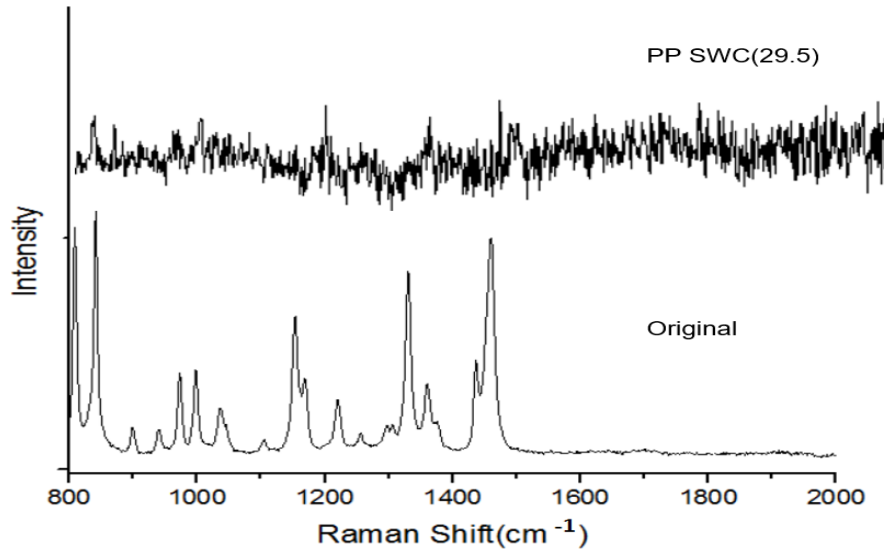


Figure 2.20: Comparative Raman spectra of PP original spectra and PP at 29.5 weeks

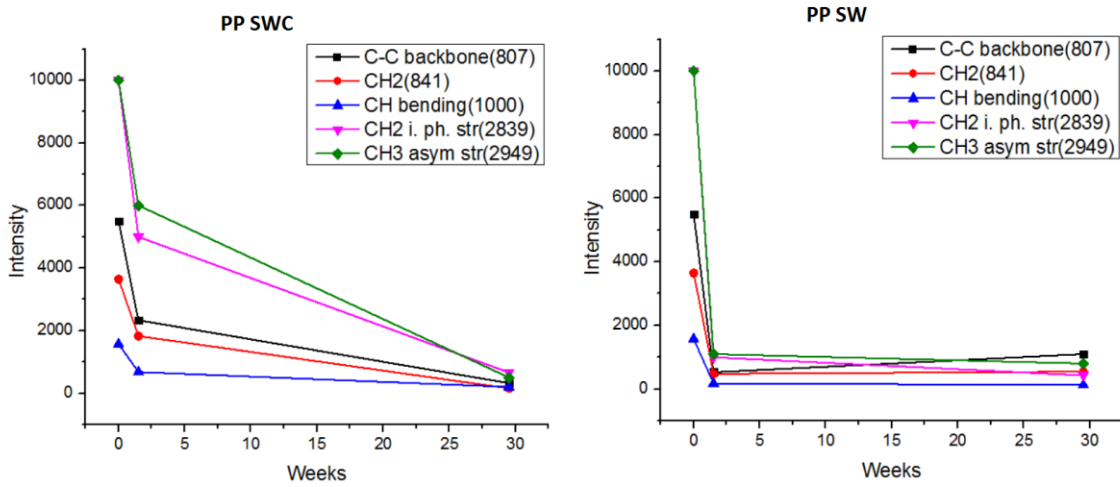


Figure 2.21: PP Raman intensity plots for SWC (left) and SW (right)

2.2.2.4 Polystyrene

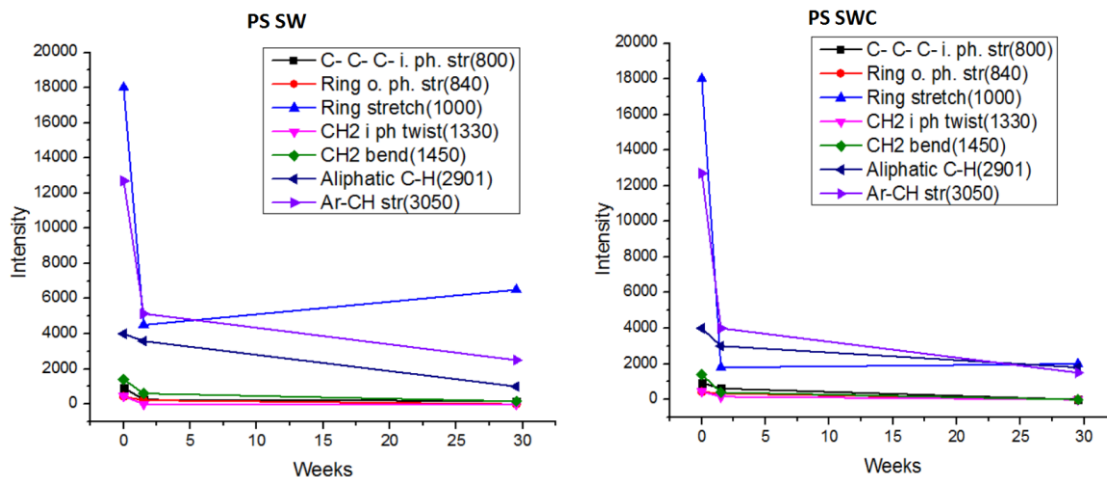


Figure 2.22: PS Raman intensity plots for SWC (left) and SW (right)

The Raman spectra for polystyrene incubated in SWC and SW solutions displayed significant differences in the peak intensities between the original sample and the sample at 29.5 weeks (Figure 2.22). A few prominent peaks were selected from the polystyrene spectra, which corresponded to its backbone, carbon- carbon chains, and ring stretches. Specifically, the peaks studied include the backbone aliphatic stretch at 2901 cm^{-1} , the aromatic C-H stretch at 3050 cm^{-1} , the symmetrical C-C-C stretch (800 cm^{-1}), and ring stretches represented by 840 cm^{-1} and 1000 cm^{-1} [13].

The samples incubated in SW and SWC displayed similar changes in peak intensities from week 0 to week 1.5. This implies that, initially, the presence of NaCl in the water is not actually causing any effect on the bond strength, but that the presence of chlorine and sunlight (UV) are the driving factors contributing to the degradation of polystyrene. However, the Raman intensities for the peaks at 840 cm^{-1} , 1330 cm^{-1} , and 1450 cm^{-1} , which represent symmetric ring stretches, symmetric CH_2 twists, and CH_2 bends, respectively,

were found to be zero in SWC solutions after 29.5 weeks. These peaks were clearly visible in the SW samples after 29.5 weeks. Hence, these bonds were susceptible to the additional chlorine present in the SWC vials. Other peaks like 1330, 2901, 1450, and 840 cm^{-1} had a lower intensity relative to the peaks at 1000 and 3050 cm^{-1} , hence, the intensity drop is not significantly seen in the above figures. In summary, all three polymers displayed significant changes in their respective Raman spectrum after incubation in SW and SWC solutions. As above, these spectral changes can be attributed to changes in sample crystallinity (for PP and HDPE), chemical composition, or surface roughness.

CHAPTER 3

SUMMARY AND CONCLUSION

3.1 Summary

In the analysis of the chlorination effects with respect to time on HDPE, PS, and PP, a variety of trends and results were observed. In HDPE, peaks corresponding to the backbone bonds were selected and analyzed for a decrease in Raman intensity. A large decrease in Raman intensity was seen between day 0 and day 9. HDPE was the most responsive towards oxidative degradation with the formation of new bonds as early as day 1 of chlorination. New bonds continued to form as the exposure time increased. Meanwhile, as the intensity of the backbone bonds decreased, the intensity of the new bonds increased and the peaks became sharper. Thermal analysis revealed that the enthalpy of melting for semi-crystalline HDPE reduced to 1/3rd of the original value and that the T_m decreased by 10 °C, indicating a weakening of the HDPE structure and possible chain cleavage.

Polypropylene had a more intense reduction in the intensity with some of the peaks being eliminated, and a distorted Raman spectrum after 5 days of chlorine treatment. The formation of C=O and C-Cl bonds indicated an oxidative attack on the PP chain. The thermal analysis of PP had a similar result as HDPE, showing signs of a weakened structure.

Polystyrene showed a similar behavior with large drops in the Raman intensity. Unlike HDPE and PP, however, it did not show crystallinity and the increase in exposure time in chlorinated solution caused a broadening of the T_g , indicating chlorine attack and

subsequent degradation. Overall, the polymers showed evidence of chlorine degradation with peak shifts, the appearance of new peaks, and flattening of old peaks.

The fall in the enthalpy and melting points because of chemical degradation can be caused by several changes to the polymer molecules, including chain scission, branching, and/or crosslinking [14]. The crystallization study done on non-degraded polypropylene and degraded polypropylene by DSC [14] found that the melting enthalpies of PP decreased with increasing incubation in chlorine solutions. A similar scenario was observed with an increase in the chlorine concentration. Similar results were seen for HDPE. There is a consistent decrease in both the T_m and ΔH_m for HDPE and PP as the chlorine concentration increased proving that the microplastics degraded and lost crystallinity. Polystyrene did not show crystallinity even in the original sample; however, the T_g decreased and the breadth of the transition increased hinting at weakened and degraded polymer chains.

The main motive of the sunlight experiments was to learn how the plastics are changing chemically as well as physically due to the attack of oxidants, like UV present in the sunlight. Specifically, they attempt to replicate the conditions the microplastics experience when they float on the surface of bodies of water throughout the globe. In all the plastics that were tested, only the most responsive bonds/peaks were selected for analysis and a large drop in the Raman intensities was observed, which can be correlated to reductions in crystallinity, oxidative degradation, or physical erosion of the sample surface [17]. In the polymers exposed to sunlight, there was no evidence of new bonds being formed or bond shifting as seen in the chlorination experiments. However, the

reduction of intensity at week 29.5 is similar in magnitude to the decrease observed after 9 days of chlorine treatment.

3.2 Conclusions

The Raman spectroscopy and DSC analyses presented herein indicate that the interaction of chlorine with the polymers is having an oxidative reaction on the plastic as well as making the polymer amorphous. The formation of new bonds with the plastic molecules in the form of new peaks is supporting the claim that chlorine oxidizes the polymer. The disinfection step in WWTP cannot be eliminated due to the benefits to society.

Therefore, there are a couple of things that WWTPs can implement to prevent contamination of the environment with microplastics:

1. Implement a process after the clarification and settling process to remove the microplastics. It can be in a form of a membrane filter that removes particles up to a few microns in diameter. This will remove the microplastics and eradicate the possibility of chlorine degrading the membrane since chlorination occurs downstream of this filtration process.
2. If the process described in bullet 1 is implemented but does not completely eradicate the microplastics problem, then another filtration process can be introduced post chlorination using polysulfone membranes, which are resistant to chlorine attack. Adding filtering processes is an efficient and effective method to remove particle with small diameters.

The above two solutions will prove effective since the plant would not have to do costly changes to their infrastructure. The addition and installation of the filtration process

would cost relatively less than a complete revamp of all the traditional processes. This small amount of money spent in adding a few processes can help in reducing the amount of damage caused to the marine life because of microplastics.

3.3 Future Work

Understanding what additives are contained in consumer products and whether they are released as a result of oxidative degradation is important. This can be researched using Gas chromatography-Mass spectrometry (GC-MS) and Gel Permeation Chromatography (GPC) to observe what chemicals are leached into the water during the chlorine treatment and to know the molecular weight of the degraded plastics, respectively. Also, a lot of consumer plastics were not studied herein, and further tests to fully identify degradation mechanisms would aid the design of effective treatment processes.

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APPENDIX A

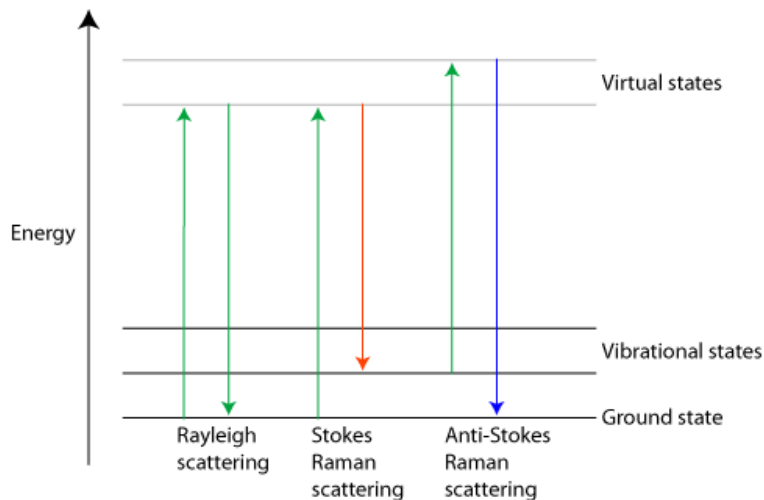
RAMAN SPECTROSCOPY FUNDAMENTALS

APPENDIX A

Raman spectroscopy fundamentals

Raman spectroscopy is based on inelastic scattering of light gathered from a sample incident with a single wavelength of light. It is a non-invasive technique used to identify the materials and involves minimum sample preparation.

A cw-laser beam (in this case, blue light of wavelength 488 nm) is focused on the surface of the sample to a lateral size of about 1 μm . The incident photon excites electrons in the sample to an excited energy state. The excited electron spontaneously returns to its ground state with a net lost energy (Stokes scattering) or gained energy (anti-Stokes scattering). The amount of energy gained or lost can be measured by collecting this scattered light, after the majority of reflected light with unchanged energy is filtered. The amount of energy gained or lost in the scattered is dependent on the molecular make-up of the sample, and the peaks are obtained at characteristic frequency shifts (measured in cm^{-1}). Hence the spectrum obtained carries information about the phonon energies in the system and can be used to fingerprint materials based on their peak positions.



Factors affecting Raman Intensities

An increase or decrease in the Raman intensity can say a tremendous amount about the condition of the substance, but the absolute intensity plot versus time cannot be termed accurate unless several factors like laser intensity, material crystallinity, thickness of the material, and surface roughness are controlled.

Thickness: The Raman intensity is a function of thickness of the material. Up to a critical value, as the material thickness increases the Raman intensity will increase. And, the chlorination on the microplastics can alter the thickness of the microplastics through chemical and physical degradation. So, without considering the thickness of each particle measured, a reliable absolute intensity plot with respect to time is not possible.

Surface Roughness: Because of inelastic scattering off of the sample surface, the smoothness play an important role in Raman analysis. The incident light is scattered from the surface and captured by the detector, which is then converted into a spectrum depending upon the energy differences between the excited electron and electron returning to the ground state. If the sample surface is uneven or rough it can result in spectral reflectance, which can also influence the Raman intensity. The chlorine attack on the microplastics is severe and it can result in abrasion on the surface of the plastic, which can result in unevenness in the plastic surface causing differences in intensity.