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Biofouling and biodegradation of polyolefins in ocean waters

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Abstract

High density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP) coupons were immersed for a period of 6 months in Bay of Bengal near Chennai Port (Port) and Fisheries Survey of India (FSI). Samples were retrieved every month and the extent of biofouling and biodegradation were monitored by measuring biological and physicochemical parameters. Dissolved oxygen and oxidation reduction potential were higher at Port than at FSI. Total suspended solids and organic matter were more on PP, followed by HDPE and LDPE indicating hydrophobic surfaces favour more biofouling. *Pseudomonas* sp., anaerobic, heterotrophic and iron-reducing bacteria were observed on polymer surface. Biofouling was found to depend on the season, loading being highest in the month of August. Chlorophyll was higher at FSI than at Port due to higher pollution levels and also being closer to the shores. Maximum weight loss was seen in LDPE (1.5–2.5%), followed by that in HDPE (0.5–0.8%) and finally in PP (0.5–0.6%) samples deployed at Port in the six month time period.

Keywords: Biodegradation; Biofouling; Polyolefin; Sea water; Fourier transform infrared spectrometry; Differential scanning colorimeter

1. Introduction

Several hundred thousand tons of plastics are discarded into the marine environment every year. It has been estimated that one million marine animals are killed every year either by choking on floating plastic items or by becoming entangled in plastic debris [1]. Polyethylenes (HDPE & LDPE) and polypropylene (PP) are the most commonly used synthetic polymers and 65% of the polymer waste in Europe is made up of these polymers. It is important to know the nature and extent of degradation of such polymers under marine conditions to address the seriousness of this problem.

Biodegradation is a process in which naturally-occurring microorganisms such as bacteria, fungi or algae act on the material. Biodegradable plastics break down completely into non-plastic and nontoxic constituents like water, CO_2, CH_4 and biological materials. Whereas synthetic polymers have been labeled as recalcitrant which means that they are completely resistant to microbial or enzymatic attack. The initial step in the biodegradation of many inert polymers that are disposed in the dump yards is photo-oxidation where oxygen in the form of carbonyl is incorporated through Norrish type I and II mechanisms. The next step is the attack of microorganisms on the carboxylic groups of the polymer, releasing two carbon chain fragments which are further used in either the anabolic or the catabolic cycle [2]. Starch containing material enhances the biodegradation process, since the rate of degradation of starch is an order of magnitude higher than that of the polymer. Several formulations containing starch and prooxidants have also been proposed to aid the degradation process [3,4]. Prooxidants help in the insertion of oxygen atom into the polymer chain. Increased surface area as well as increased oxygen permeability can also enhance degradation. During abiotic and biotic degradation, series of low

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molecular weight compounds are released into the surrounding environment and in addition, crystallinity, lamellar thickness and overall morphology of the polymer changes. The thermal oxidation of polymer results in the release of low molecular weight compounds, primarily from the amorphous region, which leaves the remaining polymer more prone to reorganisation leading to increase in crystallinity.

The rate of formation of carbonyl groups is increased by photo-oxidation, increased stress or presence of pollutants [5]. In order to initiate biodegradation, several requirements must be satisfied, the primary being that the polymer must not have an adverse effect on the organisms. This can be determined by monitoring the growth of organisms on the samples. Second, the organisms must cause a loss of integrity in the polymer; preferably this will include either a loss of mechanical strength or a decrease in the average molecular weight. There should be no effect on the polymer when the system is kept abiotic which assures that the only possible degradation mechanism in the system is due to the organisms. Finally the surface energy or forces should be enough for the organism to adhere easily.

The present study is concerned with the understanding of the process of biofouling and biodegradation of low density polyethylene (LDPE), high density polyethylene (HDPE) and polypropylene (PP) samples deployed in sea water at two different locations in the Bay of Bengal near Chennai, India for a period of 6 months. These are commercial polymers containing antioxidants and stabilizers and are widely used in marine applications.

2. Experimental

2.1. Materials

LDPE, HDPE and PP sheets of 1.5 mm thickness cut into 15×10 cm rectangles were used in the current study. The samples were left at room temperature and weighed with a precision balance. Average weight of each sample coupon was LDPE 21 g, HDPE 35 g and PP 20 g. These commercial polymer samples are used in marine applications and are obtained from Industrial Insulations Ltd., Chennai 600001, India.

2.2. Environment

The polymer samples were immersed in the ocean waters of Bay of Bengal at a depth of 3 m near Chennai Port (latitude $= 13°6' 26''$N, longitude $= 80°17'43''$ E) and Fisheries Survey of India (FSI) (latitude $= 13°6'$ N, longitude $= 80°18'$ E). The characteristic parameters such as temperature, pH, dissolved oxygen, salinity and oxidation and reduction potential (ORP) of the sea water at both the locations were measured every month. In addition, separate polymer coupons were immersed in the ocean at Port every month and removed at the end of the month. This study was done to understand the seasonal effects on biofouling and biodegradation of the polymer.

2.3. Analysis

The amount of biomass, organic matter and photosynthetic pigments namely chlorophyll a, b and c deposited on the polymer surface were monitored every month. These parameters are an indication of the extent of biofouling.

The changes in the chemical and surface properties of the polymer were monitored using Fourier transform infra red analyzer (FTIR), differential scanning calorimeter (DSC), scanning electron microscope (SEM) and atomic force microscopy (AFM). The tensile strength and weight loss of the samples were also measured every month. These experiments were carried out in triplicate with samples deployed at both the places.

The protocols are described in more detail in the following subsections.

2.3.1. Biofilm characterization

In general, the methods adopted here for biofilm analysis are based on literature references [6–11]. Exposed polymer coupons (LDPE, HDPE and PP) were collected from various sites, rinsed with filtered (0.2 μm, Millipore) and autoclaved (120 °C for 15 min) sea water from the corresponding sites. Biofilm formed was scrapped from the polymer surface using sterile nylon brush and dispersed in a fixed volume of sea water (1500 ml). Biofilm solids were measured gravimetrically [12]. Diatoms were counted on the plates as well as in biofilm samples using a colony counter. Photosynthetic groups namely chlorophyll a, b and c were estimated from biofilm samples using UV spectrophotometer (Perkin Elmer lambda 35). The filtration of the biomass was carried out through a 0.22 μm Millipore filter paper and the suspended particles were dissolved in 90% acetone.

Microbiological analysis was carried out using standard media packs prepared by HIMEDIA (Himedia Laboratories Pvt. Ltd Mumbai, India). Total viable counts (TVC) were computed using Zobell marine agar and counts of heterotrophic and iron-reducing bacteria (IR) were performed using standard microbiological methods reported by Postgate [13]. *Pseudomonas* counts were made on *Pseudomonas* agar (HIMEDIA pack) and anaerobe counts on anaerobic agar (HIMEDIA pack). Combustible organic matter in the biofilms was estimated using preignited (at 100 °C for 4 h) Whatman GFC filter paper. The results presented here are mean values of triplicate readings. The macrofoulants were removed by cleaning the surface with 10% hydrochloric acid and the samples were dried in hot air oven at 40 °C for 4 h.

2.3.2. Spectroscopy

FTIR (Fourier transform infrared spectroscopy) is used to determine the formation of new functional groups or disappearance of groups in the polymer. So degradation products, chemical moieties incorporated into the polymer molecules (branches, co-monomers, unsaturation), and presence of additives such as antioxidants can be determined. The keto carbonyl, ester carbonyl, vinyl indices were measured from the FTIR spectrum using the following formulae.

Relative intensities of the ester carbonyl band at 1740 cm^{-1}; keto carbonyl band at 1715 cm^{-1} and the double bond band at 1640 cm^{-1} (vinyl index) to that of the methylene band at 1465 cm^{-1} were evaluated [2]:

Keto carbonyl bond index $= I_{1715}/I_{1465}$;
Ester carbonyl bond index $= I_{1740}/I_{1465}$;
Vinyl bond index $= I_{1640}/I_{1465}$.

The percentage crystallinity of the polymer was measured based on the method suggested by Zerbi et al. [14].

$$\%\text{Crystallinity} = 100 - \left[\frac{\left[1 - \frac{I_a}{1.233 I_b}\right]}{\left[1 + \frac{I_a}{I_b}\right]}\right] 100$$

where I_a and I_b are absorbance values from the bands at 1474 and 1464 cm^{-1} or at 730 and 720 cm^{-1}, respectively.

2.3.3. Thermal analysis

Thermal analysis of polyolefins generally involves heating or cooling a sample at a controlled rate while monitoring some of its physical characteristics. These morphological (heat capacity, melting temperature) changes are measured by a differential scanning calorimeter (DSC) 910S, (TA instruments).

2.3.4. Contact angle

Wettability of the polymer surface was determined from contact angle. Samples supported on glass slide were analyzed using a Camtel (Royston, UK) Goniometer model FT200. The wetting liquid used was Millipore grade distilled water. Calculations were averaged from five measurements. The contact angle is an indication of the hydrophobicity of the surface, and higher the contact angle higher is the hydrophobicity.

2.3.5. Visual inspection

Microbial colony growth on the polymer surface was determined by growing these samples in various selective agar.

2.3.6. Weight loss

A simple and quick way to measure the biodegradation of polymers is by determining the weight loss. Microorganisms that grow within the polymer lead to an increase in weight, whereas growth on the surface leads to a loss of polymer integrity and hence weight loss. Weight loss is proportional to the surface area since biodegradation usually is initiated at the surface of the polymer. This method cannot be used for polymers that absorb water. Samples were weighed with an accurate four digit balance.

2.3.7. Surface changes

Scanning electron microscopy (SEM) (Joel JSM 6300) is used to detect changes in the surface morphology of the polymer due to degradation. This method can be used only to obtain a qualitative conclusion on the nature of biodegradation and cannot be used for quantification purposes. The limitation of this technique is that it is not possible to distinguish whether the changes in structure are due to the biodegradation or due to biodeterioration.

Table 1
Average water quality parameters at Port and FSI during the study period

	Water quality	FSI	Port
1	Temperature	29 ± 1.5	30 ± 4.5
2	Dissolved oxygen	55 ± 7.5	76 ± 1.5
3	pH	8 ± 0.2	7.8 ± 0.3
4	Salinity	32 ± 1.5	33 ± 1.5
5	Oxidation and reduction potentials (ORP)	84 ± 20	120 ± 30

Atomic force microscopy (AFM) was used to determine surface topography and roughness of the polymer coupons that were exposed in the sea water. The analysis was performed on multimode AFM microscope with a Nanoscope IIIa ADCS controller.

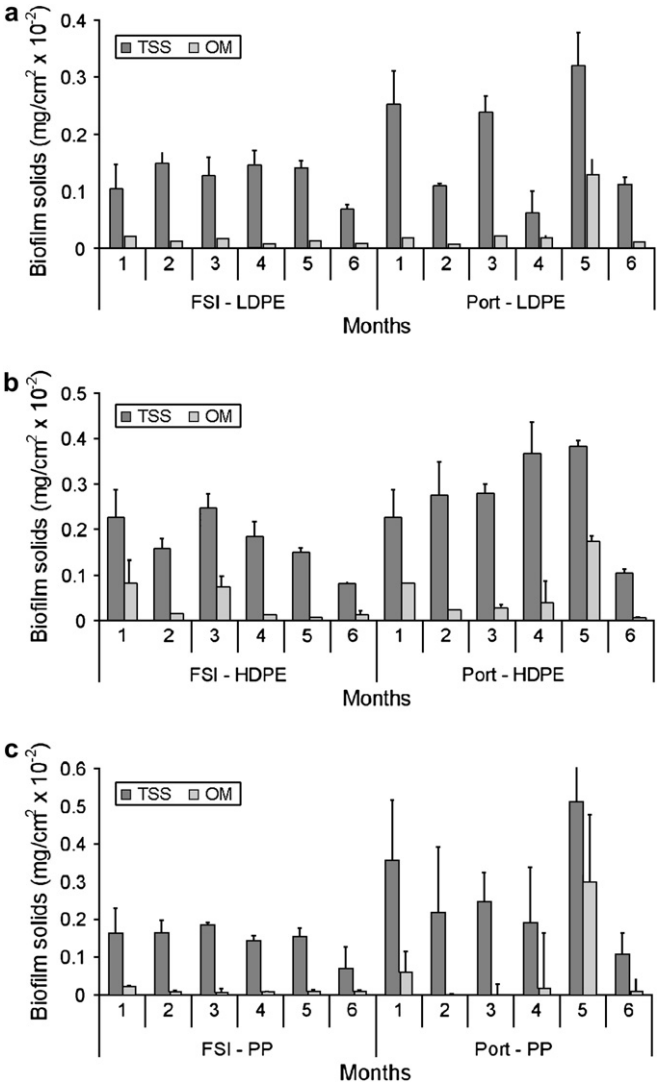


Fig. 1. Biofilm settlement on various polymers at both locations (FSI and Port): (a) low density polyethylene (LDPE), (b) high density polyethylene (HDPE), (c) poly propylene (PP).

Table 2
Seasonal effect on the three polymers at Port

Months	Biofilm solids (mg/cm^2)		Colony forming units (CFU/ml)					Chlorophyll pigments (μg/cm^2)		
	TSS × 10^{-2}	OM × 10^{-2}	TVC	PS	AN	HPC	IR	Ca	Cb	Cc
(a) Monthly biofilm data for LDPE										
April	0.252	0.018	50,000	285	0	0	0	0.160	0.056	0.129
May	0.104	0.001	10,000	1600	1800	380	0	0.311	0.317	0.094
June	0.154	0.001	9600	205	140	240	180	0.095	0.025	0.064
July	0.176	0.015	5500	5	160	170	550	0.298	0	0
Aug	0.360	0.166	28,500	585	0	195	250	0.391	0.056	0.173
Sep	0.105	0.010	19,400	585	480	445	315	0	0	0
(b) Monthly biofilm data for HDPE										
April	0.223	0.078	60,000	435	0	625	0	0.085	0.051	0.101
May	0.125	0.004	50	1400	950	350	0	0.383	0.350	0.187
June	0.246	0.325	10,800	210	180	340	520	0.209	0.126	0.411
July	0.253	0.091	12,200	0	265	125	240	0.309	0.114	0.213
Aug	0.421	0.186	15,500	160	0	195	250	0.415	0.066	0.041
Sep	0.090	0.001	19,800	160	285	1120	880	0	0	0
(c) Monthly biofilm data for PP										
April	0.356	0.059	25,300	2300	0	4000	0	0.122	0.054	0.106
May	0.081	0.001	43,000	2400	1355	355	0	0.322	0.316	0.052
June	0.191	0.012	12,200	385	155	4000	235	0.169	0.077	0.207
July	0.123	0.030	5800	0	230	150	125	0.137	0.065	0.052
Aug	0.885	0.644	29,000	840	0	290	550	0.461	0.174	0.327
Sep	0.100	0.007	44,400	840	255	1980	810	0	0	0

Biofilms: TSS – total suspended solids; OM – organic matter; TVC – total viable count; PS – *Pseudomonas* sp.; AN – anaerobic; HPC – heterotrophic plate count; IR – iron reducing bacteria; Chlorophyll: Ca – chlorophyll a; Cb – chlorophyll b; Cc – chlorophyll c.

2.3.8. Mechanical properties

The tensile properties of the dumbbell-shaped samples of dimensions $215 \times 12 \times 3$ mm were measured as per the ASTM D638 procedure on an Instron machine (no. 4204) at 30 °C, 50% humidity and cross-head speed of 25 mm/min. The impact strength was measured by following the ASTM D256 procedure and the specimen dimensions for this measurement were $6.35 \times 1.27 \times 0.35$ cm with a notch of 0.025 cm radius.

3. Results and discussion

Photograph 1 (A)–(C) show the extent of biofouling on the three polymers deployed in sea for a period of 6 months. From time to time the formed biofilm dislodges and falls into water. The photographs also reveal the presence of macrofoulants, which is seen more clearly after the removal of the biomass by scrapping with nylon brush. The macrofoulants are predominantly barnacles, hydroids and acidians, which remain strongly attached to the surface of the polymer for a long period of time. Removal of barnacles was found to be a difficult task. The degradation of the polymers manifested itself in various ways. Chemical, physical and mechanical changes occurred during the process and they were monitored by various techniques as listed above. The biofilm deposited was also characterized as described above.

Table 1 lists the water quality at the two sites during the course of study. Dissolved oxygen (DO) and oxidation and reduction potential (ORP) were significantly less at FSI when compared to Port. Oxidation and reduction potential is an

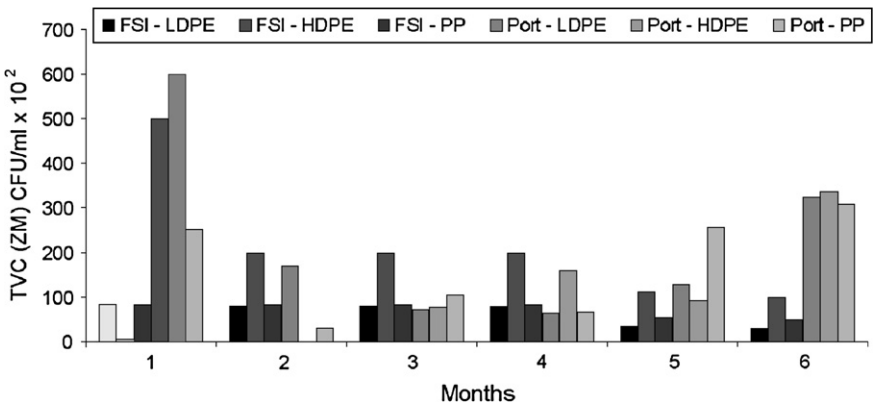


Fig. 2. Total viable counts on LDPE, HDPE and PP surfaces at both sites.

Table 3
Physicochemical analysis of the three polymers at both places

Polymer		Contact angle (°)	%Crystallinity	ΔH (°C) (%)	T_m (°C)	Tensile strength σB (MPa)	Elongation ε (%) (MPa)
LDPE	Control	58.0	87	–	128	24	224
	FSI – 6 months	61.1	83	1.22	125	–	–
	Port – 6 months	66.7	75	2.5	123	20	195
HDPE	Control	63.1	89	–	131	30	91
	FSI – 6 months	65.2	87	0.4	129	–	–
	Port – 6 months	68.6	89	0.8	125	30	88
PP	Control	64.3	90	–	168	15.45	112.9
	FSI – 6 months	64.6	86	0.4	167	–	–
	Port – 6 months	65.2	89	0.4	167	15.12	113.9

indication of effect of aeration on the sea water [15]. The lower DO and ORP observed in FSI waters when compared to Port is probably because of the presence of a village nearby in the former location. The dumping of biodegradable waste due to human activity has lead to higher oxygen demand. The accumulation of biofilm solids and organic matter on the three polymers at both the sites with time is shown in Fig. 1(a)–(c). Biofilm is generally more at Port than at FSI. Table 2(a)–(c) shows the seasonal variation of the biofouling loading on all the three polymers at Port. The biofouling loading and organic matter are highest in the month of August on all the three polymers. This is probably due to the termination

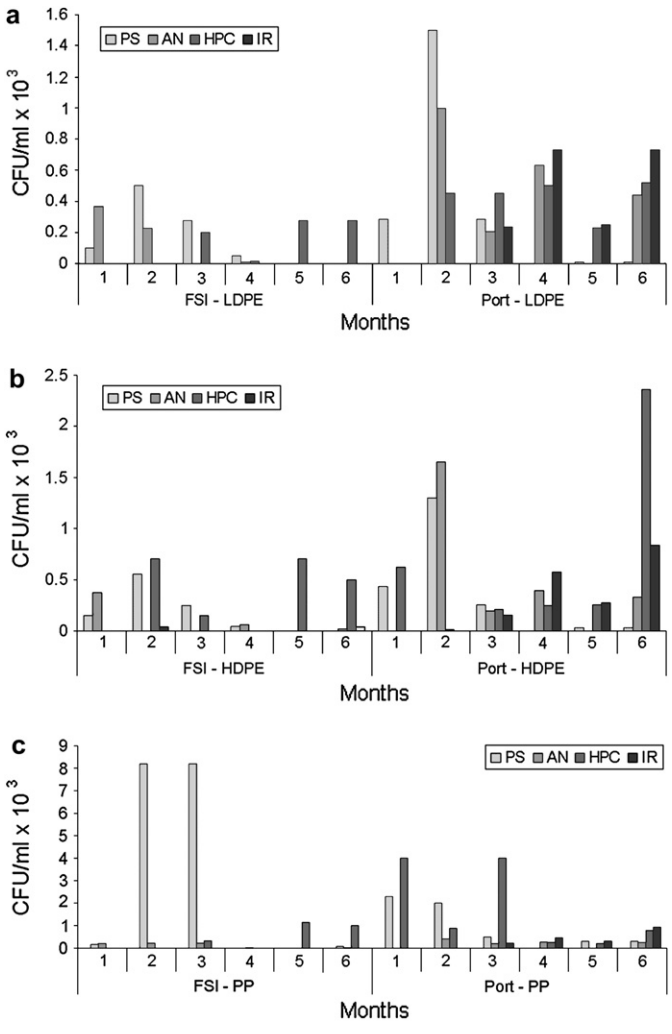


Fig. 3. Microbial colonies on polymer surfaces at both the locations (*Pseudomonas* sp, Anaerobic (AN), Heterotrophic (HPC) and iron-reducing bacteria (IR)). (a) LDPE, (b) HDPE, (c) PP.

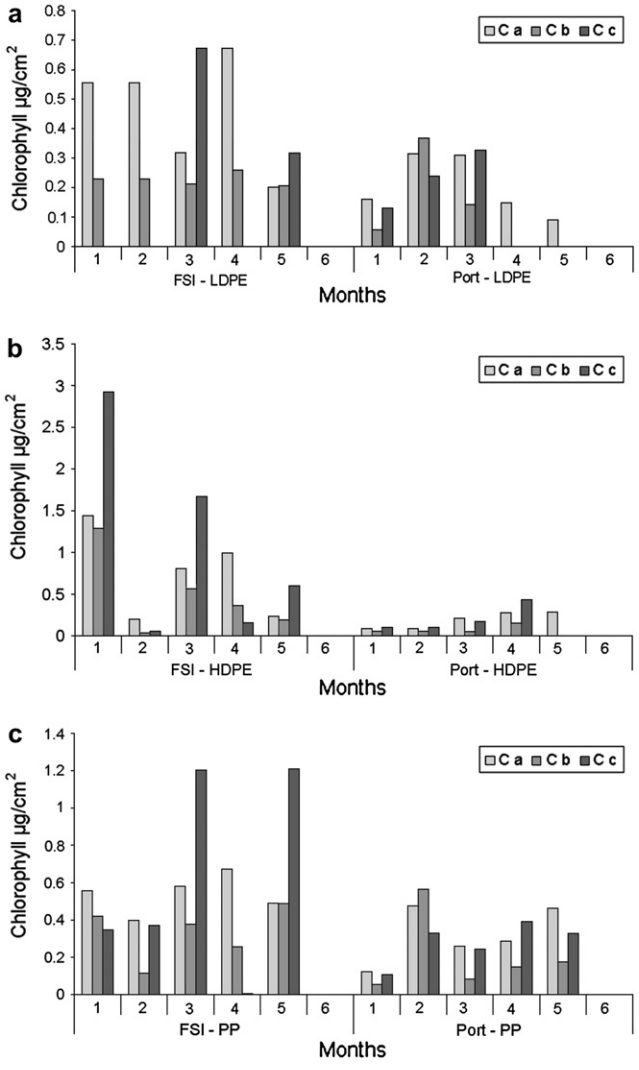


Fig. 4. Photosynthetic chlorophyll a, b and c pigments fixation on the three polymers at FSI and Port. (a) LDPE, (b) HDPE, (c) PP.

of the South West monsoon and commencement of North East winds leading to changes in ocean currents. Cumulative total viable count (TVC) is higher in Port than in FSI by a factor of 2–4 (Fig. 2). Cumulative TVC is high in the first month on all three polymers, but decreases and again starts increasing with time (Table 2) at Port. The average TVC (over the six month period) at Port is 20,500; 19,725 and 26,611 CFU/ml on LDPE, HDPE and PP, respectively. Also biofilm attachment was highest on PP in the first month, followed by that on HDPE and finally on LDPE (Fig. 1), which can be attributed to the fact that the contact angle of the control samples (which is a measure of the hydrophobicity) is lowest for LDPE, followed by that for HDPE and finally for PP indicating that LDPE is the least hydrophobic and PP the most hydrophobic (Table 3). The average amount of biofilm deposited per month on LDPE (0.192×10^{-2} mg/cm^2) is the lowest followed by HDPE (0.22×10^{-2} mg/cm^2). The average amount deposited on PP is 0.289×10^{-2} mg/cm^2, which is the highest when compared to the other two polymers. Since the microorganisms are hydrophobic, they favour hydrophobic surfaces. The amount of organic matter deposited on the surface per month also shows the same trend. Highest average deposit on PP is (0.144×10^{-2} mg/cm^2), followed by that on HDPE (0.065×10^{-2} mg/cm^2) and finally on LDPE (0.0352×10^{-2} mg/cm^2).

Microbiological analysis of biofilm revealed the presence of predominantly four different types of colonies namely, *Pseudomanas* sp (PS), heterotrophic counts (HPC), iron reducing bacteria (IR) and anaerobic (AN). Fig. 3a–c shows the cumulative data at both the sites and Table 2 shows the monthly data at Port on all the three polymers. There does not appear to be any consistent pattern of deposition of these four groups of microbes on all the three polymers at both the sites. On an average HPC and PS are more abundant than the other two organisms. Iron-reducing bacteria is mostly abundant in aerobic condition and it plays an important role in the corrosion of metals and may not be relevant on polymers. In general all the microorganisms are more predominant at Port samples than at FSI samples. This is attributed to higher dissolved oxygen in the former site than in the latter.

On an average, attachments of colonies were higher on PP, followed by that on HDPE and finally on LDPE (Fig. 3). The average attachment on PP per month at Port was 1100 and 1813 CFU/ml of PS and HPC, respectively. The corresponding values on HDPE were 560 and 450 CFU/ml and those on LDPE were 540 and 240 CFU/ml, respectively. These results clearly indicate that the formation of biofilms allow other macrofouling communities to deposit easily. Deposition of photosynthetic pigments namely chlorophyll a, b and c (Figs. 4a–c) were more at FSI when compared to at Port. Also the cumulative deposition of pigments was highest on PP and lowest on LDPE. Deposition of chlorophyll a was highest in the months of May and August on all the three polymers at Port (Table 2). Monthly samples also indicate that chlorophyll a is more predominant than b or c. Our results indicate that dissolved oxygen, biofouling and organic matter are low at FSI but chlorophyll is higher than at Port, the latter happening because of lower ORP at the site. Previous work [12,15] also observed that water pollution leads to higher chlorophyll formation.

The four different microbial colonies, namely PS, HPC, AN and IR identified on the hydrophobic polymer surface leads to fouling and they draw their carbon nutrient from the polymers. The biofilms on the polymer surfaces are heterogeneous, consisting of cell clusters with EPS and particulate matter and are

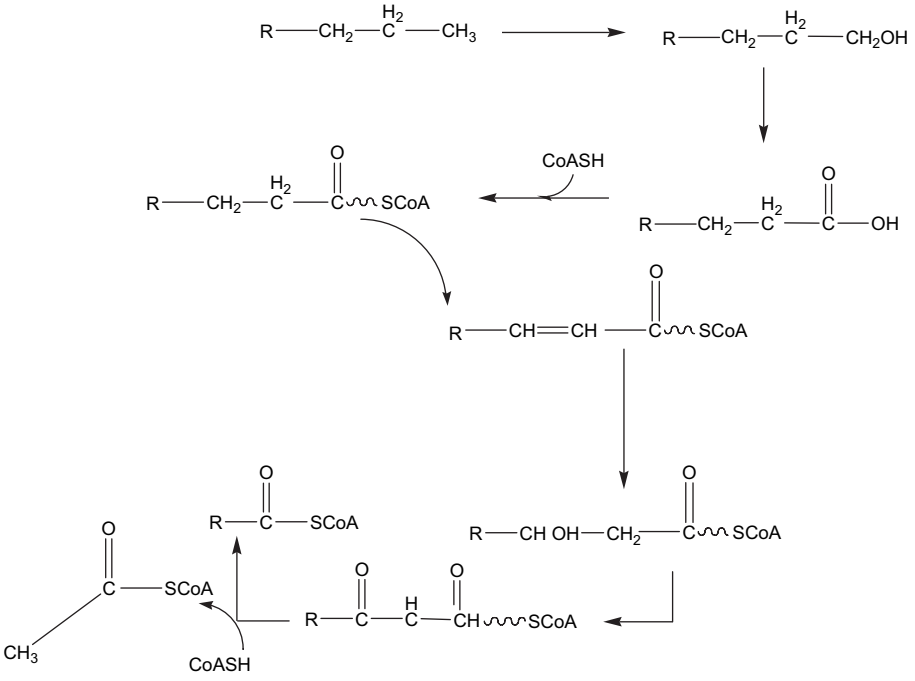


Fig. 5. Biotic paraffin degradation (H.G. Schlegel) [16,2].

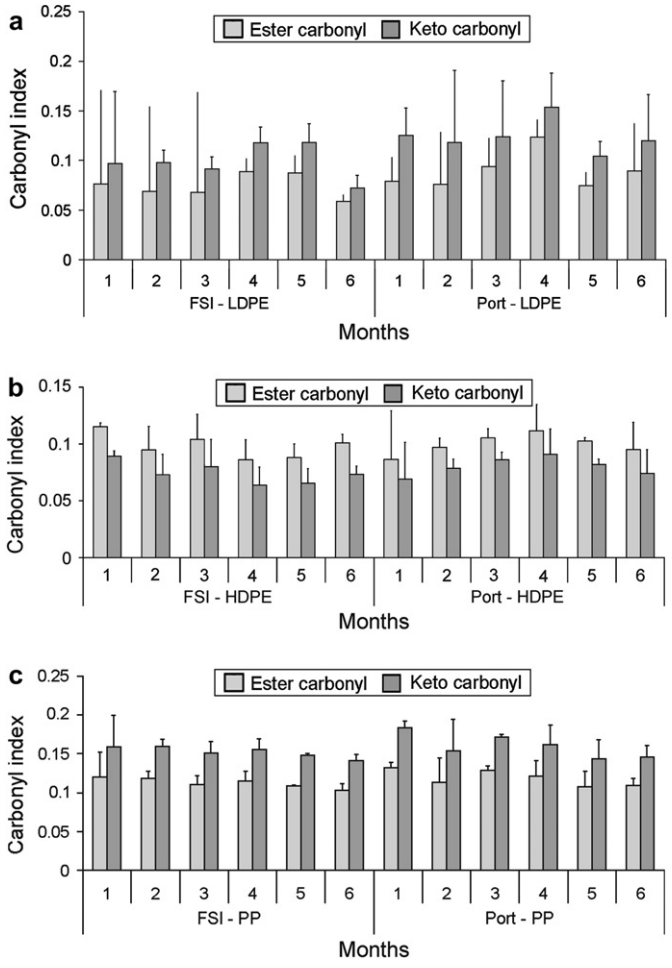


Fig. 6. Carbonyl index at both locations on the three polymers as a function of time. (a) LDPE, (b) HDPE, (c) PP.

separated by interstitial voids. The accumulation of particulate matter in biofilms was found to increase with exposure time. This is attributed to the extracelluar material produced by the bacteria.

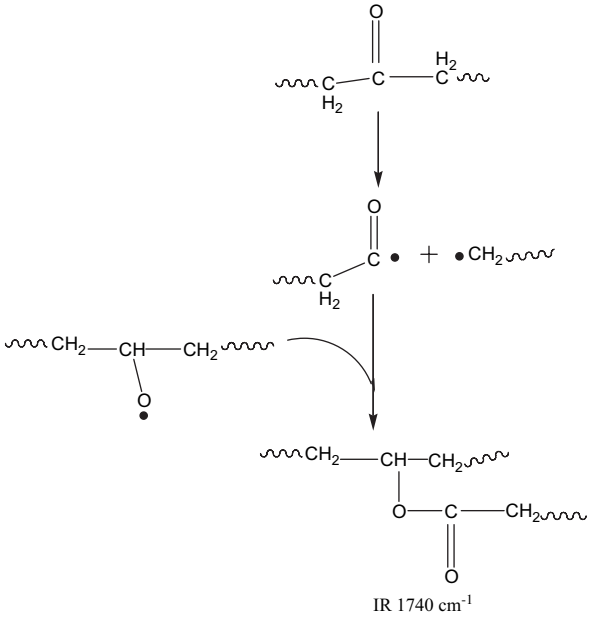


Fig. 8. Abiotic ester formation [2].

Biodegradation occurs due to the action of enzymes secreted by the living organisms such as bacteria, fungi etc. The rate of degradation is sensitive to microbial population, moisture, temperature, and oxygen in the environment. For inert polyolefins, oxidation is the initial step for the biodegradation, and the attack by microorganisms is a secondary process.

The mechanism of biodegradation of these polymers could be the same as the biodegradation of paraffins [16]. The biodegradation of paraffin starts with the oxidation of the alkane chain first to ketone, then to a carboxylic acid, and the latter then undergoes β-oxidation (Fig. 5). A mechanism for the biodegradation of polyethylene was presented in 1987 which shows similarities with the β-oxidation of fatty acids and paraffins in human and in animals [2]. In the biodegradation of polyethylene, an initial abiotic step involves oxidation of the

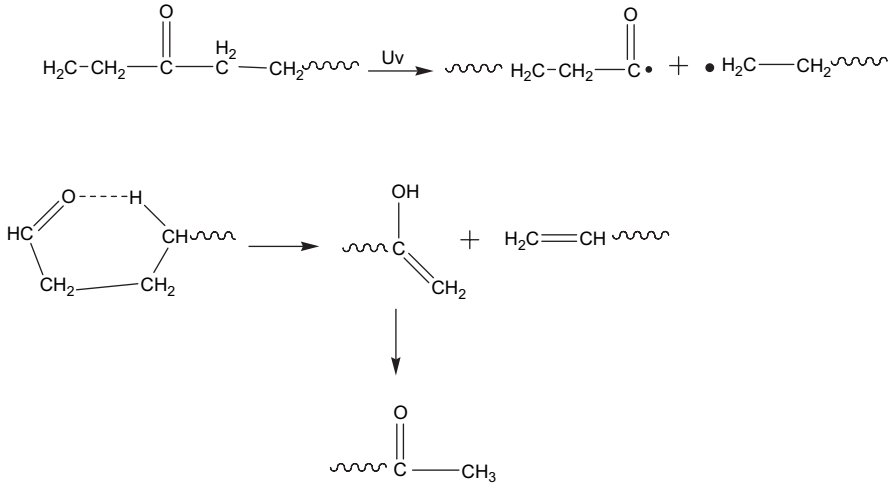


Fig. 7. Norrish type I and II degradations [2].

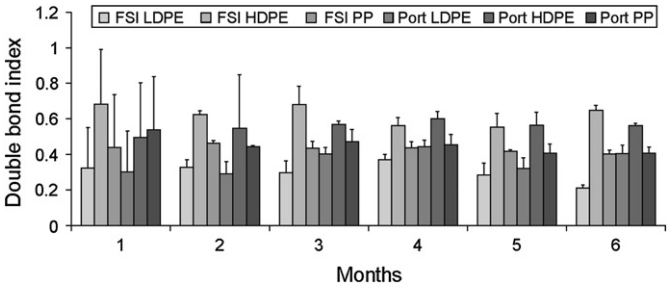


Fig. 9. Double bond index on the three polymers at both locations as a function of time.

polymer chain due to the oxygen present in the ambient, which leads to the formation of carbonyl groups. During microbial degradation, a decrease in the carbonyl groups was noted. The carboxylic acids formed react with coenzyme A (CoA) and remove two carbon fragments, acetyl-CoA, which enters the citric acid cycle and produces carbon dioxide and water as the final degradation products [2]. Photo-oxidation leads to the scission of the main chain in polymer and leads to the formation of low molecular weight products. Embrittlement and hydrophilicity due to the introduction of carbonyl groups further promotes the biodegradation of the polymer.

Exposure of polyolefins to oxygen, particularly at elevated temperatures or in the presence of sunlight leads to its oxidation. This is an autocatalytic process called auto-oxidation. Formation of carbonyl groups is dependent on various environmental factors and additives present in the commercial polyolefins. The current results (Fig. 6a–c) show that carbonyl index is generally high in Port samples when compared to FSI samples. At initial stages carbonyl index in LDPE and HDPE at Port increases, probably due to environmental factors such as UV, temperature and dissolved oxygen (abiotic factors). Prolonged stay in the ocean leads to decrease in carbonyl index probably due to biodegradation (biotic) through Norrish type mechanism (Fig. 7) or through formation of ester (Fig. 8). The rate of decrease in carbonyl index in PP is much less than the rate of decrease in the other two polymers indicating lower biodegradation. This abiotic carbonyl formation and reduced biotic degradation also leads to higher carbonyl index build up in PP. FTIR as a tool for differentiating between abiotic and biotic degradation of LDPE has also been reported by Albertsson et al. [2]. Others have also observed that in the abiotic environment, a continuous increase in the amount of carbonyl compounds with exposure time is seen, contrary to the observed decrease in the biotically aged samples [17–19]. Norrish type II reaction (Fig. 7) leads to the formation of double bonds in the polymer chain. Fig. 9 shows the changes in the double bond (vinyl) index with time at both the locations as a function of time. The vinyl index is lowest for LDPE when compared to HDPE and PP probably because of chain scission. A combination of abiotic and biotic degradation is observed in the marine environment and the rate of biotic degradation is very slow in PP (Fig. 6c) at both places when compared to HDPE (Fig. 6b) and LDPE (Fig. 6a). Formation of

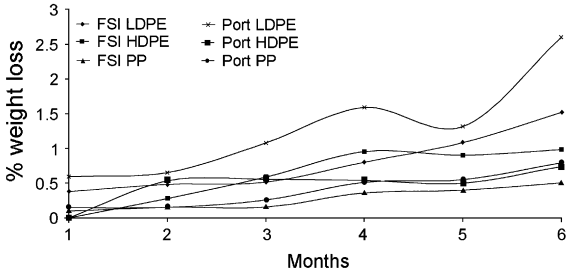
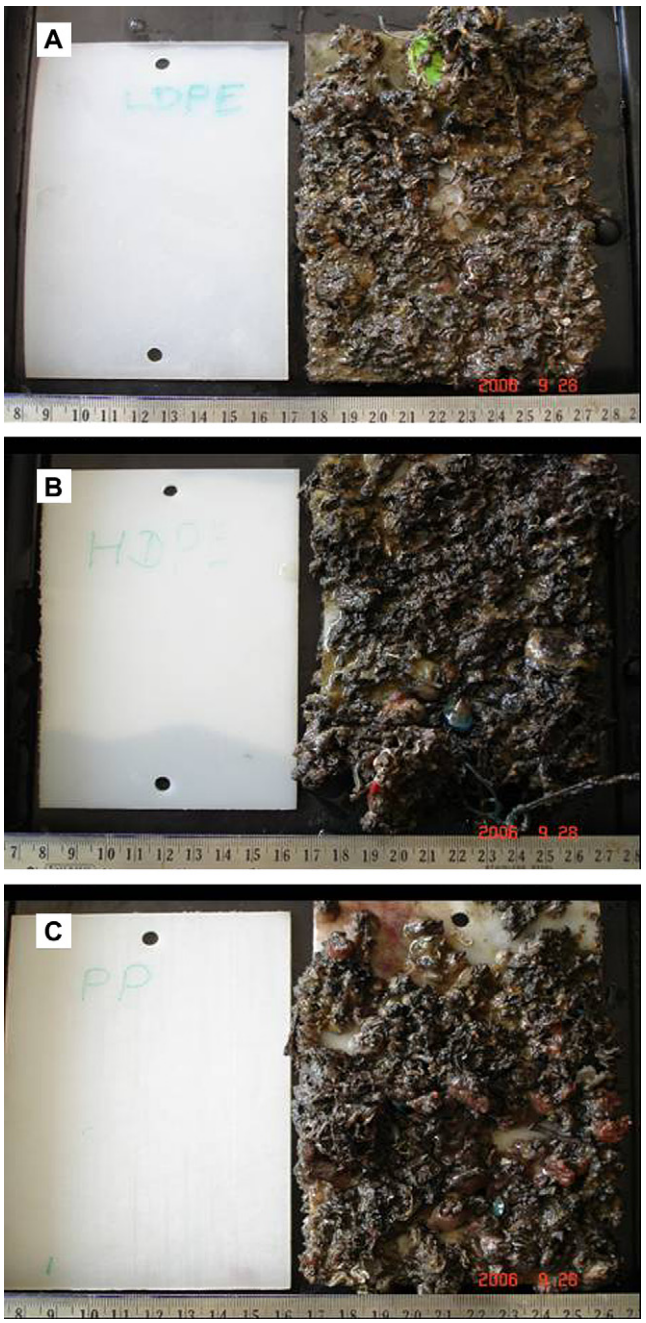
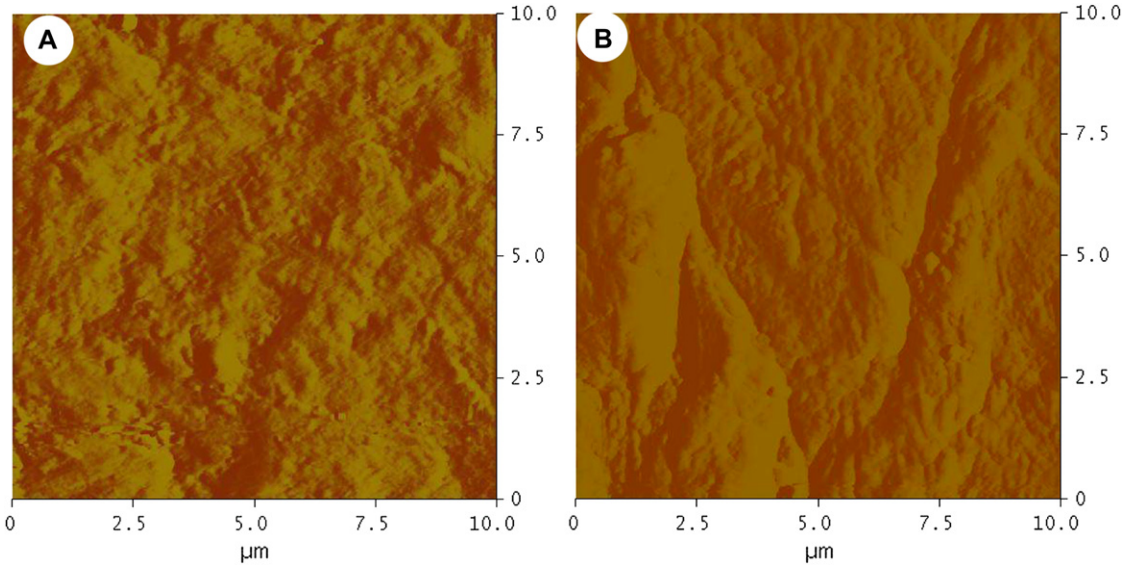


Fig. 10. Weight loss on the three polymers at both locations as a function of time.



Photograph 1. (A) LDPE, (B) HDPE, (C) PP.

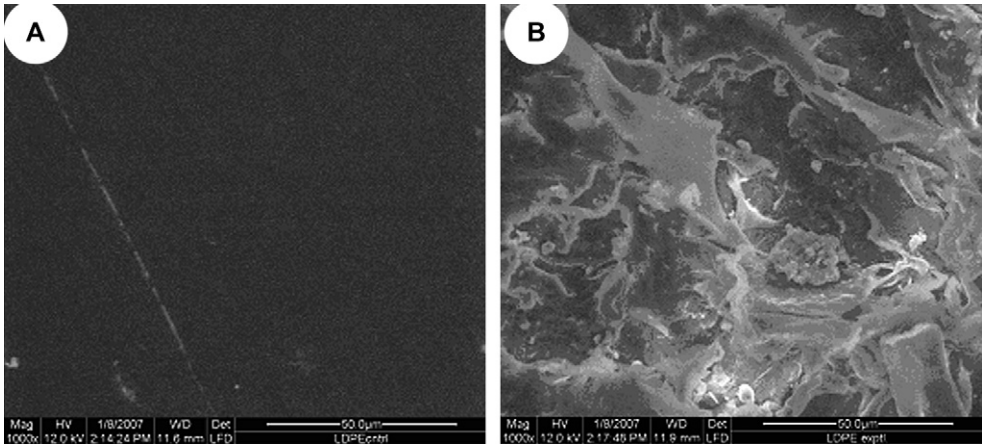


Photograph 2. AFM pictures of LDPE samples (A) control and (B) 6 months in ocean.

ester and keto carbonyl has also been reported as major products formed during abiotic oxidation of polymer under UV light, thermal or enzymes such as oxidoreductase [20].

The utilization of low molecular weight carboxylic acids as a carbon source by thermophilic fungi commonly found in composting refuse had been reported by Karlsson and Albertsson [20]. These dicarboxylic acids had, however, been formed through partial oxidation of polyethylene by boiling it with nitric acid. These studies were extended to include polypropylene and polystyrene [21]. The absence of carboxylic acids in biotically aged LDPE samples is thus a confirmation of the biodegradation mechanism proposed in 1987 [2]. Dexter and Culberson [22] observed that the DO content in the sea water may be the major influence on degradation. They commented that the oxygen levels increased due to photosynthesis by marine plants and by the action of the waves, while the oxygen level decreased due to demand for oxygen by the microorganisms. In our studies Port is observed to have more waves and ocean currents than FSI, hence DO was higher in the former location than the latter. The results clearly indicated that the rate of biodegradation was higher at Port than at FSI.

Photographs 2 and 3 show the AFM and SEM pictures, respectively, of the LDPE surface before and after it was deployed in Port for 6 months. The corresponding average roughness of the polymer surface was 80.2 and 76.08 nm, respectively. Decrease in percentage crystallinity with time in LDPE was observed, more at the Port than at FSI. Increase in contact angle was observed in LDPE and HDPE samples located at Port. A reduction in tensile strength and elongation was also observed in LDPE (Table 3). Percentage weight loss was highest with LDPE samples deployed in Port (Fig. 10) (about 2.5% in 6 months), followed by HDPE (1.5%) and then with PP (0.5%). *Pseudomonas* and



Photograph 3. SEM pictures of LDPE samples (A) control and (B) 6 months in ocean.

Clostridium (anaerobic) microorganisms have been reported to degrade LDPE and HDPE under *in vitro* conditions [5]. These organisms have been observed in the biofilms in the present field studies as well. It is reported that the rate of biodegradation of polyethylene in Baltic Sea environment was found to be 2.7% in 12 months [23].

4. Conclusion

Microorganisms are involved in the degradation of polymers under both aerobic and anaerobic conditions. The current study has revealed that biological analysis which includes measurement of biofilm solids, amount of organic matter, total viable bacterial count and chlorophyll deposited are effective tools for understanding biofouling under *in vivo* conditions. Analysis of functional groups, melting temperature, percentage crystallinity, hydrophobicity, mechanical strength and surface morphology of polyolefines show that they degrade in tropical sea water (Chennai Port and FSI). Maximum degradation was seen in Chennai Port, when compared to FSI, which was due to higher dissolved oxygen and higher oxidation and reduction potential at the former site than at the latter site. The weight loss was higher in LDPE (2.5% weight loss in 6 months) followed by that in HDPE (0.75%) and then in PP (0.5%).

Polyolefins are widely used in ship gears, hulls, bearing and in other marine and industrial applications. Previous study reported the exposure of starch blended polyethylene films in Baltic Sea. They observed 2.7% weight loss and decrease in the tensile strength from 18 to 14 MPa in 12 months period while there were no changes observed in 6 months [23]. Albertsson and Karlsson [24] found that polyethylene buried in soil had a weight loss of 3.5% in 10 years. These low rates are in agreement with the argument of Otake et al. [25] that 10 years is a relatively short period for the biodegradation of synthetic polymers such as polyethylene. The present experimental results show a weight reduction of 2.5% in unblended LDPE and decrease in tensile strength from 24 to 20 MPa in 6 months under tropical conditions. Starch blended polymers are reported to degrade at a higher rate when compared to unblended polymer. Hence the current study indicates that higher biodegradation levels can be expected in tropical conditions probably because of higher ambient temperature, DO levels and microorganisms.

Initial abiotic conditions lead to introduction of oxygen in the polymer. Formation of carbonyl groups aids the microorganisms to take up the degradation process further. A decrease in carbonyl index and presence of double bonds in the FTIR spectra clearly indicate that the degradation is due to the action of microorganisms. The degradation appears to follow the Norrish type II mechanism. Hydrophobic nature of the surface helps in easy attachment of hydrophobic microorganisms. Seasonal effects were seen on the amount of biofilm attached on the polymer surface. In the current study no efforts were made to isolate fungi that were also found in the biofilm.

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