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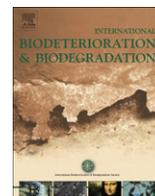**16** PUBLICATIONS **131** CITATIONS

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Biofouling and stability of synthetic polymers in sea water

Trishul Artham [a], M. Sudhakar [a], R. Venkatesan [b], C. Madhavan Nair [c], K.V.G.K. Murty [c], Mukesh Doble [a],*

[a] Department of Biotechnology, Indian Institute of Technology Madras, Chennai, Tamilnadu 600036, India
[b] OSTI, National Institute of Ocean Technology, Chennai, India
[c] Life Sciences Division, AU-KBC Research Centre, MIT Campus, Chennai, India

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ABSTRACT

Commercial synthetic polymers namely Polycarbonate (PC), Low density polyethylene (LDPE), High density polyethylene (HDPE), and Polypropylene (PP) coupons were immersed for a period of 12 months (Feb 2006 – Feb 2007) in Bay of Bengal, East coast, India. Samples were retrieved every month and the extent of biofouling and biodegradation were monitored. Biofouling was found to depend not only on the season but also on the chemical nature of the polymer. Surface energy of all the four polymers is positively correlated with fouling only at the initial stages (three months) while surface roughness had a negative correlation. The later increased during the study period. Total suspended solids and organic matter were more abundant on HDPE, followed by PP and LDPE, indicating that among polyolefins hydrophobic surfaces (lower surface energy) favor biofouling over one year. Maximum fouling was observed on polycarbonate during initial three months. Chlorophyll *a* showed a decreasing trend during the study, as secondary foulers such as *Balanus amphitrite*, were dominant after the monsoon (6th month in the present study). Maximum weight loss was seen in LDPE (1.9%), followed by that in HDPE (1.6%), PC (0.69%) and finally in PP (0.65%) samples in the 12 months time period. FTIR spectra of PC displayed a decrease in carbonate carbonyl index, while an initial increase and a decrease in carbonyl index of polyolefins as a function of time indicated biodegradation.

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1. Introduction

Plastics are synthetic organic polymers that are produced worldwide at a rate of 100 million tons per year and are increasing day by day (Thompson et al., 2004). The increased consumption over time has led to escalating levels of plastic in the marine environment via industrial discharge, littering and terrestrial runoff (Derraik, 2002). Most polymers are highly persistent in the marine environment and only degrade slowly via photocatalysis when exposed to ultra-violet radiation. Pegram and Andrady (1989) had observed 12% and 26% reduction in tensile properties of polyethylene and polypropylene respectively when exposed to sea water for a period of one year. The retardation in weathering was attributed to the slow build up of heat in the samples in sea water. Polyolefins and thermoplastic polyesters have been used as organic spray coatings to prevent corrosion on steel in marine waters (Singh et al., 2007). It is important to know and understand the stability of these polymers under natural marine environments to either address the environmental cause or to use them in any other application such as organic coatings to prevent corrosion.

Any material immersed in aqueous environments or under high humidity conditions is equally susceptible to biofouling and biodegradation (Gu, 2003). Biofouling has been recognized as a widespread problem in design and operation of processing equipment. Earlier studies have focused on the biological characterization of microfouling products developed on various surfaces immersed in marine waters (Baier, 1980; Bhosle et al., 1989). During the initial period of immersion the nature of the substratum influences the composition of the microfouling organisms (Characklis and Cooksey, 1983). There are a number of reports on impact of surface energy and surface roughness on the fouling on substrates immersed in sea water (Zhao et al., 2005; Audrey et al., 2006). Strong hydrophobic low energy surfaces are said to be preferable in industrial and marine biofouling control because of their stability and lower interactions with living cells (Vladkova, 2007). It is even reported that materials with surface energies anywhere between 20 and 30 mN m^{-1} are favorable antifouling materials (Robert and Brady, 1999). Only few reports are available that study the effect of biofouling on the surface energy and surface

roughness of the polymer. Little is known about the alterations of surface properties of polymers associated with the fouling. Such data will be of great importance to understand the fouling phenomena in natural environments. In the present study an attempt has been made to correlate the fouling parameters to the surface characteristics of the polymer during the course of the study and further determine the stability of these polymers exposed to sea water for one year.

Atomic force microscopy (AFM) was combined with surface analytical techniques to investigate the rarely addressed issue of the effect of biofouling on the surface properties of few widely used polymers namely, LDPE, HDPE, PP and polycarbonate. The exposure of these polymers to sea water resulted in fouling which in turn led to modification of their morphology and surface properties.

2. Materials and methods

2.1. Materials

LDPE, HDPE, PP and Bisphenol A polycarbonate (PC) (Lexan®) sheets of 1.5 mm thickness cut into 150×100 mm coupons were used in the current study. Average weight of each sample coupon was LDPE 21 g, HDPE 35 g, PP 20 g and PC 35 g. These polymers were obtained from Industrial Insulations Ltd., Chennai 600001, India and used as supplied.

2.2. Environment

The polymer samples were tied to fiber reinforced racks and were vertically submerged in the ocean waters of Bay of Bengal at a depth of three meters near Fisheries survey of India (FSI) (Latitude = 13°7′34″N, Longitude = 80°17′49″E) from February 2006 to February 2007. The racks were fixed to plastic buoys filled with polyurethane foam. A total of 36 coupons (3 samples for each month) were used for each polymer. The characteristic parameters of the sea water such as temperature, pH, dissolved oxygen (DO) and salinity, at the study site were measured every quarter using a Hydrolab Quanta (HACH, USA). Polymer samples, in triplicate were removed every month and the extent of biofouling and their physicochemical parameters were analyzed.

2.3. Biofilm characterization

Exposed polymer coupons were retrieved from the site every month in sample bottles containing pre-filtered (0.2 μm, Millipore) and autoclaved (120 °C for 15 min) sea water. Biofilm formed was scraped from the polymer surface using a nylon brush as suggested by Sharma et al. (1990) and dispersed in 1500 ml of sterile sea water. Parameters such as total suspended solids (TSS), combustible organic matter (OM) and chlorophyll *a* were estimated to assess the development of biofilm since these parameters were known to hold a key role in biofouling (Bhosle, 2005).

The total suspended solids were estimated from the biofilm samples based on the method reported by Parsons et al. (1984). Typically, a sample of 20 ml was filtered through a pre-ignited (400 °C, 4 h) and pre-weighed whatman GF/C filter paper, dried at 100 °C for 1 h and reweighed to get the dry weight of the residual biomass. Organic matter was estimated after oven-drying of samples to a constant weight and subsequent combustion in a muffle furnace at 350 °C for 1 h. Then OM was calculated from the subtraction of weights before and after combustion. All samples were cooled to room temperature in a desiccator before any weight determinations. Samples for photosynthetic pigment chlorophyll *a*, which represents the algal growth, were stored at −20 °C until analysis. Around 15 ml of water sample containing scraped biofilm

suspension was filtered through a 0.22 μm Millipore® filter paper and the filtrate was dissolved in 90% acetone for extracting the chlorophyll *a*. The samples were incubated for 12 h at 4 °C in the dark after which the absorbance at 630, 645, 665 and 700 nm was measured using a UV spectrophotometer (Perkin Elmer, Lambda 35).

The adhered remains of macrofoulants were removed from the polymer by cleaning the surface with 10% hydrochloric acid and then dried in hot air oven at 40 °C for 4 h before characterizing it.

2.4. Polymer characterization

The changes in the chemical and surface properties of the polymer were monitored based on the following methods.

2.4.1. Surface wetting properties

Contact angle is an indication of the hydrophobicity of the surface, and higher is its value higher is the hydrophobicity. It was measured using the sessile drop method with an Easy Drop Contact Angle Measuring goniometer (Kruss, Germany). The polymer film was supported on a glass slide and a drop of Millipore® grade distilled water was placed on it using a syringe. The image of the drop was processed by DSA2 software which calculated both the left and right contact angles of the drop made with the surface to an accuracy of $\pm 0.1°$. It was measured on five different locations on the polymer and the average values were reported here.

Contact angles were also measured using three test liquids namely double distilled de-ionized water, diiodomethane (Sigma, India) and formamide. DSA2 software was used to calculate the surface energy of the polymer by Owens method (Owens and Wendt, 1969). The total surface energy of a solid, γ_s, can be expressed as the sum of contributions from dispersion γ_s^d and polar γ_s^p force components of the polymer. These can be determined from the contact angle (θ) data of polar and non-polar liquids with known dispersion and polar parts, by the equation

$$\gamma_{lv}(1 + \cos \theta) = 2\sqrt{\gamma_s^d \gamma_{lv}^d} + 2\sqrt{\gamma_s^p \gamma_{lv}^p}$$

where γ_{lv} is the surface tension of probing liquid while γ_{lv}^d and γ_{lv}^p are dispersive and polar components respectively of the surface energy of probing liquid.

Contact angle hysteresis (CA hys), a measure of surface heterogeneity of the polymer, was calculated as the difference between advancing (θ_a) and receding (θ_r) contact angles (Schmidt et al., 2004) as given below

$$\text{CA hys} = \gamma(\cos \theta_r - \cos \theta_a)$$

where γ is the surface tension of the probing liquid (Water = 72.6 mN m^{-1})

2.4.2. Surface changes
The surface topography and the roughness of the polymer coupons that were exposed to the sea water were measured with an atomic force microscope (AFM). Typically, the sample was mounted on a piezoelectric scanner and the surface was scanned using a Nanoscope III AFM microscope with an ADCS controller in contact mode within an area of 20 μm² with a silicon nitride cantilever.

2.4.3. Fourier transform infrared spectroscopy
Fourier transform infrared (FTIR) spectra, which are used for detecting the formation of new functional groups or change in the amount of existing functional groups, were recorded on a Jasco N4200 spectrometer at a resolution of 4 cm^{-1} in the frequency

Table 1
Water quality parameters at FSI during the study period.

Period	Season	DO[a] mg ml^{-1}	pH	Salinity ppt	Temperature °C
Apr-06	Summer	3.27	7.88	33.53	29.48
Jul-06	Pre-monsoon	4.56	7.94	33.92	28.10
Oct-06	Monsoon	3.65	8.12	34.23	28.30
Jan-07	Post-monsoon	4.08	8.04	31.17	28.42

[a] DO = Dissolved oxygen.

range of 4000–400 cm^{-1}, calibrated with polystyrene standards. The analysis was performed using HATR (Horizontal Attenuated Total Reflectance) mode by accumulating 32 scans. The readings were taken in triplicates and the mean and standard deviation are presented here.

The keto carbonyl, ester carbonyl, vinyl indices for the polyolefins were measured from the FTIR spectra using the following formulae

Keto carbonyl bond index $= I_{1715}/I_{1465}$

Ester carbonyl bond index $= I_{1740}/I_{1465}$

Vinyl bond index $= I_{1640}/I_{1465}$

where relative intensities at 1740 cm^{-1}, 1715 cm^{-1}, 1640 cm^{-1} and 1465 cm^{-1} correspond to ester and keto carbonyl, double bond (vinyl index) and methylene bands respectively (Albertsson et al., 1987).

The methyl index for polycarbonate was calculated by taking the ratio of absorbances at 2915 and 1508 cm^{-1}. The former peak corresponds to the stretching frequency of methylene carbon, while the later peak corresponds to bending frequency of aromatic sp^2 carbon. This latter peak is assumed to be the internal standard, since it is reported that the phenyl stretching vibrations are not affected significantly even under strong ionic irradiation (Gagnadre et al., 1993). Carbonate carbonyl index (CC index) (ratio of carbonate bond at 1778 cm^{-1} to aromatic CH stretching at 1508 cm^{-1}) for PC was calculated using two-point base method (ASTM E 168-99). This method would eliminate the error that would occur during baseline correction.

2.4.4. Weight loss

A simple and quick way to determine the biodegradation of polymers is by measuring the weight loss. This method cannot be used for polymers that absorb water. Samples were weighed with an accurate four digit balance before deployment and after removing from the ocean and cleaning them as described in Section 2.3.

2.5. Correlation analysis

Correlation between the biofouling parameters and surface energy, surface roughness and contact angle hysteresis were developed using Microsoft® Excel 2003 software.

Fig. 1. Map showing the location of the Sampling site on Indian coast.
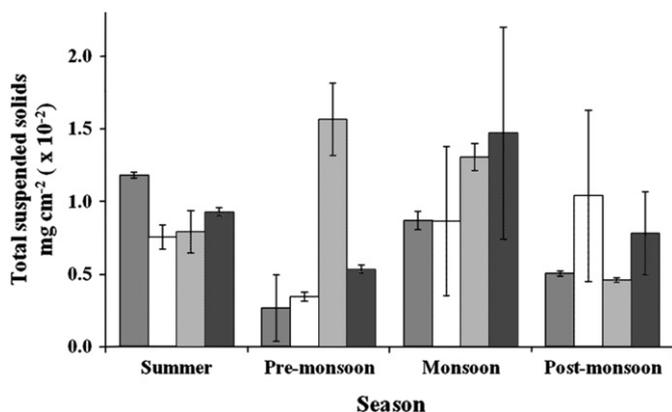
Fig. 2. Biofilm settlement in terms of total suspended solids (TSS) on polymers at FSI. (■ Polycarbonate; □ LDPE; ▨ HDPE; ■ PP).

Fig. 4. Cumulative photosynthetic pigment Chlorophyll *a* in the biofilm on different polymers during various seasons. (■ Polycarbonate; □ LDPE; ▨ HDPE; ■ PP).

3. Results

3.1. Characterization of the biofilm

The average sea water quality parameters measured during the course of the study at FSI are presented in Table 1. The experimental site (Fig. 1) being close to the shore with high human anthropogenesis had lower dissolved oxygen values than the recommended levels of 5 mg ml^{-1} (COMAPS, 2006). Figs. 2 and 3 show the total suspended solids and organic matter respectively on all the polymers. Chlorophyll *a* (which represents the amount of algal and photosynthetic bacteria) was highest during the summer (Mar–May 2006) (Fig. 4).

Seasonal effect on accumulation of the total suspended solids was observed during the current study. Initially, during the summer (Mar–May 2006) a buildup in the amount of TSS was observed on all polymers. The total suspended solids and organic matter were more on HDPE, followed by PP and LDPE. During the first three months, it was observed that polycarbonate which was more polar and hydrophilic than polyolefins, had higher TSS and OM, but as the seasons changed a buildup of fouling on polyolefins was observed. On an average over 12 months, polycarbonate had higher amount of algal deposition than polyolefins. Among the three polyolefins, hydrophobicity seems to have a role in the amount of algal deposition in the three months sample. Apart from barnacles, other foulants like mussels, tube worms and hydroids were also observed however, their relative amou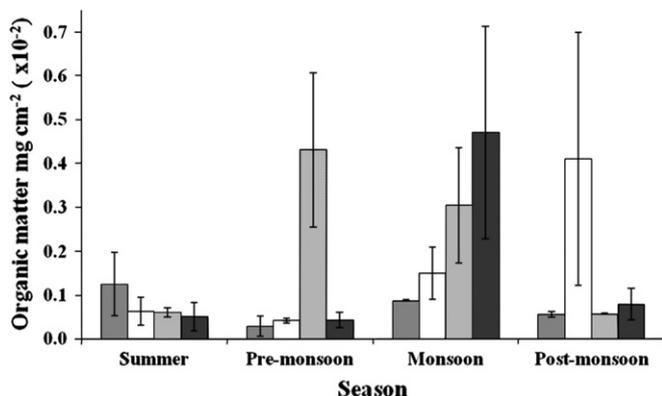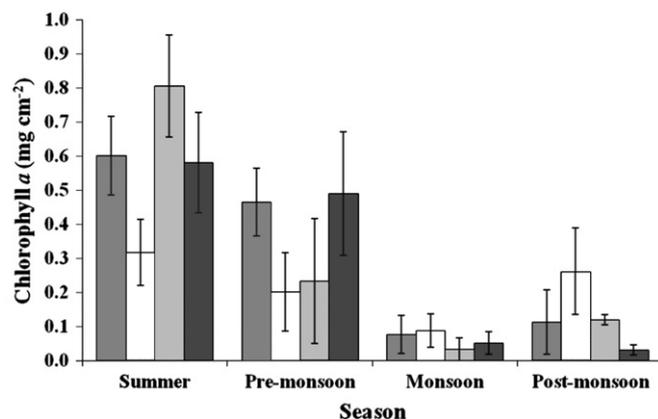nts varied from one month to the other. In the present study the thickness and number of macrofoulers were not quantified.

3.2. Surface characterization

Table 2 presents the measured root mean square values of surface roughness, surface energies and contact angle hysterisis for all the four polymers after various periods of exposure to sea water. Generally an increase in the surface roughness was observed over the exposure period.

Surface energy of polyolefins remained almost constant during the study period. In the case of polycarbonate, an increase in surface energy and a reduction in its contact angle were observed. Contact angle hysterisis, a measure of surface heterogeneity, did not show any trend for any of the polymers during the study.

3.3. Correlation studies

There was a strong positive correlation between surface energy and total suspended solids during the first three months (Table 3)

Fig. 3. Biofilm settlement in terms of organic matter (OM) on polymers at FSI. (■ Polycarbonate; □ LDPE; ▨ HDPE; ■ PP).

Table 2
Measured surface characteristics of polycarbonate and polyolefins during 12 months exposure to sea water.

Sample	Duration (months)	Roughness (nm)	Surface energy (mJ m^{-2})	Contact angle hysteresis
PC	Control	4.38	40.58	28.8
	3	30.93	41.82	22.4
	6	24.29	46.09	8.6
	9	44.93	46.52	32.2
	12	320.59	47.89	18.3
LDPE	Control	60.19	38.58	18.7
	3	117.68	37.95	28.7
	6	158.43	36.95	9.5
	9	199.52	34.93	16.2
	12	224.84	38.79	27.4
HDPE	Control	62.75	38.52	26.0
	3	90.82	36.88	17.6
	6	67.17	37.85	25.9
	9	224.41	36.84	20.9
	12	119.61	38.00	12.9
PP	Control	45.96	35.16	39.0
	3	90.36	37.23	26.9
	6	122.89	32.37	20.4
	9	184.59	31.79	17.7
	12	73.17	34.16	30.7

Table 3
Correlation analysis between surface properties of four polymers with biofouling for three months, in terms of total suspended solids and Chlorophyll *a*. [numbers in brackets indicate correlation for 12 months].

Parameters	Surface Roughness	Surface energy	Contact angle hysterisis	TSS	Chlorophyll *a*
Roughness	1.00				
Surface energy	−0.69 (−0.45)	1.00			
CA hysterisis	−0.29	0.78	1.00		
TSS	−0.99 (−0.05)	0.80 (−0.64)	0.44	1.00	
Chlorophyll *a*	−0.05 (−0.96)	0.64 (0.40)	0.40	0.18	1.00

while surface roughness had a strong negative influence on fouling. Poor correlation was observed between surface properties and biofouling during the rest of the study period probably because the conditioning film had stronger effect on successive fouling. A negative correlation was observed between surface energy and surface roughness between these polymers.

3.4. Weight loss

Low density polyethylene showed 1.9% weight loss followed by HDPE (1.6%), PC (0.69%) and PP (0.65%) in 12 months (Fig. 5). The rate of biodegradation of polyethylene in Baltic Sea environment was found to be 2.7% in 12 months (Rutkowska et al., 2002). These findings indicate that among polyolefins, PP has the highest stability towards the sea water and so does PC. The rather small percentage weight loss and varied values among polymers may be due to the type and densities of the marine microbes which had preferentially adhered to them in the seawater.

3.5. FTIR

Fig. 6a and b shows the changes in the ester and keto carbonyl indices of polyolefins as a function of time. These indices were highest for PP during monsoon season. In the case of polyolefins, variation in the indices and amount of total suspended solids seems to have a direct correlation. As discussed earlier, during monsoon season higher amounts of TSS was observed on all the polymers. Fig. 6c shows the changes in the double bond (vinyl) index as a function of time. Generally, the vinyl index is lower for LDPE when compared to HDPE and PP probably because of chain scission. In the case of polycarbonate, a decrease in the carbonate carbonyl index
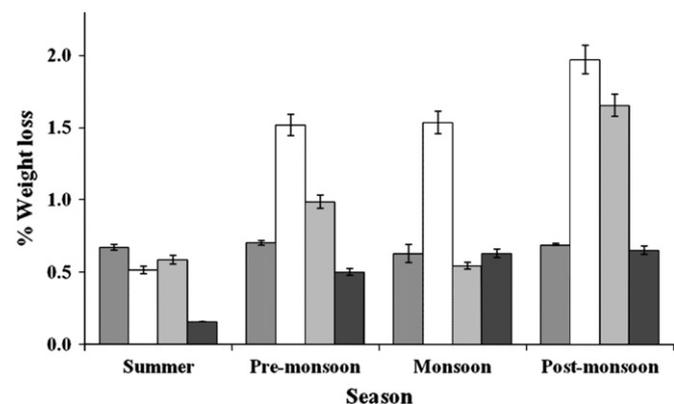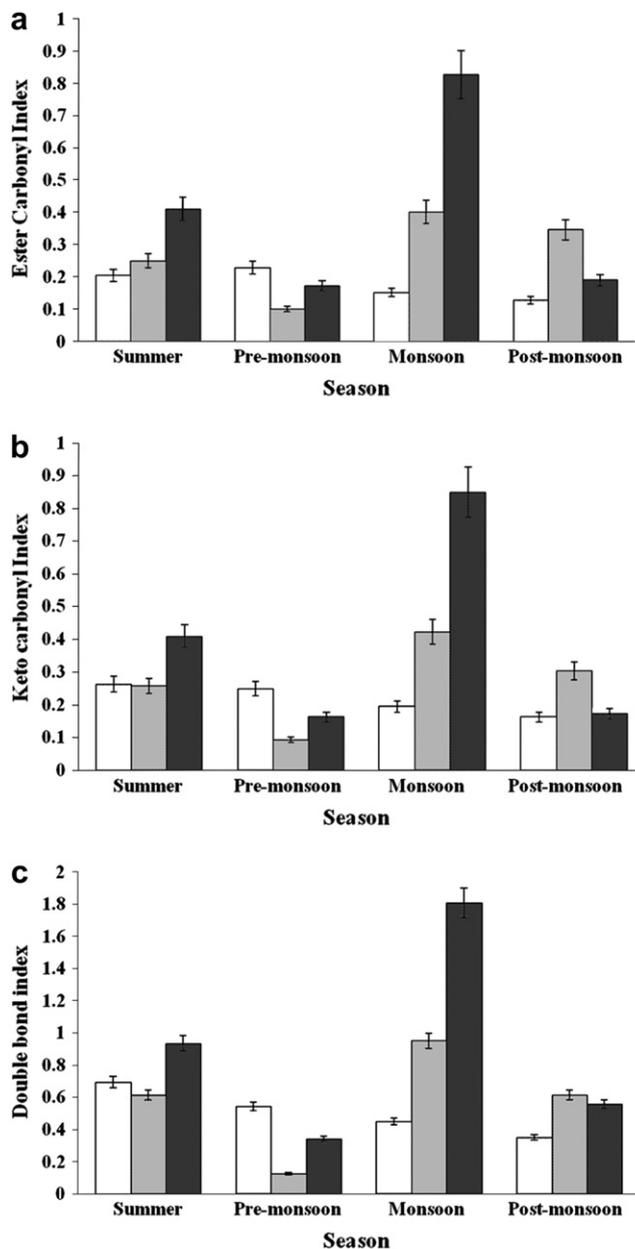

Fig. 6. FTIR indices for polyolefins as a function of different seasons (a) Ester carbonyl index (b) Keto carbonyl index (c) and Double bond index. (□ LDPE; ▨ HDPE; ■ PP).

was clearly observed during the 12 months period (Fig. 7), while there was a negligible change in the methyl index.

4. Discussion

Sea water parameters provide information on the biodegradation environment of which dissolved oxygen plays an important role in the amount of biofouling (Sudhakar et al., 2007). Lower DO levels can lead to higher chlorophyll formation (Pearsall and Mortimer, 1939; Parsons et al., 1984) which is an indication of the abundance of the autotrophs in the biofilm. Biofilm is also constituted of total suspended solids whose accumulation is in turn dependent on the season (Anderson, 1995). One possible reason for the observed variation in the biofilm solids among the months could be due to continuous fouling and dislodgment of biomass from the surface (Anderson, 1995; Aziz et al., 2001).
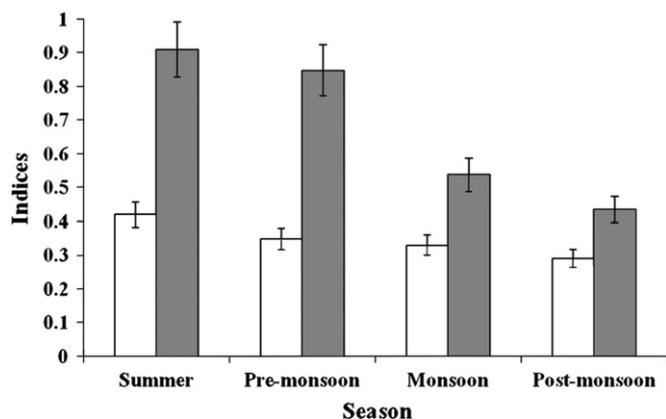

Fig. 5. Cumulative weight loss observed for various polymers during 12 months exposure to sea water. (▨ Polycarbonate; □ LDPE; ▨ HDPE; ■ PP).

Fig. 7. FTIR indices for □ methyl and ■ carbonate carbonyl index of polycarbonate.

Bacterial adhesion to surfaces in sea water is controlled to a large extent by physicochemical surface properties of the substrata and the bacteria, rather than by biological processes (Absolom et al., 1983). When these surfaces are exposed to the marine environment, they are rapidly covered by a conditioning film. This is the very first stage of biofilm formation (Bradshaw et al., 1997; Taylor et al., 1997) prior to the arrival of microfoulers and macrofoulers (Compère et al., 2001). It has been proposed that the original substratum surface properties such as roughness, surface energy and hydrophobicity shape the microfouling events through the intermediary of these conditioning films. These microfoulers in turn, based on the season (DeSouza et al., 2005), affect the incoming macrofoulers.

Kerr and Cowling (2003) suggested that surfaces with root mean square roughness of 5–25 nm will have a minimum fouling. The initial surface roughnesses of all the polymers used in the current study were in a range of 30–120 nm suggesting a higher fouling build up during the study. Moreover the surface roughness of the polymers over the period increased due to action of foulers.

Surface energy of polycarbonate has also increased during the study while there was a negligible change in polyolefins. The increase was attributed to the higher contribution by polar component of surface energy (Vernhet and Bellon-Fontaine, 1995). Schneider (1996) reported that conditioning films modify the surface energy of the substrate by creating a new interface whose physicochemical properties may be controlled by the substratum, by film or by the interaction of both. In addition, all the polymers used in the current study have higher surface energies than the proposed minimal bioadhesive range (20–30 mN m^{-1}) when exposed to sea water (Dexter, 1979). In the current study it was observed that hydrophobic surfaces favor fouling. Similar findings were reported earlier (Pringle and Fletcher, 1983). A negative correlation was observed between roughness and surface energy of polymers during the first three months. Similar findings were reported by others (Brewer, 1984).

A change in contact angle hysterisis, which is a measure of surface heterogeneity, gives an indication of departure of meta-stable state at solid–liquid–vapor interface from equilibrium (Schmidt et al., 2004). This is known to be effected by the thermodynamic and kinetic equilibrium of the testing liquid on the material surface and it is due to the reorientation of the polymer molecules when in contact with the liquid. Since the polymers used in the present study are rigid there was no trend observed in the CA hysterisis.

Biofilms on polymer surfaces not only change its surface characteristics but also can have disastrous effects leading to degradation (Cappitelli and Sorlini, 2008). It is reported that generally polymer biodegradation proceeds via surface attack by the bacteria (Mueller, 2006) present in the biofilm. In the present study, over the 12 months exposure of polymers to sea water, a considerable change in the various FTIR indices was observed among the polymers. The changes among different indices are due to biotic and abiotic factors of the sea (Sudhakar et al., 2007). Such changes imply that new functional groups are formed, which in turn, due to their polar nature, bring about a change in the surface energies of the polymers. It is well known that auto-oxidation due to abiotic factors leads to the formation of new functional groups such as esters and keto groups (oxidation of polyolefins). These functional groups reduce the hydrophobicity assisting the fouling process (Orr et al., 2004; Hadad et al., 2005). Prolonged stay in the ocean leads to a decrease in carbonyl index probably due to biodegradation (biotic) through Norrish type mechanism or through formation of ester. Norrish type II reaction leads to the formation of double bonds in the polymer chain (Albertsson et al., 1987; Albertsson and Karlsson, 1990). In case of polycarbonate a reduction in carbonate carbonyl index could be due to the hydrolysis of the carbonate bond due to long exposure to sea water (Artham et al., 2008).

The correlation studies corroborated with the available literature only during the first three months of analysis implying that biofouling is a more complex phenomenon than understood and should be dealt case-to-case basis. The current results suggest that surface properties alone do not determine the biofouling on these artificial surfaces. The whole process of fouling is like a feed-back mechanism where fouling alters the surface properties of the substrate and that in turn affects further fouling in a dynamic manner.

5. Conclusions

The exposure of polymers to seawater for the duration of one year invariably led to biodeterioration and biodegradation and change in their physicochemical properties.

A decrease in carbonyl index and presence of double bonds in the FTIR spectra clearly indicate biodegradation. In case of polyolefins hydrophobic nature of the surface favors fouling. Seasonal effects were seen on the amount of biofilm attached on the polymer surface. Among polyolefins, PP with lowest weight loss indicates that it is most stable. Year long studies spanning different seasons are required to establish the stability of polymers in sea water.

Apart from the biofilm characterization, physicochemical parameters such as surface energy, surface roughness and contact angle hysterisis which are evaluated in the present study help us to understand the stability of substrates in sea water.

Acknowledgements

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