

EFFECT OF THERMO-PHOTOCATALYTIC PROCESS USING ZINC OXIDE ON DEGRADATION OF MACRO/MICRO-PLASTIC IN AQUEOUS ENVIRONMENT

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Abstract: More than 320 million tons of plastics are produced annually, and the rate of plastic waste generation steadily increases by 3.9% per year. Introduction of plastic waste into water bodies may lead to many adverse environmental impacts as the plastic debris is very stable and generally requires a longer time to degrade. Over a period of time, bulk plastic debris will slowly degrade into small fragments known as macroplastics (particles size >5mm) and microplastics (particles size <5mm). Accumulation of this newly emerging class of pollutants potentially decreases the efficiency of the existing water treatment system. Therefore, improvement on the existing water treatment technique is required. This study aimed at investigating the effect of using the UV-assisted thermo-photocatalytic reaction on the degradation of polypropylene (PP) macro- and microplastics in an aqueous environment for 6 hours. ZnO nanoparticles (<50 nm) were employed as the photocatalyst. 2³ Full Factorial design was carried out in order to identify the correlation between the reaction temperature (35-50 °C), size of PP plastic (25-100 mm²) and the catalyst dosage (1-3 g/L) factors and their influences on the weight loss of macro/micro-plastics. Maximum plastic weight loss of 7.8 wt% was achieved at 50°C, 1 g/L ZnO and 25 mm² of PP plastic. The interaction between temperature and size must be taken into consideration.

Keywords: Microplastic, macroplastic, thermo-photocatalytic, zinc oxide, aqueous environment .

Introduction

More than 320 million tons of plastic products made of polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and many more are produced annually (Benckiser, 2019). Unfortunately, the plastic wastes generated from household materials and industrial sectors steadily increase by 3.9% per year while almost 12,000 million tons of the wastes have escaped from the waste management cycle and ended in the landfills or discarded into water bodies such as river, lake or ocean (Clean Malaysia, 2016; Valavanidis, 2016). This is undesirable since plastic waste does not decompose or degrade naturally, so they could last for several decades in our valuable water resources if no proper handling is carried out (Bandara *et al.*, 2017).

Introduction of plastic waste into water bodies may lead to many adverse environmental impacts as the plastic debris is very stable and generally requires a longer time to degrade. Over a period of time, bulk plastic debris will slowly degrade into small fragments known as macroplastics (particles size >5mm) and microplastics (particles size <5mm) (Piehl *et al.*, 2018). Microplastics can be classified as primary and secondary microplastics. Primary microplastics are small plastic particles which are deliberately produced in this size for use in cosmetic or abrasive products while secondary microplastics are generated during degradation processes (Shim *et al.*, 2017). The fragmentation of plastic macro debris into smaller pieces is promoted by the action of the hydrolysis, photodegradation, mechanical or physical degradation of plastic.

Several conventional ways to increase degradation of plastics include biodegradation, photodegradation, thermooxidative degradation and thermal degradation approaches (Andrady, 2011). However, these time consuming processes are applied for promoting the fragmentation of plastic waste in a dry condition in the presence of microbial agents, weathering under direct exposure to UV light and chemical decomposition under high temperature (above 100 °C). The rate of plastic fragmentation process may vary depending on the plastic's chemical and thermal stability as well as exposure time to degradation agents (Lambert & Wagner, 2016; Portillo *et al.*, 2016; Weinstein *et al.*, 2016). Noticeable degradation of plastic is commonly observed after weathering test for up to 6 months.

The concern due to the presence of macro or microplastic pollutants in aquatic ecosystems has been highlighted in many recent studies. Accumulation of this newly emerging class of pollutants potentially decreases the efficiency of the existing water treatment system. As a result, many water or wastewater treatment facilities have now become the sink and source of microplastic pollution (Kay *et al.*, 2018; Prata, 2018). Larger plastic debris are generally removed by physical removal process including filtration and sedimentation but the treatment of macro or micro plastic suspended in water is relatively limited. Therefore, improvement on the existing water treatment technique is required to reduce the impacts.

Photocatalytic degradation of polymers stands out as one of the most promising methods because photocatalysis could be viable, inexpensive and energy efficient for polymer degradation (Tofa *et al.*, 2019a). Photocatalysis is a light-mediated redox process. In the presence of appropriate light energy, nanostructured semiconductors excited thus leading to the creation of excited pairs. It will react with surrounding water/moisture to produce superoxides and hydroxyl radicals which are highly reactive species that promote the oxidation of organic species including polymers (Tofa *et al.*, 2019b). Attempts to evaluate the

efficiency of photocatalytic treatments of plastic waste in aqueous medium have been previously and most current works extensively focus on the use of TiO₂ as photocatalyst material over a range of polymers. Ali *et al.*, (2016) explored the use of TiO₂ nanotubes to photocatalytically enhanced degradation of low density PE (LDPE) under UV light. Their findings show that 78% of PE degrades in 15 days of reaction. Bandara *et al.*, (2017) reported the degradation of plastic over TiO₂ and ZrO₂ under sunlight. In this case, the degradation of PE and PP were studied in terms of its morphology and changes in carbonyl index. They reported that both PE and PP undergo progressive oxidation process which promotes fragmentation and decomposition of its structure. Similar observation was emphasised in the work by Zhao *et al.*, (2008). Employment of modified TiO₂ enhances the photocatalytic degradation of PE under sunlight irradiation. During photocatalytic degradation process, direct attack of polymer surface by highly oxidizing radicals in the form of reactive oxygen species (ROS) causes oxidation and breakage of polymer chains. The decomposed chains leached from the bulk as intermediate and simpler compound. A study by Abo *et al.*, (2016) supported that the photocatalysis process can further degrade the by-product from plastic waste decomposition such as Bisphenol A to more than 98% using TiO₂, ZnO and SnO₂. Although the presence of photocatalyst significantly accelerates the degradation of plastic in water, the treatment time required to achieve satisfactory percentage of plastic removal or degradation is relatively longer compared to the physical removal process like filtration. Some plastic wastes are designed to be highly durable and chemically stable at ambient temperature, thus chemical degradation of plastic through photocatalytic treatment alone is not sufficient to shorten the reaction time. Furthermore, the performance of a photocatalysis system strongly relies on the perfect combination of operating parameters such as temperature, intensity of light, catalyst dosage, dissolved oxygen level and initial concentration of pollutant. Therefore, of the rate decomposition could be maximised

by conducting the treatment under optimum conditions.

The present work therefore extends previous studies by investigating the effect of thermo-photocatalytic process using ZnO on degradation of plastic in aqueous environment. In this work, the photocatalytic treatment using reactive ZnO photocatalyst was performed at elevated temperature (up to 50 °C) to promote the photodegradation of plastic debris in water. ZnO was chosen because of its known photocatalytic efficiency. Laxma in his review highlighted that the ZnO has similar band gap energy (3.37 eV) to TiO₂ and its electron mobility is much higher than that of TiO₂ at a lower cost (Laxma *et al.*, 2018). The thermo-photocatalytic technique is proposed as an alternative method to accelerate the decomposition of macro-plastics in the wastewater system. It may assist in reducing the plastic accumulation problem in the water system. The findings from this study may also improve the understanding on the impact of reaction temperature and the amount of catalyst loading on decomposition of macro/micro-plastics.

Materials and Methods

Materials

Commercial ZnO nanoparticles with a particle size of ~50 nm (99.9%, Sigma–Aldrich) were employed as the photocatalyst. Commercially available macro-plastic particles made up of polypropylene (PP) plastic and the plastic sheets were manually cut into small pieces with the dimension 25 mm² and 100 mm² and were denoted as the micro-plastic and macro-plastic.

Photocatalytic Testing

Photodegradation of 25 mm² and 100 mm² PP plastic in 1000 mL aqueous samples was achieved using batch- slurry photoreactor equipped with an air pump (1.6 L/min) and an ultraviolet lamp with 11 watts of UV-C radiation. The photoreactor was partially immersed in a water bath with temperature controller (GTSONIC Model VGT-1620QTD) to maintain the reaction

temperature at a selected setting. The schematic diagram of the experimental set-up is shown in Figure 1. This work evaluates the degradation of PP plastic under the spectrum of 254 nm at elevated temperature. The macro or microplastic prepared was mixed with 1 or 3 g/L of ZnO in a beaker and was immersed in a water bath for further treatment. Based on our preliminary work, loading the reactor with less than 1 g/L of ZnO in nano-scaled was insufficient to give noticeable effects on the plastic removal process whereas exceeding the load above 3 g/L ZnO produced very turbid solution that hindered penetration of light. Infact, the excess catalyst agglomerated as sediment at the bottom of the reactor. The reaction time was set at 6 hours and the reaction temperature was set up at 35°C or 50°C. The selected reaction time and temperature range simulate the operation of a vast majority solar thermal collector. In the future work, the elevation of operating temperature can be achieved by using a solar thermal collector which converts solar radiation to heat. In addition, increasing the solution temperature above 80 °C is impracticable due to safety issue and excessive energy usage. The efficiency of the thermo-photocatalytic process in aqueous environment was determined by calculating the difference in weight of PP in percentage plastic before and after the experimental work in percentage as expressed in Equation 1,

$$\text{Weight loss (\%)} = \frac{W_i - W_f}{W_i} \times 100 \quad (1)$$

where W_i is the initial weight of PP plastic before treatment and W_f is the final weight of PP after photodegradation treatment. In order to study the impact of multiple treatments, the microplastic (25 mm²) was treated continuously for five repeated cycles in presence of 1 g/L ZnO at 50°C. The weight loss of PP plastic was measured after each cycle.

Characterisation Techniques

The surface morphology of PP plastics before and after the treatment was studied by scanning electron microscopy (SEM) (Philip XL40). The

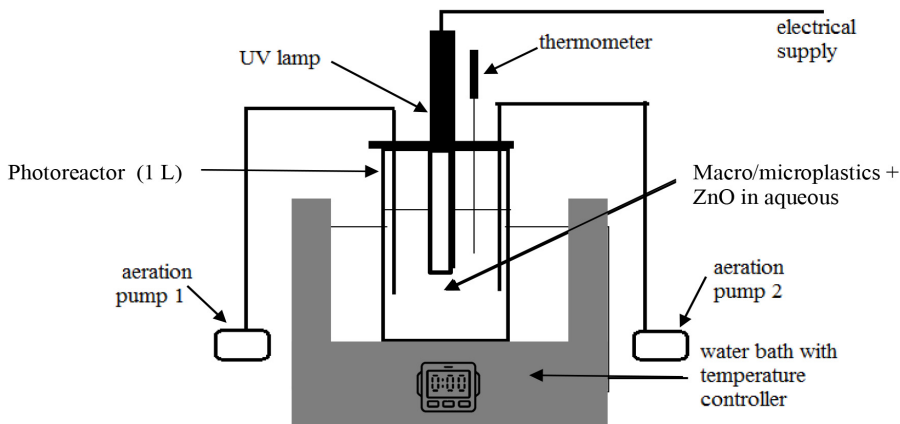


Figure 1: Schematic diagram of the photoreactor set up

PP plastic was mounted on carbon tape and gold coated prior to study. Surface functionalities of the sample were identified by Fourier transform infrared spectroscopy (FTIR) (IR Tracer-100). The data were collected over the range 500 to 4000 cm^{-1} with a resolution of 4 cm^{-1} . Thermogravimetric analyser (TA Instrument Q50) identified the mass loss of the PP sample over time and relative to temperature change. The temperature was increased from 20°C to 500°C at a rate of 10°C/min under compressed air purging and macro plastic using thermo-photocatalytic technique. In this work, the 2³ full factorial design was adapted to statistically analysed the individual and interaction effects of the reaction temperature, the plastic's size and the ZnO catalyst dosage factors on the weight loss of PP during the course of a thermo-photocatalytic treatment. The data was analysed using MiniTab® 16 Statistical software. Reaction temperature was set at 35 and 50°C; while PP macro- and microplastic were cut into 25 and 100 mm². 1 and 3 g/L of ZnO were employed as the photocatalyst. The highest and lowest value were denoted as +1 and -1. 24 sets of experiments were conducted with

three replicates and the data is summarised in Table 1.

Results and Discussion

2³ Full Factorial Analysis

24 sets of experiments were conducted with three replicates using 2³ Full Factorial design and were analysed using MiniTab® 16 software. The results are summarised in Table 1.

The statistical calculation and regression were performed using MiniTab software. The coefficients for individual and interactive effect of each coefficient and the probability for the full 2³ factorial designs are tabulated in Table 2. ANOVA analysis is provided in Table 3. All factors are statistically significant as the P value is smaller than 0.05. According to the coefficient value, reaction temperature shows a positive impact on the percentage of plastic weight loss. In contrast, the size of PP plastic and the catalyst dosage factors show a negative impact. The first-order model with all possible interactions is shown in Equation 2. This model equation has a very satisfactory fitting as the $R^2=0.9769$ and the $R^2(\text{adj})=0.9721$.

$$\% \text{Weight Loss} = 4.394 + 1.115 * T - 1.321 * \text{SIZE} - 0.207 * \text{DOSE} - 0.565 * T * \text{SIZE} \quad (2)$$

where T is the temperature factor, SIZE is the plastic size factor and DOSE is the catalyst dosage factor in their corresponding coded forms.

Table 1: Experimental design matrix and results using 2³ full factorial technique

Run	Coded Experiments Matrix			Weight Loss (%)
	Temperature (T)	Plastic Size (SIZE)	Catalyst Dosage (DOSE)	
1	-1	1	-1	2.48
2	-1	1	1	2.48
3	-1	-1	1	3.44
4	-1	-1	-1	4.43
5	1	1	1	3.00
6	1	1	-1	3.90
7	1	-1	1	7.39
8	1	-1	-1	7.35
9	-1	1	1	2.42
10	1	1	-1	3.92
11	-1	1	-1	2.43
12	-1	-1	-1	4.00
13	1	-1	1	7.80
14	1	1	1	3.50
15	-1	-1	1	3.94
16	1	-1	-1	7.89
17	-1	-1	1	3.90
18	1	1	-1	3.92
19	-1	1	-1	2.89
20	-1	-1	-1	4.50
21	-1	1	1	2.44
22	1	-1	-1	7.50
23	1	-1	1	6.44
24	1	1	1	3.50

Table 2: Estimated effects and coefficients for % weight loss

Term	Effect	Coef	SE Coef	T	P
Constant	-	4.394	0.06455	68.08	<0.001
T	2.230	1.115	0.06455	17.27	<0.001
Size	-2.642	-1.321	0.06455	-20.46	<0.001
Catalyst	-0.413	-0.207	0.06455	-3.20	0.005
T*Size	-1.130	-0.565	0.06455	-8.75	<0.001

Table 3: Analysis of variance (ANOVA) for % weight loss

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main effects	3	72.7329	72.7329	24.2443	242.46	0.000
T	1	29.8374	29.8374	29.8374	298.39	0.000
Size	1	41.8704	41.8704	41.8704	418.73	0.000
Dose	1	1.0251	1.0251	1.0251	10.25	0.005
2-Way Interactions	1	7.6614	7.6614	7.6614	76.62	0.000
T*Size	1	7.6614	7.6614	7.6614	76.62	0.000
Residual Error	19	1.8999	1.8999	0.1000		
Lack of Fit	3	0.1739	0.1739	0.0580	0.54	0.663
Pure Error	16	1.7260	1.7260	0.1079		
Total	23	82.2942				

Individual plots of the impact of reaction temperature, plastic size and catalysts dosage were generated as shown in Figure 2. High reaction temperature favours the decomposition of PP plastic thus leading to the increment of percentage of weight loss. Heat can influence plastic degradation in several possible ways. Heat can cause thermal oxidative degradation on polymers. However, the polymer must be heated to a sufficiently high temperature that can cause breakage of chemical bonds. Kang *et al.*, (2019) reported that microplastic (about 10% to 54%) decomposed when heated for 8 hours at a temperature between 100 °C to 160 °C. In the context of this study, exposure of PP to the temperature lower than 50 °C was not adequate to cause direct thermal decomposition of PP. However, it is proposed that the temperature influences the rate of photo-oxidation reaction on PP. As suggested by Gogotov and Barazov (2012), mild heat treatment (~70 °C) promotes rapid breakdown of polymer chains during photo-oxidation process. Synergistic application of UV-photocatalysis (mediated on ZnO catalyst) and heat generated different oxidised product on the surface of PP, thus making it more vulnerable to subsequent radical attacks.

PP plastic in smaller size (microplastics) promotes the decomposition process while the

amount of catalyst loaded has a little impact. The plastic size factor has interaction effect with the temperature. The influence of plastic size effect on PP decomposition is more prominent at high temperature. The interaction plot in Figure 3 suggests that the combination of high reaction temperature (50 °C) and low size of PP plastic (25 mm²) resulted in high PP weight loss. It was determined that the decomposition of microplastic (25 mm²) was the highest (7.89%) upon the introduction of 1 g/L of ZnO and the reaction was carried out at 50°C. The trend observed in this experiment is comparable to the result reported in Ariza-Tarazona *et al.*, (2019) that used N doped TiO₂ for degrading high density polyethylene (HDPE). Plastic loss during photodegradation process signified that the PP surface underwent gradual decomposition process. The highly oxidizing radicals namely the •OH and •O₂⁻ radicals photogenerated on the ZnO surface could aggressively attack the polymeric chains on PP and cause it to oxidised. In comparison to the findings in Ariza-Tarazona *et al.*, (2019), the treatment time required for decomposing 7 wt% HDPE is relatively longer (20 hours) as the reaction takes place under 25 °C in the presence of TiO₂. PP treated in this study on the other hand lost similar weight in only 6 hours.

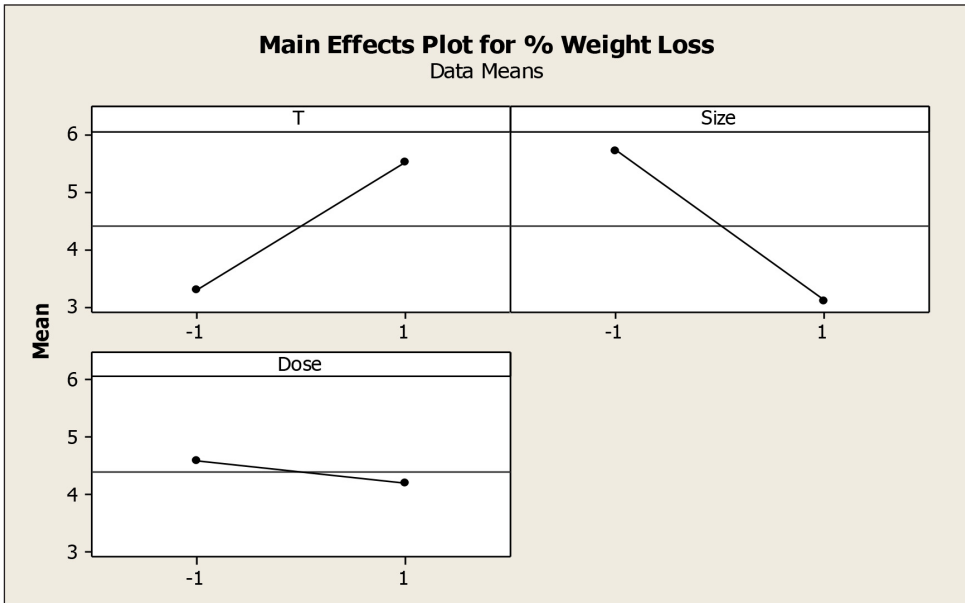


Figure 2: Plot for % weight loss

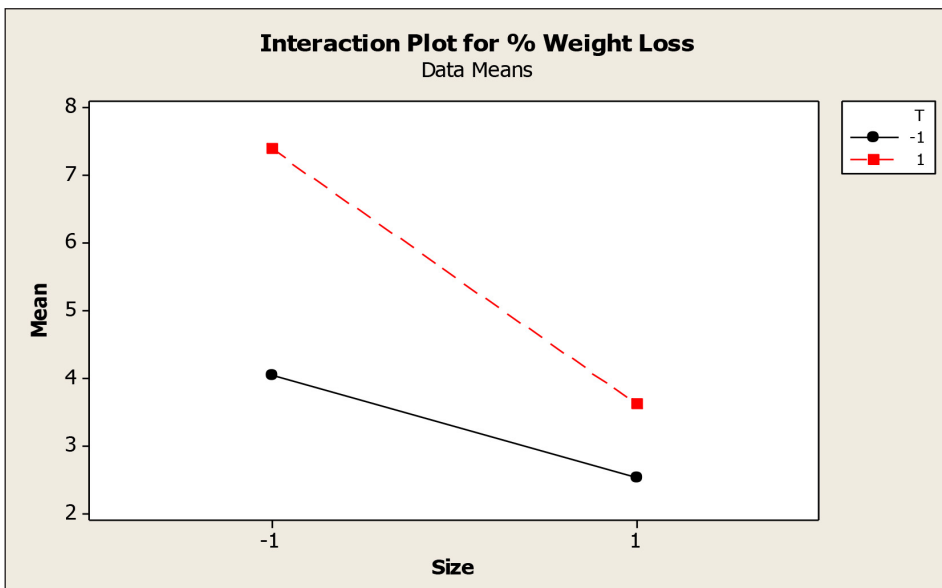


Figure 3: The interaction plot between PP size and reaction temperature and its impact on percentage of weight loss

The contour plots and surface response are shown in Figure 4 and the interaction between all factors were analysed. Based on the finding, it can be predicted that the synergy between the factor of PP plastic size and the reaction temperature factor are very significant. High

PP plastic weight loss (>7%) is achieved by carrying thermo-photocatalytic treatment on small PP plastic pieces (25 mm²) at high temperature (50 °C) or low ZnO catalyst dosage (1 g/L).

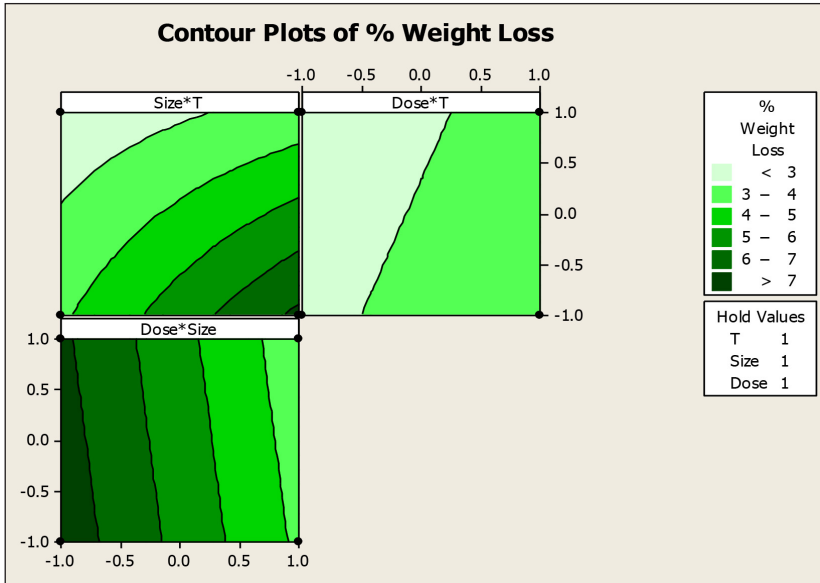


Figure 4: Contour plots of Size*T, Dose*T and Dose*Size

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) used in this study is able to determine the decomposition of PP plastic. It was reported that the PP plastic exhibits low melting points at $164 \pm 1 \text{ }^\circ\text{C}$ (Majewsky *et al.*, 2016). As can be seen from the TGA curve shown in Figure 5, the thermal decomposition process of PP starts at a temperature of 178°C and the maximum weight loss occurs in the range of 200 to 300°C . No obvious weight loss was detected at 35

and 50°C . This observation suggests that the weight loss measured during the treatment was solely due to the photodegradation reaction. Elevation of reaction temperature up to $50 \text{ }^\circ\text{C}$ possibly alters the activity on ZnO catalyst surface which encourages generation of radical species or promotes the oxidation reaction rate on plastic surface. In addition, exposure to that temperature weakened the chemical bonds in PP, thus increased the effectiveness of radical attacks.

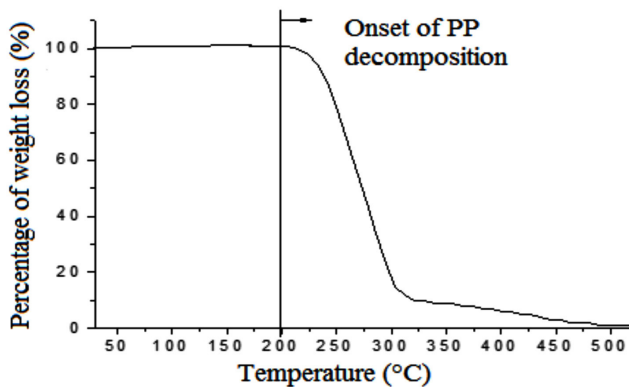


Figure 5: TGA analysis of PP plastic

SEM Analysis

Figure 6 (a) shows the SEM micrograph of untreated PP plastic. Microcracks, cavities and interconnected holes were detected forming on the surface of treated PP (as shown in Figure 6(b) and (c)). In agreement with Ali *et al.*, (2016), the development of these surface defects indicates the occurrence of polymer degradation or oxidation. Small cracks and isolated holes ($<3 \mu\text{m}$ diameter) were observed on the PP surface treated at 35°C in the presence of 3 g/L ZnO catalyst. The size of the microcracks grew to approximately more than $15 \mu\text{m}$ diameter as the plastic was treated at 50°C using 1 g/L ZnO catalyst. The overall surface of the plastic was also becoming rough and irregular. The ZnO suspension initiates the photocatalysis process under UV light and it leads to aggressive oxidation of polymer chains that later creates holes or cracks.

The Influence of Cyclic Thermo-photocatalytic Treatment on Polypropylene

The impact of cyclic thermo-photocatalytic treatment on PP plastic degradation was tested over 25 mm^2 plastic in presence of 1 g/L of ZnO and 50°C . The experimental works has been repeated for five cycles and the percentage of PP plastic weight loss has been summarised in Figure 7. As expected, high percentage of weight loss was observed on the increase of the number of treatments from 7.4% to 37.8% . With more cycles, the plastic weight loss was higher. It is recommended that the number of treatment cycles can be prolonged to more than 5 cycles in future studies to further confirm the trend.

PP plastic is considered strong and has a good thermal resistance. The morphology of the plastic started to crack after the first treatment. The SEM micrograph of PP plastic after being treated for five times as indicated in Figure 8. The damage of the PP surface increases with

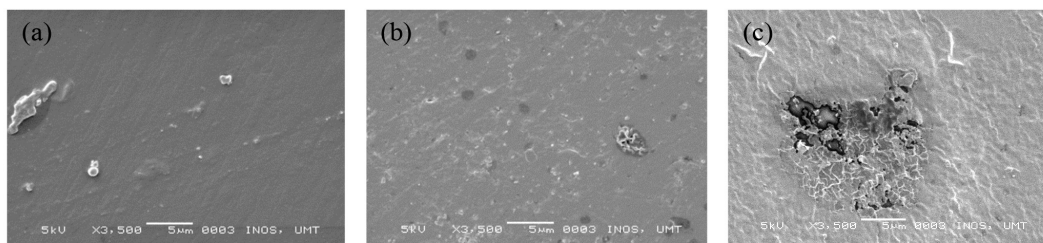


Figure 6: The SEM micrograph of (a) untreated PP plastic; (b) PP plastic treated using 3 g/L ZnO at 35°C and (c) PP plastic treated using 1 g/L ZnO at 50°C

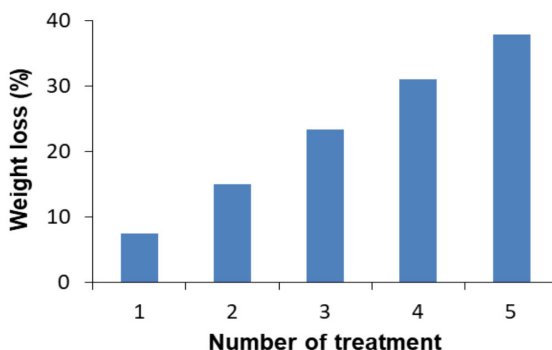


Figure 7: Percentage of plastic weight loss with number of thermo-photocatalytic treatment cycles

increased exposure to light source and longer reaction time (Bandara et al., 2017).

Thermophotocatalytic process is expected to cause oxidative degradation of PP microplastics due to simultaneous thermal exposure and radical attacks by photogenerated reactive oxygen species on ZnO surface illuminated

with UV. FTIR analysis has been performed to confirm the oxidative degradation of PP upon treatment. Figure 9 shows the comparison between the spectrum of untreated PP and the PP treated with thermophotocatalytic process for 5 cycles.

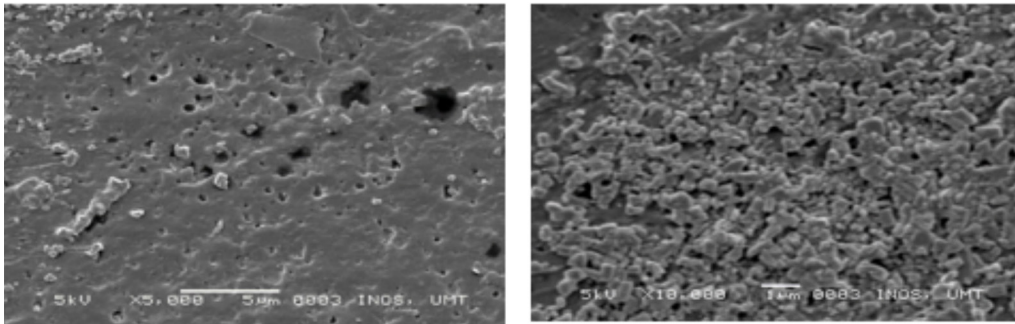


Figure 8: The SEM micrograph of PP plastic (25 mm²) treated using 1 g/L ZnO at 50°C after 5 cycles of thermo-photocatalytic treatment

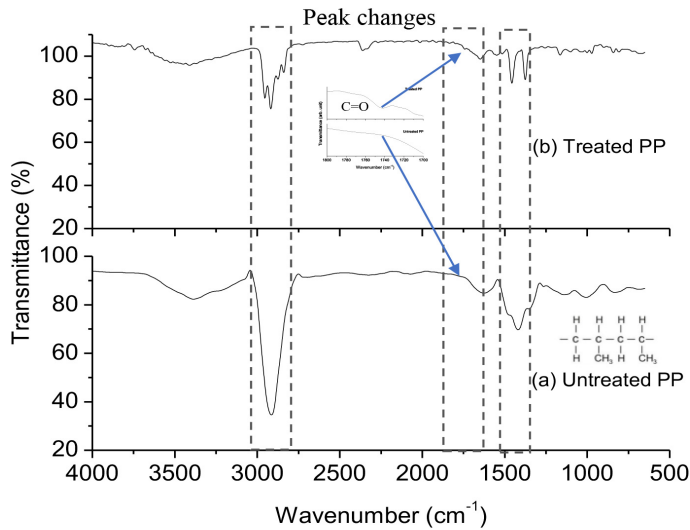


Figure 9: Wave number in diagram

Table 4: The peaks detected from FTIR spectra of (a) untreated PP plastic and (b) 25 mm² PP plastic treated with 1 g/L ZnO at 50°C after being treated for 5 times.

	Peak (cm ⁻¹)	Assignment	References	
Untreated PP	833	Rocking vibration of -CH	Fang <i>et al.</i> , 2012; Chun <i>et al.</i> , 2015; Jung <i>et al.</i> , 2018	
	1006	Rocking vibration of -CH ₃		
	1141	Wagging/Rocking of CH or CH ₃		
	1354	Symmetrical bending vibration of -CH ₃		
	1419	Symmetrical bending vibration of -CH ₃		
	1618	C=C stretching vibration		Longo <i>et al.</i> , 2011
	2914	Asymmetrical bending vibration of -CH ₂		Fang <i>et al.</i> , 2012; Chun <i>et al.</i> , 2015; Jung <i>et al.</i> , 2018
	3377	Hydroxyl (-OH) group		Longo <i>et al.</i> , 2011
Treated PP (After 5 cycles of treatment)	840	Rocking vibration of -CH	Fang <i>et al.</i> , 2012; Chun <i>et al.</i> , 2015; Jung <i>et al.</i> , 2018	
	1022	Rocking vibration of -CH ₃		
	1161	Wagging/Rocking of CH or CH ₃		
	1375	Symmetrical bending vibration of -CH ₃		
	1456	Symmetrical bending vibration of -CH ₃		
	1647	C=C stretching vibration		Longo <i>et al.</i> , 2011
	*1743	(new peak merge)		Barbes <i>et al.</i> , 2014; Mylläri <i>et al.</i> , 2015; Longo <i>et al.</i> , 2011; Sellin & Campos, 2003
	*1832	Carbonyl (C=O) from ketone groups		
	2918	Asymmetrical bending vibration of -CH ₂		Fang <i>et al.</i> , 2012; Chun <i>et al.</i> , 2015; Jung <i>et al.</i> , 2018
	*2926	(new peak merge) C-H stretching from linear aliphatic chain		Longo <i>et al.</i> , 2011
	3410	Hydroxyl (-OH) group		

An untreated PP molecule is made from polymerization of propene monomer (C₃H₆) in which the non-polar methyl groups are attached to its long carbon chains. Based on previous works, oxidative degradation of PP is associated to the presence of oxidized polar functional groups such as carbonyl (C=O), hydroxyl (-OH), (C-O) and (C-OH) (Barbes *et al.*, 2014; Mylläri *et al.*, 2015; Longo *et al.*, 2011; Sellin & Campos, 2003). Action by radiation, thermal exposure

and/or oxidising agents particularly reactive oxygen species (•OH, •O₂) are responsible for the introduction of these new functional groups to the PP during degradation process. Based on FTIR result, important changes occurring in the region of 1600 to 3500 cm⁻¹ was thoroughly analysed. It was noticed that several new peaks emerged at 1743, 1832 and 2926 cm⁻¹ in treated PP. Consistent with Longo *et al.*, (2011), Mylläri *et al.*, (2015) and Sellin and Campos

(2003), the appearance of these peaks could be associated with the presence of ketone groups. The presence of hydroxyl (-OH) groups around 3400 cm^{-1} in the spectrum of treated PP also indicates the surface of the PP has oxidised with more carboxyl groups (-COOH) and alcohol. Therefore, the FTIR analysis confirmed that upon treatment with thermal-photocatalytic process using ZnO, oxidative degradation of PP occurred. Combination of heat, UV irradiation and chemical attack by reactive oxygen species induced by ZnO photocatalyst had effectively promote degradation of PP.

Conclusion

Degradation rate of PP macro and microplastics suspended in an aqueous environment has been significantly affected by the UV-assisted thermo-photocatalytic reaction over ZnO at elevation of reaction temperature. ZnO photocatalyst which was activated by UV light induced the photogeneration of reactive radical species (superoxides or hydroxyl radicals). These highly oxidising agents rapidly attacked and oxidised the polar functional groups on PP. The photodegradation rate of PP was further promoted by increasing the reaction temperature ($\sim 50^\circ\text{C}$). As a result, fragmentation of macro- and microplastic was accelerated. The 2^3 full factorial analysis statistically proved that the reaction temperature, size of PP plastic and interaction of both variables are important factors that need to be taken into consideration. However, the ZnO catalyst dosage has a little impact on the PP plastic degradation. The decomposition of microplastic (25 mm^2) was the highest (7.89%) upon the introduction of 1 g/L of ZnO and the reaction was carried out at 50°C . In addition, the degradability of microplastics increased linearly with increasing number of treatment; in which 38% of PP plastic was degraded after being treated for five cycles. With similar number of treatment cycles, the percentage of PP weight loss can be maximised if the treatment was conducted on microplastics with much smaller size ($<25\text{mm}^2$). This would be an advantage to treat microplastic debris in

actual wastewater which commonly ranging from 25mm^2 to 1 nm^2 . All these work contributed to the knowledge in improving the microplastic degradation from the influence catalyst loading, influence of reaction temperature and influence of microplastic size.

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