ORIGINAL PAPER

Visible light photocatalytic degradation of microplastic residues with zinc oxide nanorods

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Abstract

Microplastics have recently become a major environmental issue due to their ubiquitous distribution, uncontrolled environmental occurrences, small sizes and long lifetimes. Actual remediation methods include filtration, incineration and advanced oxidation processes such as ozonation, but those methods require high energy or generate unwanted by-products. Here we tested the degradation of fragmented, low-density polyethylene (LDPE) microplastic residues, by visible light-induced heterogeneous photocatalysis activated by zinc oxide nanorods. The reaction was monitored using Fourier-transform infrared spectroscopy, dynamic mechanical analyser and optical imaging. Results show a 30% increase of the carbonyl index of residues, and an increase of brittleness accompanied by a large number of wrinkles, cracks and cavities on the surface. The degree of oxidation was directly proportional to the catalyst surface area. A mechanism for polyethylene degradation is proposed.

Keywords Microplastic · Low-density polyethylene · Photocatalysis · Zinc oxide · Nanotechnology · Visible light

Introduction

Recent studies have shown the ubiquitous distribution of fragmented plastics of sizes less than 5 mm, typically referred to as microplastics, in the biosphere, due to years of improper disposal of plastic materials, mismanagement and negligent littering (Eerkes-Medrano et al. 2015, Van Cauwenberghe et al. 2015, Auta et al. 2017). A small fraction of larger sized plastic materials are recovered, incinerated or recycled for further use. The rest of the plastics end up in landfills, waterways, drainage systems and wastewater plants. Wastewater treatment plants have been identified as one of the major potential sources of microplastics pollution in aquatic systems mainly contributed by consumer plastics, industrial abrasion, air blasting media, cosmetic products, textiles, medicines as well as the breakdown of larger particles (Bergmann et al. 2015; Talvitie et al. 2015). Several studies have suggested advanced treatment technologies for the removal of microplastics from wastewater treatment system (Talvitie et al. 2017). Research is also focusing on the development of sustainable, bio-based plastic polymers (Kuswandi 2017; Brandelli et al. 2017).

Existing approaches for handling waste plastic materials are thermal, catalytic, mechanical, chemical, ozonation and photo-oxidative degradation (Klein et al. 2018); yet studies showed that photocatalysis could be viable, inexpensive and energy efficient for polymer degradation. Photocatalysis is a light-mediated redox process, wherein nanostructured semiconductors excited with appropriate light energy lead to the creation of exciton pairs, which react with surrounding water/moisture to produce highly reactive species like superoxides and hydroxyl radicals that can effectively oxidize organic species including polymers (Ali et al. 2016; Qi et al. 2017; Çolak et al. 2017; Baruah et al. 2016).

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Amongst popular metal oxide photocatalysts, ZnO stands out to be the most promising owing to its band gap (3.37 eV), excellent optical properties, high redox potential, better electron mobility and non-toxicity. In addition, ZnO is easy to synthesize and can be formed into different shapes and sizes using facile low-temperature hydrothermal growth processes (Qi et al. 2017; Baruah and Dutta 2009; Çolak et al. 2017). 'Nano' sized materials are of great importance due to high surface to volume ratio compared to bulk materials as photocatalysis is a surface-driven phenomenon (Baruah et al. 2016).

In this study, ZnO nanorod photocatalysts were used to degrade LDPE film (residual), which is an abundant microplastic pollutant in wastewater systems (Talvitie et al. 2017). Suitability of photocatalysis as a process to degrade solid phase LDPE residues in water was evaluated and a possible chemical pathway has been proposed.

Materials and methods

Reagents

Zinc acetate dihydrate [$Zn(CH_3COO)_2$, molecular weight: 219.5 g/mol], Zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$, molecular weight: 297.47 g/mol]and Hexamethylenetetramine [$C_6H_{12}N_4$, molecular weight: 140.19 g/mol] were purchased from Sigma-Aldrich. Commercially available, solid LDPE film of 50 μm thicknesses was used for the degradation studies.

Growth of zinc oxide nanorods

Zinc oxide (ZnO) nanorods were hydrothermally grown on glass substrates (Baruah and Dutta 2009). Briefly, a seed ZnO layer was formed by spray pyrolysis of 10 mM $Zn(CH_3COO)_2$ at 1 mL/min on clean microscopic glass slides placed on a hot plate at 350 ºC. ZnO nanorods were grown by subsequently placing the seeded substrates in a chemical bath of equimolar solutions of hexamine and zinc nitrate hexahydrate in DI water for 5 h at 90 °C, followed by post-synthesis annealing in air at 350 °C for 1 h.

Experimental set-up for photocatalytic degradation of low-density polyethylene film

Photocatalytic degradation of low-density polyethylene (LDPE) film of size (1 cm × 1 cm) was carried out for 175 h in a petri dish containing the photocatalyst and deionized water. A 50 W dichroic halogen lamp in ambient air was used for visible light illumination ($\approx 60–70$ klux) from a distance of 10 cm (supporting info. Fig. S1).

Characterization techniques

Scanning electron microscope (SEM) (ZEISS Ultra 55) was used for the determination of surface morphology and size ranges of catalysts. A digital microscope (Leica: DFC295) fitted with a 3.0 megapixel camera was used for observing the morphological changes over the surface of the exposed LDPE film.

Dynamic mechanical analyser (DMA) was used to determine mechanical changes within the polymer at molecular levels. Both controlled, and pre-stressed LDPE films were exposed to a sinusoidal stress and strain at different temperatures (-20 ºC to $+100$ ºC) at 1 Hz frequency. Storage modulus (E_s) that represents the elastic behaviour of polymer was calculated as in Eq. (1).

Storage modulus,

$$E_s = \sigma / \in * \cos\beta \qquad (1)$$

where $\sigma =$ maximum stress, $\epsilon =$ maximum strain and $\beta =$ phase angle in radian between the dynamic stress and the dynamic strain in a visco-elastic material subjected to a sinusoidal oscillation.

Fourier-transform infrared (FTIR) spectroscopy (Nicolet is 10: Thermo scientific) was used for the qualitative observation of molecular changes of the functional groups. The effect of photocatalytic oxidation was monitored by determining both carbonyl and vinyl indices; carbonyl index being the ratio of areas under the absorbance peaks at 1712 cm^{-1} and 1372 cm^{-1}; vinyl index being the ratio of the area under the absorbance of vinyl group at 909 cm^{-1} to the area under the same reference peak (Ali et al. 2016).

Result and discussion

Morphological variations of photodegraded low-density polyethylene films

Cracks and spots on the low-density polyethylene (LDPE) film where the photo-mediated oxidation process was prevalent after 175 h of exposure can be visually observed from optical images shown in Fig. 1. Chromophoric groups, manufacturing defects and weak links act as initiation sites for the oxidation process, in turn leading to degradation of the molecular bonds upon prolonged photocatalytic exposure (Yousif and Haddad 2013). Few cracks observed on the control LDPE film might be introduced from manufacturing processes.

Fig. 1 Microscopic images of **i** as received low-density polyethylene (LDPE) and photo-irradiated LDPE for 175 h in contact with nanorods **ii** ZnO (3 mM_5 h) **iii** ZnO (10 mM_5 h), **iv** ZnO (20 mM_5 h) exhibiting the development of cracks, holes and spots
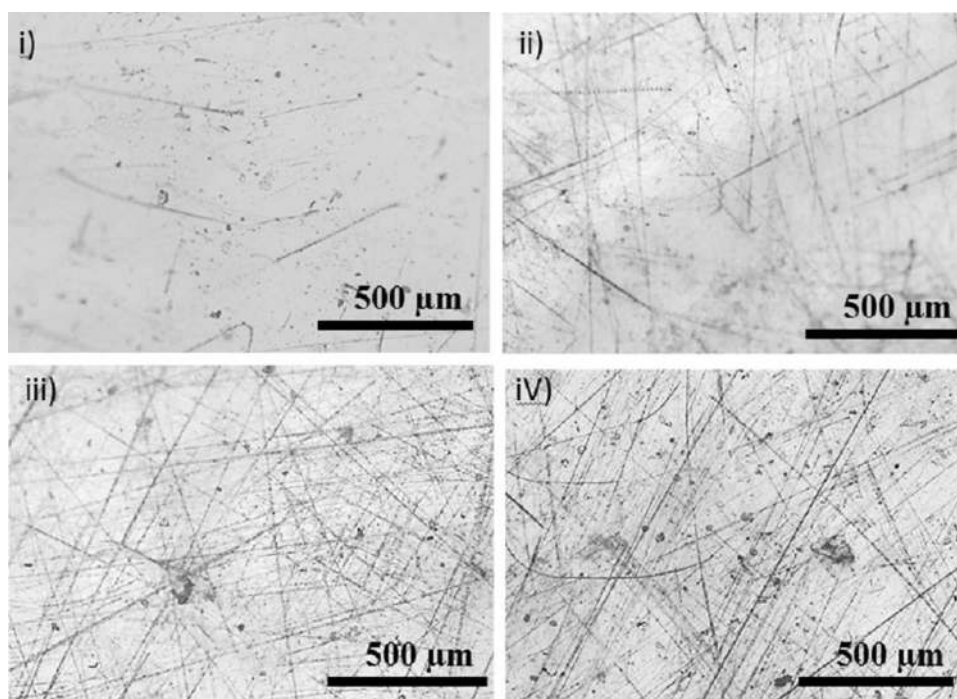
It is generally agreed that excitation of the photocatalyst under optimum light energy leads to the formation of hydroxyl radicals, which have a high oxidation capacity for degrading organic pollutants. Hence longer rods, which by virtue of their increased surface area can generate higher number of radicals, lead to a higher degradation of the LDPE film surface. Further evidence of the LDPE oxidation is also provided by DMA analysis.

Surface topography and composition of designed catalysts

Scanning electron microscopy (SEM) micrographs show that the ZnO nanorods were 250 to 1750 nm long varying in width from 34 to 65 nm for the precursor concentrations of 3 mM, 5 mM, 10 mM and 20 mM, leading to increment of total effective surface area to 6.5, 22, 49 and 55 cm^2, respectively (supporting info. Fig. S2 and Table S1). This suggests that longer rods have higher effective surface area and could be more effective for microplastics degradation.

Changes in visco-elastic properties of photocatalysed low-density polyethylene films

Dynamic mechanical analyser (DMA) analyses the storage modulus (E_s) as a function of temperature, where E_s represents the energy stored with increasing temperature per cycle of sinusoidal deformation, which in turn represents the changes in the visco-elastic properties of the LDPE films. As shown in Fig. 2, temperature-dependent
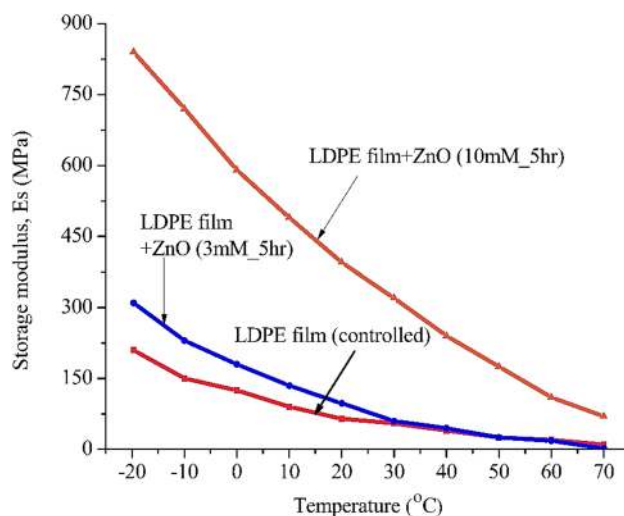

Fig. 2 Variation in the elastic properties of low-density polyethylene films upon photo-irradiation in the presence of zinc oxide (ZnO) (3 mM_5 h), ZnO (10 mM_5 h) catalysts. It can be noted that higher value of storage modulus (E_s) reveals the alteration to more stiffer and tougher elastic properties due to photocatalysis in comparison with non-irradiated (control) film

variations of the storage modulus for the films irradiated in the presence of photocatalysts showed a marked increase in E_S, indicating increased stiffness. The degree of stiffness for same level of photo-irradiation was observed to be a function of the rod length, again indicating to the hypothesis that higher surface area leads to a more effective photocatalytic performance. In fact, E_s values for the
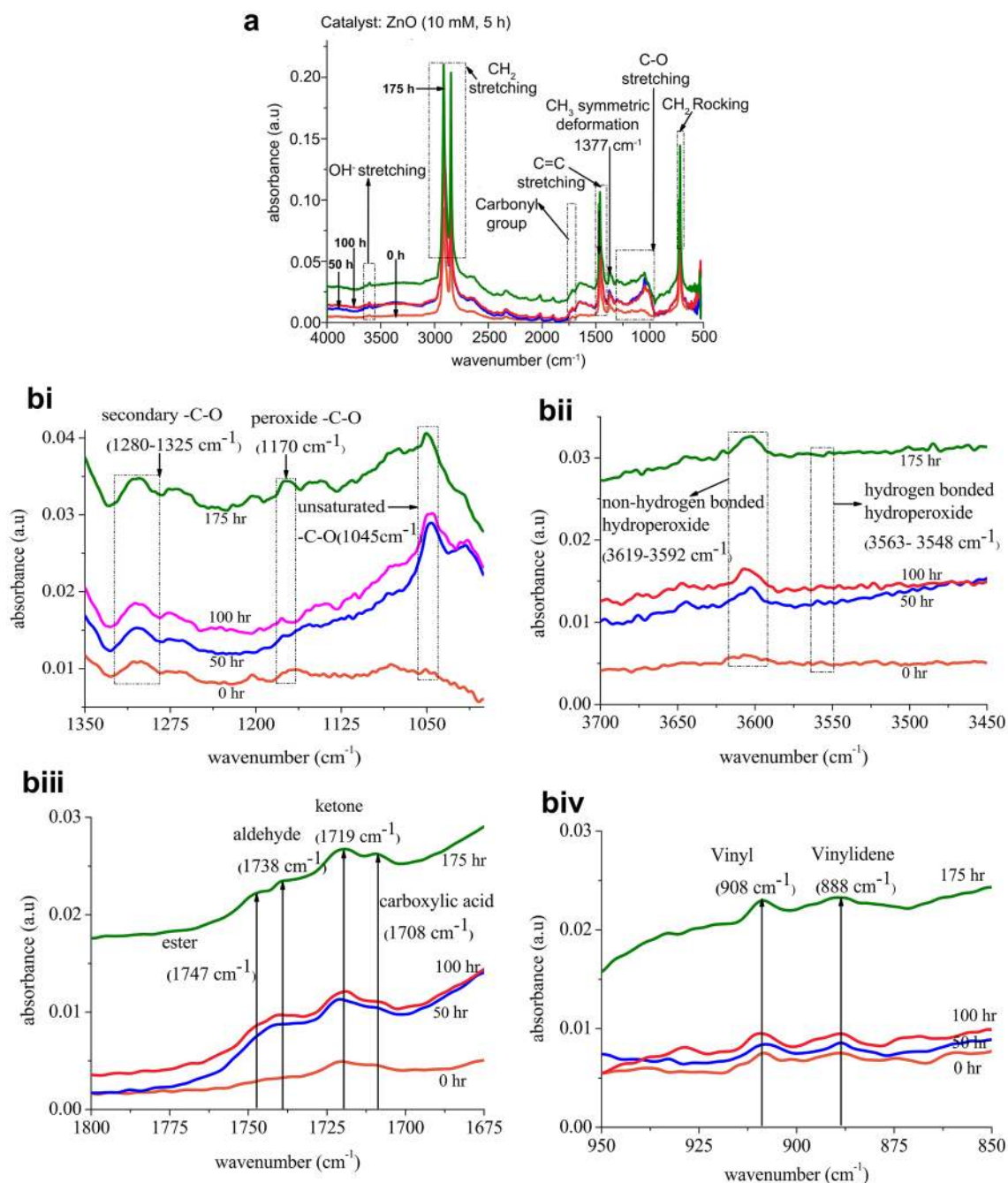
Fig. 3 a FTIR spectra of low-density polyethylene film over 175 h of visible light photocatalysis in the presence of ZnO (10 mM_5 h) nanorods. **b** Evolution of different functional groups **i** peroxides, **ii** hydroperoxides, **iii** carbonyl and **iv** unsaturated groups during photocatalysis process

20 mM ZnO photocatalyst sample could not be extracted as the sample ruptured due to non-sustenance of the pre-stress while performing the measurements. Hence, it gives a clear indication that the irradiated films lose their elasticity due to chain scission within the polymeric matrix, as a result of photocatalytic oxidation (Sebaa et al. 1993; Briassoulis 2005).

Temporal changes of chemical properties during photocatalysis of low-density polyethylene films

To better understand the LDPE degradation phenomenon, the samples were characterized using time-dependent FTIR spectroscopy as shown in Fig. 3. Baselines were extracted

from the control (non-irradiated) LDPE with characteristic vibrational peaks at 710 cm^{-1}, and 719 cm^{-1} (rocking deformation of –CH$_2$), 2847 cm^{-1}, 2915 cm^{-1} (symmetric and asymmetric –CH$_2$ stretch), 1462 cm^{-1}, 1472 cm^{-1} (–C=C– stretch), and 1377 cm^{-1} (weak symmetric deformation of –CH$_3$ group) (Gulmine et al. 2002; Ali et al. 2016; Socrates 2004). Chemical transformation during the photodegradation resulted in the formation of new functional groups like carbonyl, hydroperoxide, peroxides and unsaturated groups within the bands from 1700–1760 cm^{-1}, 3600–3610 cm^{-1}, 1100–1300 cm^{-1} and 880–920 cm^{-1}, respectively, which is in agreement with previous studies (Gardette et al. 2013; Luongo 1960; Qin et al. 2003).

A closer observation of the vibrational bands (Fig. 3b) leads to a better understanding of the degradation mechanism. The formation of bonded and non-hydrogen-bonded alcohol species was confirmed by the stretching peaks at 3553 cm^{-1} and 3606 cm^{-1}. Primary (1170 cm^{-1}), secondary (1280–1325 cm^{-1}) and double-bonded (1048 cm^{-1}) peroxide groups were also observed. Fairly broad and clear peaks observed at 1708 cm^{-1}, 1719 cm^{-1}, 1738 cm^{-1} and 1747 cm^{-1} that can be assigned to carboxylic acid, ketones, aldehyde and esters belonging to carbonyl groups (Kumanayaka 2010; Socrates 2004). It has been previously suggested that photo-oxidation of ketones results in the formation of unsaturated vinylidene and vinyl groups at 888 cm^{-1} and 909 cm^{-1}, respectively (Gardette et al. 2013). Interestingly, vinylidene groups seem to form rapidly before decaying and vinyl groups increase simultaneously with the generation of ketones, due to Norrish type II reactions, which is a part of the photocatalytic degradation process.

Photocatalytic degradation indices

The evolution of carbonyl and vinyl groups are the main indicators for monitoring the degree of degradation of a polymer. Table 1 shows the carbonyl and vinyl indices of the LDPE films after photocatalysis with different catalysts, wherein a 30% increase in the CI and VI indexes for longer

Table 1 Carbonyl index (CI) and vinyl index (VI) of low-density polyethylene (LDPE) films after 175 h exposure to visible light in the presence of different photocatalysts for monitoring the degree of degradation where higher values suggest better oxidation
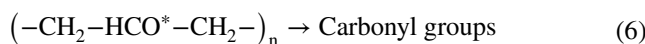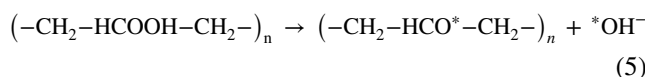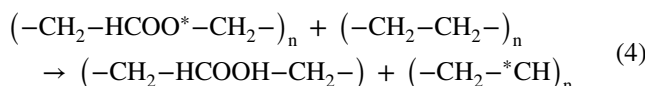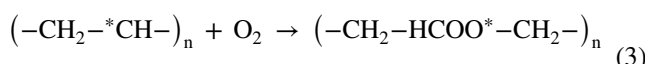
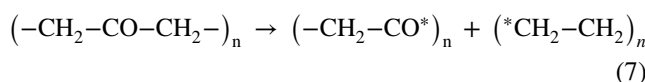| Parameters	Control (non-irradiated) LDPE	LDPE+ZnO (3 mM_5 h)	LDPE+ZnO (10 mM_5 h)	LDPE+ZnO (20 mM_5 h)
CI	0.71	1.17	1.38	1.51
VI	0.51	0.9	1.12	1.3

Zinc oxide (ZnO)

ZnO rods clearly demonstrates the photocatalytic improvement with catalyst surface area. Initial carbonyl and vinyl values of 0.71 and 0.51 indicate the presence of inherent chromophoric groups which are the primary initiators for the degradation (Ali et al. 2016; Yousif and Haddad 2013).
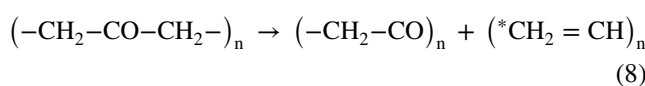
Proposed degradation mechanism

Based on the results obtained in this study, the following degradation pathway for the LDPE film is proposed. The generated hydroxyl and superoxide radicals from catalyst initiate degradation at weak spots (like chromophoric groups, defects) of the long polymeric chains to generate low molecular weight polyethylene alkyl radicals (Eq. 2), followed by chain breaking, branching, crosslinking and oxidation of LDPE. Subsequently (Eqs. 3–5), peroxy radicals are formed with oxygen incorporation, followed by the abstraction of hydrogen atoms from the polymeric chains to form hydroperoxide groups. The hydroperoxide groups are the foremost oxygenated products that regulate the rate of photocatalytic degradation, wherein their dissociation into alkoxy radicals undergoes successive reactions to generate carbonyl and vinyl group containing species (Eqs. 7–8), which in turn lead to chain cleavage. Hence the presence of carbonyl and vinyl groups confirms the photo-oxidative degradation of LDPE films in the presence of catalysts that terminates by generating volatile organic compounds like ethane and formaldehyde. However, further oxidation can lead to complete mineralization to produce carbon dioxide and water as explained below (Hartley and Guillet 1968; Shang et al. 2003; Liang et al. 2013).
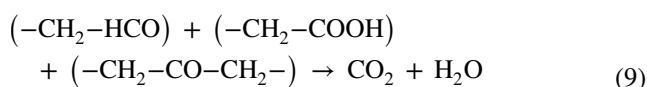
$$\left(-CH_2 - CH_2-\right)_n + {}^*OH^- \rightarrow \left(-CH_2 - {}^*CH-\right)_n + H_2O \tag{2}$$

$$\left(-CH_2-{}^*CH-\right)_n + O_2 \rightarrow \left(-CH_2-HCOO^*-CH_2-\right)_n \tag{3}$$

$$\begin{aligned}\left(-CH_2-HCOO^*-CH_2-\right)_n &+ \left(-CH_2-CH_2-\right)_n \\ &\rightarrow \left(-CH_2-HCOOH-CH_2-\right) + \left(-CH_2-{}^*CH\right)_n\end{aligned} \tag{4}$$

$$\left(-CH_2-HCOOH-CH_2-\right)_n \rightarrow \left(-CH_2-HCO^*-CH_2-\right)_n + {}^*OH^- \tag{5}$$

$$\left(-CH_2-HCO^*-CH_2-\right)_n \rightarrow \text{Carbonyl groups} \tag{6}$$

Norrish type I

$$\left(-CH_2-CO-CH_2-\right)_n \rightarrow \left(-CH_2-CO^*\right)_n + \left({}^*CH_2-CH_2\right)_n \tag{7}$$

Norrish type II

$$\left(-CH_2-CO-CH_2-\right)_n \rightarrow \left(-CH_2-CO\right)_n + \left({}^*CH_2 = CH\right)_n \tag{8}$$

$$\begin{aligned}(-CH_2-HCO) + (-CH_2-COOH)\\+ (-CH_2-CO-CH_2-) \rightarrow CO_2 + H_2O\end{aligned} \quad (9)$$
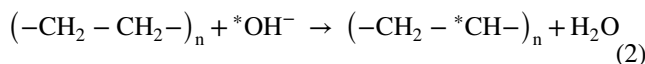
Conclusion

This study successfully demonstrates the degradation of microplastic fragments, low-density polyethylene film (LDPE) in water using visible light excited heterogeneous ZnO photocatalysts. Photocatalytic LDPE oxidation led to formation of low molecular weight compounds like hydroperoxides, peroxides, carbonyl and unsaturated groups, resulting in increased brittleness along with wrinkles, cracks and cavities on the LDPE surface. Furthermore, catalyst surface area was found to be important towards enhancing the LDPE degradation. The results provide new insights into the use of a clean technology for addressing the global microplastic pollution with reduced by-products.

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