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Research Article

A primary study on the degradation of low-density polyethylene treated with select oxidizing agents and starch

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Abstract

Polyethylene has become an integral part of our contemporary lives. The neoteric versatile nature of polyethylene is used in constructing various applications. Out of the plastic waste discarded, 60% of the plastic waste enters landfills. The polyethylene discarded in the soil and water on exposure to the environment forms macroplastics (>2.5 cm), mesoplastics (5 mm - 2.5 cm) and microplastics (<5 mm). Microplastics in the water and soil are observed to have lethal and ecotoxicological effects on aquatic and terrestrial organisms. They enter the food chain and permeate into the food that one eats. In order to address this impending concern, the present study aimed to treat plastics to form a degradable, safe and earthy material. The dissolved polyethylene was treated with starch and was made to react with oxidizing agents such as hydrogen peroxide, nitric acid and acetic acid to lower its inert ability to withstand its degradation. The effect of starch and oxidizing agents on dissolved low density polyethylene was subsequently analysed. The analysis of treated polyethylene showed a decrease in its crystallinity percentage by 6.19 and an increase in its functional groups on reaction with solvent trichloroethylene made to react with starch and oxidizing agents. In the present research, tests were conducted to obtain the various methods that can be utilized to reverse the inert ability of polyethylene. The prevailing recycling model that uses antioxidation techniques is counterproductive since it was found that such techniques appeared to make the polyethylene more resistant to further degradation. In this study, the polyethylene was dissolved in the solvents, such as xylene and trichloroethylene, to make the polyethylene more susceptible to reactants and hence a viable model for treating polyethylene.

Keywords: Polyethylene, Plastic degradation, Oxidation reactions, Thermo-oxidation reaction

INTRODUCTION

Polyethylene (PE) has found its application in the soil and has formed mulching waste that harms the soil health. The various organisms in the soil have been affected due to the effects of PE on the moisture, air and nutrients which are essential for survival (Liu *et al*., 2014). Plastic, on exposure to the environment forms plastic particles with size less than 5mm called microplastics (MPs). These MPs have the ability to pollute the environment and biota (Zhang *et al*., 2017; Chen *et al*., 2020a; Wong *et al*., 2020). When inhaled, the fibrous microplastics containing contaminants like plasticizers and dyes enter the lungs, leading to carcinogenicity and mutagenicity (Gaspéri *et al*., 2018; Wong *et al*., 2020).

Polyethylene is a highly defiant and inactive material; therefore, they are broken down very slowly under environmental conditions. This polyethylene is thermally stable as its backbone contains carbon bonded with hydrogen. Polyethylene can be low-density polyethylene (LDPE) and high-density polyethylene (HDPE). The low-density polyethylene is the kind of plastic used in food packaging (Ghatge *et al.,* 2020). These are prepared by polymerizing ethylene at high pressure. When discarded, these plastics enter the landfills as they get exposed to sunlight and undergo weathering forming secondary particulate plastics (microplastics). The secondary particulate plastics can act as a vector to transport toxics. These aged particulate plastics (microplastics) can adsorb higher amounts of trace elements since they contain dissolved organic matter, increased surface area, developed functional groups and have undergone modification over the period of time to adsorb particles (Bradney L *et al*., 2019). The cultivated land can have high levels of particulate plastics (microplastics). Any change in the pH causes the adsorption of various elements. The particulate plastics or microplastics with dissolved organic matter carry trace elements that can cause biomagnification in a living organism. Particulate plastics (microplastics) are pristine as they are non-reactive and can be less harmful when compared to particulate plastic with dissolved organic matter as the metals it carries can further result in toxic effects on the living organism (Bradney *et al*., 2019; Muncke *et al*., 2021). Thus, the inert plastic material can act as a long-term vector to transport contaminants.

Polyethylene can undergo oxidation or antioxidation reactions under suitable conditions. Polymer products are produced to have longevity. These PE, on exposure to oxygen present in the air, its molecular weight, oxidative stability, appearance, and thermal stability degrade with time. Thus, polymers are fabricated by crosslinking them with antioxidants. Antioxidants are added into polyethylene in the right combination to increase its stability and reduce autoxidation degradation reaction (https://polymer-additives.specialchem.com/selection-guide/antioxidants-stabilizers-selection-for-polyolefins-pp-pe; https://global.ihs.com/doc_detail.cfm?item_s_key=00021050). Polyethylene is more susceptible to thermo-oxidative degradation reactions in the presence of air and increased temperature. Thus, antioxidants or reducing agents used as stabilizers are added to polymers during their polycondensation to increase thermo-oxidative stability. As the concentration of stabilizers increased in the polymers, their melting point also increased (Karayannidis *et al.,* 1994). Oxidation in polyethene is prevented for three years in the presence of antioxidants. Antioxidants are responsible for giving toughness to polyethylene on exposure to radiation (Currier *et al.,* 2018). Antioxidants like RECYCLOBYK® 4371 by BYK along with co-stabilizers are added to polyethylene on recycling to increase their shelf life by 24 months (https://polymer-additives.specialchem.com/product/a-byk-recyclobyk-4371?src=sg-overview-iframe; BRUGGOLEN® TP-H1804 by Brüggemann) can increase the shelf life of polyethylene by 12 months from discolouration and provide mechanical strength (https://polymer-additives.specialchem.com/product/a-bruggemann-bruggolen-tp-h1804?src=sg-overview-iframe).

Oxidation of polyethylene can affect the chemical and mechanical strength of polyethylene (Nowak *et al.,* 2011; Pegram *et al.,* 1989; Sudhakar *et al.,* 2008). In the earlier work on the oxidation of polyethylene, its surface adhesion properties were modified for increased adhesion of antioxidants on the surface to enhance their mechanical strength (Zander N *et al.,* 2009). During production or recycling of polymers antioxidant are added to reduce the degradation of polymers. The antioxidants in PE must be deactivated to allow oxidation of polyethylene (Billingham N C 2009). Thus, deterioration reactions can be made possible by introducing oxidation reactions that can weaken the physical properties of polymers. Polymers on heating in the presence of oxidizing agents can favour oxidation reactions. In an antioxidation reaction, hydrogen is added to allow reduction or antioxidation reaction. Introducing oxygen as oxidizing agents are can propagate oxidation reactions (Karayannidis *et al.,* 1998).

PE can undergo oxidative decomposition when in liquid state (Oluwoye I *et al.,* 2015). The solvent molecules would penetrate the surface area of polyethylene, resulting in swelling on the layer between the polyethylene layer and solvent layer (Wong *et al.,* 2014). Nitric acid is known to be a good oxidizing agent and also assists in the disintegration of polyethylene as polyethylene has a long chain and semi-crystalline morphology (Ghatge *et al.,* 2020; Chaudhary *et al.,* 2022).

In this experiment, polyethylene was dissolved in a suitable solvent. The dissolved PE was treated with starch and oxidizing agents like hydrogen peroxide, nitric acid and acetic acid to undergo thermo-oxidative degradation reaction of polyethylene with induced heat. The swelling of PE would further allow the penetration of reactants, making them more vulnerable to reactions. In this study, efforts were made to identify an ideal solvent with a suitable oxidizing agent to degrade polyethylene. Thus, the present work aimed to introduce the thermo-oxidative reaction on inert dissolved polyethylene with starch and oxidizing agents like hydrogen peroxide, nitric acid and acetic acid to convert polyethylene into a more vulnerable product.

MATERIALS AND METHODS

Materials

Polyethylene packaging material was purchased from Synpack Slide N Zip Private Limited, Bangalore-58, Karnataka, India. The solvents used were xylene and trichloroethylene. The oxidizing agents used were hydrogen peroxide, nitric acid and acetic acid. These chemicals were procured with analytical grade. Trichloroethylene and acetic acid from S D Fine, xylene, hydrogen peroxide, nitric acid from Fisher/ Qualigens and starch from Nice brand. Suitable protective equipment was used while handling the reactants.

Treatment of polyethylene

Polyethylene was weighed and dissolved in solvents such as xylene and trichloroethylene. The solvent that was taken was observed for its boiling point and its swelling ratio. The solvent with low boiling temperature and a high swelling ratio with polyethylene was considered an ideal solvent (Fujimatsu *et al.,* 2012). The dissolved polyethylene was treated with starch and oxidizing agents. The purpose of including starch at 30% of

Table 1. Swelling ratio of trichloroethylene, xylene and polyethylene in three trials

	Polyethylene treated with trichloroethylene	Polyethylene treated with xylene	Untreated polyethylene
Swelling ratio	2.1	1.5	1
	2.1	1.5	1
	2.1	1.5	1

the weight of polyethylene in the process was to decrease the mechanical strength of polyethylene (Amin *et al.,* 2012).

Swelling ratio

The swelling ratio of treated polyethylene was analysed in triplets (Table 1) compared to untreated polyethylene. The swelling value indicates the molecular weight of cross-links between polymer chains. The greater the swelling ratio, the higher their interaction between the solvents and oxidizing agents with polyethylene. The polyethylene was treated with a different solvent and its difference in its swelling was observed (Anandhan S *et al.,* 2009). The swelling ratio (Wang *et al.,* 2022) was calculated as follows:

Swelling Ratio: $S = W1 / W2$ Eq.1

Where, W1 is the weight of treated PE with its reactants and W2 is the weight of treated PE air-dried. Increase in the swelling of polyethylene indicates the reduction in the entanglement of polyethylene chains. Trichloroethylene had a higher swelling ratio of 0.6 when compared to that of xylene.

Statistical analysis

The experiment was performed three times, i.e., in triplets and with their results in ± SD. One-way ANOVA was used to conduct statistical importance. Less than 0.05 was considered (Khaleghi M *et al.,* 2020). The p-value using unpaired Student's t-test obtained here between treated polyethylene and untreated polyethylene was 0.029798, which was statistically important.

RESULTS AND DISCUSSION

Comparison between the dissolution of polyethylene with trichloroethylene and xylene:

The present study indicated that the dissolution of polyethylene in solvents like xylene, trichloroethylene underwent solvent diffusion. 60ml of trichloroethylene could dissolve 3g. of polyethylene at a temperature of 83.4^0C and 60ml of xylene can dissolve 3.2g. of polyethylene at a temperature of 97^0C. Trichloroethylene could dissolve 3g. pf polyethylene at a temperature of 13.6^0C less than that of xylene. Trichloroethylene had its swelling ratio 0.6 more than that of xylene. Thus, according to Fujimatsu *et al.* (2012), the solvent that took low boiling point and high swelling ratio was considered an ideal solvent. Therefore, trichloroethylene showed better dissolution as it dissolves polyethylene at a lower temperature and high swelling ratio and thus was taken as an ideal solvent (Fig. 1).

Dissolution and oxidation of polyethylene with swelling ratio

The dissolved polyethylene treated with starch and oxidizing agents like hydrogen peroxide, nitric acid and acetic acid showed a swelling effect. The polyethylene was dissolved in xylene at a boiling temperature of 97^0C and then treated with the starch and oxidizing agents showed a swelling ratio of 1.5. Polyethylene dissolved in trichloroethylene showed boiling temperature of 83.4^0C and was then treated with the starch and oxidizing agents with a swelling ratio of 2.1. Thus, trichloroethylene had a higher swelling ratio. 60ml of trichloroethylene could dissolve 3g of polyethylene at a temperature of 83.4^0C and 60ml of xylene could dissolve 3.2g of polyethylene at 97^0C. Therefore, trichloroethylene showed better dissolution as it dissolved polyethylene at a lower temperature.

XRD analysis of treated and untreated PE

The analysis was done by XRD- pattern analysis software of Origin 2020. The percentage of crystallinity of treated and untreated polyethylene was calculated by integration method analysis. In this method, the straight background line was compared with the area under the entire curve. The percentage is calculated using the following equation,

Percentage crystallinity = (area under the crystallinity peaks/ area under all peaks)*100 Eq. 2

(https://mcl.mse.utah.edu/xrd-crystallinity-by-integrati on/)

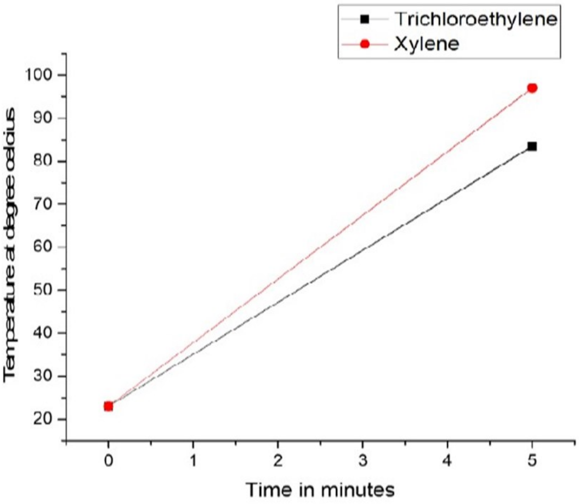

Fig. 1. *Comparison between the dissolution of polyethylene with trichloroethylene and xylene.*

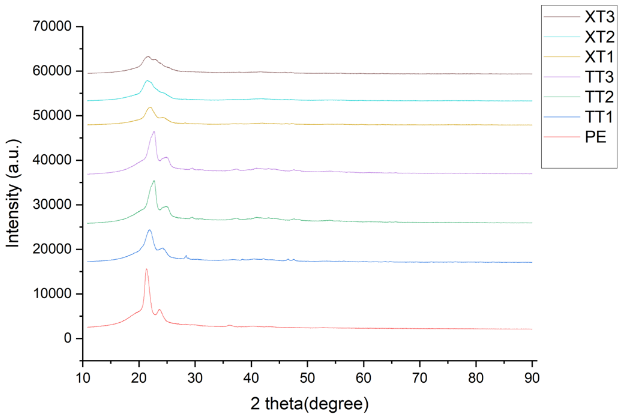

Fig. 2. *XRD analysis of polyethylene: untreated polyethylene (PE), polyethylene dissolved in trichloroethylene treated with starch and oxidizing agents (TT1, TT2, TT3) and polyethylene dissolved in xylene treated with starch and oxidizing agents (XT1, XT2, XT3).*

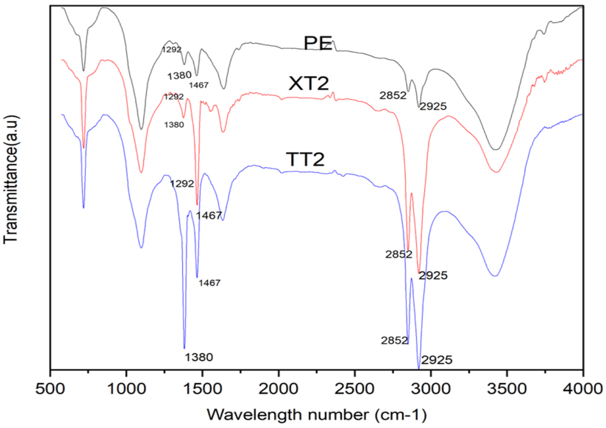

Fig. 3. *KBr-FTIR analysis of polyethylene. PE is untreated polyethylene. TT2 is polyethylene dissolved in trichloroethylene and treated with starch and oxidizing agents. XT2 is polyethylene dissolved in xylene and treated with starch and oxidizing agents.*

Change in crystallinity of treated polyethylene

XRD-pattern analysis software using Origin 2020 (Fig.2), the graph of all the treated and untreated PE was compared. The untreated polyethylene according to equation 2, showed crystallinity percentage of 48.48. The treated polyethylene with trichloroethylene had a crystallinity percentage of 42.29. The treated polyethylene with xylene had a crystallinity percentage of 55.51. Thus, according to XRD-pattern analysis trichloroethylene can decrease the crystallinity of polyethylene by a percentage of 6.19. According to XRD-pattern analysis, the dissolution of PE with trichloroethylene shows a decrease in crystallinity of PE. The percentage of crystallinity for PE treated with trichloroethylene and starch decreased when compared to that of untreated PE and PE treated with xylene and starch.

FTIR analysis of treated and untreated PE:

Chaudhary *et al.* (2022) in their experiment on polyethylene with nitric acid found the formation of peaks after treatment indicated to be associated with the deterioration of polyethylene. Roy *et al.* (2008) found significant changes in the amorphous 1300 cm^{-1} and O-H stretching regions indicating multiple oxidation products. In this study untreated polyethylene (PE) and treated polyethylene (XT2, TT2) in Fig. 3 and Table 2 were observed at a spectral range between 500-4000 cm^{-1}. The increase in peaks around 1380 cm^{-1}, 2852 cm^{-1} and 2925 cm^{-1} associated with O-H group increased and an increase in 1380 cm^{-1} indicated an increase in amorphous nature showed in samples of polyethylene treated with trichloroethylene starch and oxidizing agents. This indicated the presence of many oxidative oxidation products of polyethylene. 1467 cm^{-1} associated with C-H group, showed a tendency to increase in XT2 and TT2 samples. These spectral differences between polyethylene treated with xylene, trichloroethylene and untreated polyethylene showed that polyethylene treated with trichloroethylene was more affected in the treatment process.

Change in the functional group of treated polyethylene

In this study of untreated polyethylene (PE) and treated polyethylene (XT2, TT2) in Fig. 3 and Table 2 of spectral range between 500-4000 cm^{-1} were observed. Poly-

Table 2. FTIR peak values, class and functional group in untreated polyethylene and treated polyethylene(https://instanano.com/all/characterization/ftir/ftir-functional-group-search/)

Sl.No.	Wave number (cm^{-1})	Functional Group	Class
1	1292	C-N stretching, C-O stretching	Aromatic amine, aromatic ester
2	1380	C-H bending, O-H bending	Aldehyde, alcohol, phenol
3	1467	C-H bending	Alkane
4	2852	O-H stretching, N-H stretching, C-H stretching	Carboxylic acid, amine salt, alcohol, alkane
5	2925	O-H stretching, N-H stretching, C-H stretching	Carboxylic acid, amine salt, alcohol, alkane

ethylene treated with trichloroethylene had increased peaks at O-H group around the range 1380 cm^{-1}, 2852cm^{-1} and 2925 cm^{-1} and an increase in peak in amorphous nature at 1380cm^{-1} and increase in peak 1467 cm^{-1} associated with C-H group. The polyethylene treated with xylene and untreated polyethylene did not show any transition at 1292 cm^{-1} at the crystalline phase. But polyethylene treated with trichloroethylene changed as it did not peak at 1292 cm^{-1} crystalline phase.

Conclusion

From the results obtained in comparison with polyethylene treatment with xylene and trichloroethylene used as a solvent trichloroethylene was an ideal solvent, better dissolution with increased functional groups and decreased crystallinity. As for future engagement, this method can be further analysed with different solvents and oxidizing agents to make polyethylene more degradable and less harmful to the environment and biota.

Conflict of interest

The authors declare that they have no conflict of interest.

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