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Anionic surfactant induced oxidation of low density polyethylene followed by its microbial bio-degradation

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ABSTRACT

Hydrocarbon solubilization ability of surfactants was utilised for the deterioration of polyethylene during its thermal oxidation. Carbonyl index of polyethylene treated with Sodium dodecyl sulphate (SDS) at 60 °C for 1 month was found to be higher than thermally oxidised polyethylene as observed in FTIR study. Moreover, higher oxidation of polyethylene was witnessed after treatment of control polyethylene with 1%–10% of sodium dodecyl benzene sulphonate, sodium stearate, sodium octyl sulphate and sodium dodecyl sulphate at 60 °C for 1 month. Oxidation level of polyethylene treated by surfactant was higher as the availability of soluble oxygen and chain scission increased due to the attachment of surfactant to the polyethylene surface. Weight loss of 7.006 ± 0.05%, 1.76 ± 0.05% and 0.83 ± 0.05% were maximum which was achieved after bacterial treatment of oxidised polyethylene with 6%, 8% and 10% SDS, with *L. fusiformis* using peptone for 1 month, respectively. Along with weight loss after bacterial incubation, a decrease in the amount of carbonyls and an increase in the amount of unsaturated hydrocarbon were observed for the conversion of carbonyls into unsaturated hydrocarbon through biotic Norrish-type mechanisms. The biodegradation through β-oxidation mechanisms, by which oxidised polyethylene molecule was utilised to produce necessary energy for bacteria, was confirmed by a decrease in intrinsic viscosity and a decrease in the viscosity average molecular weight (M_v) of bacterially treated polyethylene. Nevertheless, an increase in the amount of carbonyls was observed after 1 month of bacterial incubation of polyethylene treated with SDBS and thermally oxidised polyethylene which was due to oxidation by oxidative enzymes released by *Lysinibacillus fusiformis*.

1. Introduction

Polyethylene has emerged as one of the most used plastic materials around the world since its first production in 1939, replacing metals and glasses. Main advantages of polyethylene such as durability, resistant towards several chemicals and cheap production leads to its widespread use which ultimately resulted in the major environmental pollution of the environment. Polyethylene is highly hydrophobic due to the absence of any polar groups into the carbon hydrogen backbone which makes polyethylene resistant towards microbial attack (Nowak et al., 2011). It is reported that less than 0.5% carbon might be mineralised in 100 years when polyethylene is thrown away into the environment and after natural ageing of polyethylene under sunlight for 2 years, only 1% of carbon could be mineralised in the same period of time (Jeon and Kim, 2014). For this reason, the high rate of polyethylene production since last decades is effecting the high rates of waste polyethylene deposition into the environment (Harshvardhan and Jha, 2013; Restrepo-Flórez et al., 2014). These accumulated polyethylene is the major environmental pollutant and major constituent of municipal wastes (Santo et al., 2013). Maximum amount of total polyethylene waste is low density polyethylene, which is mainly used in thin transparent polyethylene bags and are discarded after short periods of use (Harshvardhan and Jha, 2013; Skariyachan et al., 2015).

Bio-degradation of waste polyethylene can be a solution to the problem that arises from the increasing rate of polyethylene deposition in the environment. Several approaches including thermal degradation and photo-oxidative degradation have been

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studied by researchers to find an efficient method of degradation for polyethylene waste (Piiroja and Lippmaa, 1989; Qin et al., 2003). Among these methods, biodegradation of polyethylene by microbial strain is environmental friendly and one of the most studied methods (Restrepo-Flórez et al., 2014). Biodegradation of polyethylene mainly consists of two steps: oxidation of polyethylene for introduction of polar groups into the carbon-hydrogen backbone to enhance microbial attachment to the polyethylene surface and biodegradation of that oxidised polyethylene (Albertsson et al., 1987). Photooxidition by irradiation with U.V. light at temperature above 50 °C, thermal and chemical oxidation are the few examples of abiotic oxidation generally used for oxidation of polyethylene (Yamada-Onodera et al., 2001). Pre-oxidation of polyethylene, prior to biodegradation by fungi, has been done by two methods – first, by accelerated aging at 70 °C under U.V. light for 29 days and the second by thermal treatment at 105 °C and 150 °C for 5 days (Manzur et al., 2004). Before biodegradation, polyethylene has been photooxidised by natural weathering for 93 days, followed by thermal treatment at temperature ranging from 45 °C to 65 °C for 200 days (Corti et al., 2010). Loss of ductility and mechanical integrity of polyethylene after treatment at 60 °C for 15 days is reported by (Benítez et al., 2013). Further, low density polyethylene has been thermally oxidised at 80 °C for 15 days prior to biodegradation by fungal strain (Volke-Sepulveda et al., 2002). Additionally, polyethylene has been thermally oxidised at 150 °C for 5 days as the pre-oxidation step of the biodegradation study (Volke-Sepúlveda et al., 1999). Thus, thermal oxidation of polyethylene is a very effective and extensively used method. In case of commercial polyethylene, hydroperoxides and carbonyl groups formed during high temperature manufacturing processes generally makes polyethylene vulnerable towards thermal oxidation (Khabbaz et al., 1999). However, improvement of oxidation rate is necessary for the effective increase in polyethylene biodegradation rate (Jeon and Kim, 2015).

Previously we reported the oxidation of polyethylene by biosurfactant produced by *B. licheniformis* at 37 °C. Bio-surfactants are mainly amphiphilic molecules produced by microbial species and have the ability to solubilize the hydrocarbon (Zhou and Rhue, 2000). Loss of oxidised amorphous region has been observed during the oxidation of polyethylene in the presence of bio-surfactant (Mukherjee et al., 2015). Chemical surfactants are chemically synthesized and are expected to be much more effective than biosurfactant for inducing oxidation of polyethylene. Some chemical surfactants have very low critical micelle concentration (CMC) i.e., have higher solubilization ability at a very low concentration and are also biodegradable. Such a chemical anionic surfactant, sodium dodecyl sulphate has been used to remove crude oil from soil at 50 °C for 14 days (Thomas and White, 1989; Urum et al., 2004). The chemical surfactants as well as bio-surfactants have been used extensively in enhanced oil removal application by increasing solubilization of petroleum materials (Mulligan et al., 2001). Hydrocarbon solubilization ability of biodegradable chemical surfactant (ionic and non-ionic) is never been used for the oxidation of polyethylene and this ability can be utilised during thermal oxidation of polyethylene to improve its oxidation level. Surfactants can be used at higher concentration than their CMC to get higher rate of hydrocarbon solubilization. Simultaneous oxidation and solubilization of oxidised polyethylene into aqueous media during thermal oxidation in the presence of chemical surfactant, may lead to higher amount of deterioration at the surface of polyethylene, resulting more microbial biodegradation. Non-ionic surfactant like Tween 80 is used during biodegradation of polyethylene. LDPE has been mixed with 0.5% of tween 80 and subjected to biodegradation to increase availability of the polyethylene to microbes (Albertsson et al., 1993). Previously, it was shown that pre-oxidised LDPE has been subjected to biodegradation in the presence of non-ionic surfactant and increased biodegradation rate is observed in this case (Karlsson et al., 1988). However, surfactant especially anionic surfactant is never used for inducing oxidation of polyethylene at room temperature or at high temperature.

In our earlier study, efficient biodegradation of oxidised polyethylene by *L. fusiformis* bacterium has been observed (Mukherjee et al., 2016). The same bacterium is also used for biodegradation of oxidised polyethylene in the present report.

Till now, there is no report of using chemical surfactant (non-ionic and ionic) during thermal oxidation of polyethylene at 60 °C. In this present report, polyethylene was kept with anionic, cationic and non-ionic chemical surfactants separately at 60 °C for 1 month to study the effect of oxidizing ability and hydrocarbon solubilization ability of surfactant on polyethylene. All the chemical surfactants used in this study are bio-degradable. During oxidation at 60 °C in the presence of these chemical surfactants, a small part of oxidised polyethylene was solubilized into the aqueous media which was identified by GC-MS analysis of the aqueous solution. After oxidation, polyethylene was incubated with *Lysinibacillus fusiformis* for 1 month, for the study of microbial biodegradation of polyethylene.

2. Materials & methods

2.1. Test materials

Daily used 0.01 mm thick, post-consumer transparent colourless low density polyethylene bags were collected from the dry waste bins of Kolkata Municipal Corporation. Three pre-consumer and three post-consumer LDPE transparent bags are taken (Gonzalez et al., 2011). These bags were then cut into rectangular pieces (5 mm × 5 mm) and washed with soap water and distilled water, consecutively. Then, these pieces were kept in 70% (v/v) ethanol solution for 30 min and then washed again with water, followed by drying at 50 °C till fixed weight of polyethylene were obtained. The viscosity average molecular weight of each post-consumer and pre-consumer bags were same. The polyethylene films were 10 μm thick and the viscosity average molecular weight (M_v) was 24079.27. In GC-MS analysis of chloroform extract of untreated pre and post-consumer LDPE bags, three anti-oxidants were identified which were enlisted as anti-oxidants used in polyethylene in a report by Dopico-García et al. (2007) and these anti-oxidants were listed in Table 1. As post-consumer bags were collected from dry waste bins within hours of its discard, no biodegradation or oxidation had been taken place which was confirmed by same M_v of LDPE before and after use. Presence of similar chemicals were also

Table 1
GC-MS analysis of chloroform extract of control unoxidized polyethylene.

Compound name	Con_PE
Antioxidants:	
Phenol, 2,4-bis(1,1-dimethylethyl)-	Y
Pentanoic acid, 5-hydroxy-, 2,4-di-t-butylphenyl esters	Y
Phenol, 2,6-bis(1,1-dimethylethyl)-	Y
CH_2 group:	
Tetracosane, (24C)	Y
Eicosane	Y
Heptadecane	Y
Hexadecane	Y
Tetradecane	Y
Dodecane	Y
Benzene, 1,3-bis(1,1-dimethylethyl)- (6C)	Y
Benzene, 1,4-bis(1,1-dimethylethyl)-	Y
m-Cymene, 5-tert-butyl-	Y