International Biodeterioration & Biodegradation 65 (2011) 276–284

Contents lists available at ScienceDirect

International Biodeterioration & Biodegradation

journal homepage: www.elsevier.com/locate/ibiod

Fouling and stability of polymers and composites in marine environment

Thangavelu Muthukumar [a], Adithan Aravinthan [a], Karunamoorthy Lakshmi [a], Ramasamy Venkatesan [b], Loganathan Vedaprakash [b], Mukesh Doble [a,*]

[a] Department of Biotechnology, Indian Institute of Technology Madras, IIT Campus, Adayar, Chennai 600036, Tamil Nadu, India
[b] National Institute of Ocean Technology, Chennai 600100, India

ARTICLE INFO

Article history:
Received 31 July 2010
Received in revised form
22 November 2010
Accepted 22 November 2010
Available online 28 December 2010

Keywords:
Surface energy
Hardness
Biofouling
Total suspended solids
FTIR
AFM

ABSTRACT

Effect of biofouling on various polymers and composites such as, Polyurethane (PU), Silicone rubber (SR), Polyester (PET), Glass Fiber Reinforced Polymer (GFRP), Carbon fibre Reinforced Plastic (CFRP) and Syntactic foams (SF) deployed for a period of one year in marine waters at a depth of 1 m was studied. These materials find wide marine applications. SR with lowest surface energy was the least fouled. Maximum barnacle attachment was seen on hard surface (GFRP) and minimum on flexible surface (SR). Attachment of barnacles and polychaetes are positively correlated with surface energy. Fouling load is positively correlated with Surface energy and hardness. The surface energy, hardness and tensile strength reduced while surface roughness considerably increased during this period. Maximum gravimetric weight loss was seen in PET (7.49%) followed by PU (4.25%) and minimum in CFRP (0.45%). Maximum thermogravimetric weight loss was observed in PET (73.5% at 400 °C) followed by PU (71.1%) and least in SR (2.4%). Fourier Transform infrared spectrum revealed that carbonyl/oxidation indices decreased for PET, GFRP, CFRP, and SR indicating biotic degradation. The same index increased for PU indicating abiotic oxidation.

1. Introduction

The most serious problem faced by the marine industry is biofouling. All surfaces under aquatic environment gets fouled due to the attachment of marine flora and fauna. A complex community of microorganisms and macrofoulants including biomacromolecules are involved during this process. The initial step in this process is the formation of a biofilm which is made up of carbohydrate, proteins, exopolysachrides and microorganisms, etc. Due to this, the material experience a series of discrete physical, chemical and biological changes (Baier, 1984; Geesey and White, 1990; Ford et al., 1991; Gu, 2003). The macrofoulants include barnacles, hydroides, algae bryozoans, mussels, and polychaetes, which attach later on this biofilm or conditioning film. This film alters the surface characteristics of the base material (Sudhakar et al., 2007).

Polymers and composites are commonly used in marine applications. Varieties of materials with different surfaces are developed in an attempt to reduce biofouling and bioadhesion, but still there is a dire need to find a perfect antifouling surface. Baier et al. (1983) reported that the surface energy of a material significantly influences the bacterial adhesion process. In previous studies from our lab we have observed that surface energy and season play a role in the biofouling of synthetic polymers deployed in tropical marine sea water (Sudhakar et al., 2007; Artham et al., 2008; Artham and Doble, 2009).

Polyurethanes (PU) are a remarkable class of polymers which exhibit a wide range of mechanical properties, and physical behaviour (Hepburn, 1992). These materials find increasing applications at sea. In the fishing industry selectivity grids, oceanographic appliances including fenders and tubing on underwater vehicles and underwater antenna protection gears are fabricated with PU (Loaec et al., 2006).

Fiber reinforced composite materials have been the alternatives for metal, steel and wood in many applications because of their low cost to weight savings, improved life cycle, high specific tensile and compressive strength, good fatigue and corrosion resistant (Couchman and Mouritz, 2006). Glass Fiber Reinforced Polymer (GFRP) are predominantly used as a light weight material in a wide variety of marine applications including parts in ship, boat, patrol boats, underwater sea pipes and fishing trawlers. Broad scale usage of GFRP is seriously hindered by the lack of experimental data and, understanding of its durability aspects in the marine environment (Apicella et al., 1983; Smith, 1990). Carbon fibre Reinforced Polymer (CFRP) is also used because of its delamination resistant properties. Syntactic foams (SF) because of their buoyancy property are used in

* Corresponding author. Tel.: +91 44 2257 4107; fax: +91 44 22574102.
E-mail address: mukeshd@iitm.ac.in (M. Doble).

0964-8305/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ibiod.2010.11.012

boat hulls, deep-sea exploration, and autonomous underwater vehicles.

Polyester resins (PET) are widely used in marine applications, mostly with glass fibers, in reinforced composite structures. They have been used as organic spray coatings to prevent corrosion of steel in marine waters (Singh et al., 2007). They are cheap, have good physical strength, excellent handling characteristics, and high heat resistance and have versatile use. Their curing process and mechanical properties can be changed by modifying the monomer in the polyester chain (Visco et al., 2008).

The present study investigates the role of surface characteristics of these polymers and composites on the formation of biofilm and biofouling, and the subsequent changes they undergo when they are immersed in marine water for 12 months. Biodegradation/biodeterioration of wide range of synthetic polymers (polyolefin, polycarbonate) in field and in lab has been reported (Sudhakar et al., 2007; Artham et al., 2008; Artham and Doble, 2009; Muthukumar et al., 2010). These studies could help in identifying the properties of the surface which affect fouling and hence in the long run help in designing antifouling surfaces. The current study will also help in ascertaining their stability in such field conditions.

2. Materials and methods

The materials used in this study namely, Polyester [Isopthalic Polyester Resin (PET)], Glass Fiber Reinforced Polymer [Glass Fiber – Chopped Strand Mat (CSM 450); Resin – Isopthalic Polyester Resin (GFRP)], Carbon fibre Reinforced Plastic [Carbon fibre – T 300; Matrix – Epoxy resin LY 556; Hardner – HY 951 (CFRP)], Syntactic foam [Matrix – Araldite GY 257; Hardner – Arudur HY 951; Filler – Glass Spheres (SF)], except for Polyurethane [Polyether based Polyurethane (PU)] and Silicone rubber [Polysiloxane Polymer (SR)], are commercially available and are purchased from Industrial Insulations Ltd., Chennai-600001, India. They are mainly used in marine applications. Syntactic foam was obtained from NIOT, Chennai. They were cut into uniform size (100 × 75 mm). All materials except for SF were of 0.3 cm thick, while the latter was 1.4 cm thick. The coupons were cleaned with 70% v/v ethanol and dried in a hot air oven at 50 °C for 24 h. They were left at room temperature and weighed with Sartorius Precision balance (Germany).

Dumbbell shaped tensile coupons of dimensions 215 × 12 × 3 mm (as per ASTM D256) were prepared and were also subjected to the same studies. All the samples were deployed in the surface waters (at a depth of 1 m) of Bay of Bengal at Ennore Port Limited Chennai, India at a Latitude of 13°15′48″ N and a Longitude of 80° 20′28″ E. The coupons were tied vertically in a polypropylene frame. Each frame consisted of all the six materials in triplicate. The frames were tied to a floating raft made of High Density Polyethylene. This study was conducted from July 2008 to July 2009. Each frame was retrieved once every two months for analysis. The samples were photographed using a Digital Still Camera (Sony, model No: DSC-H2) immediately after removal from the frames. Similar samples were prepared and were also left undisturbed in the laboratory which acted as controls.

2.1. Seawater parameters

During the sampling period, temperature, salinity and dissolved oxygen of the sea water were measured using a pre-calibrated water quality monitoring system (Hydrolab, Quanta Instruments, USA).

2.2. Analysis

The biological and physical characterization of the biofilm formed on the material surfaces, namely fouling load, total suspended solids, carbohydrate, protein, chlorophyll a, ATP (Adenosine triphosphate) and total viable count were measured once every two months. It is well documented that these parameters constitute the biofilm. The change in the physiochemical properties of the materials were analysed using a Thermogravimetric (TG) and differential thermal analyser (TGA), Fourier transform infra red spectroscopy (FTIR) and Atomic force microscopy (AFM). The tensile strength, surface energy, and weight loss of the samples were also analysed. All analysis was performed in triplicates.

2.3. Biofilm characterization

The polymer coupons were retrieved from the field and carried to the laboratory in a sampling jar containing 500 ml of 0.2 μm (Millipore) filtered and autoclaved sea water. Total fouling load of the sample was calculated by measuring the wet weight of the polymer without cleaning along with the biofilm, micro and macrofoulants. Then the solids deposited on the test coupons were scraped with the sea water using a sterile nylon brush (Bhosle et al., 1989) and stored at −20 °C. The macrofoulants settled on the surface of the polymers were removed using 10% hydrochloric acid and then the coupons were dried in a hot air oven at 40 °C for 4 h (Artham et al., 2009).

The total suspended solid (TSS) in the biofilm was estimated from the sample based on the method reported by Parsons et al. (1984). A sample of 10 ml was filtered through a pre-weighed GF/C filter (47 mm, 0.22 μm), dried at 100 °C for 1 h and reweighed to get the dry weight of the residual biomass. The amount of chlorophyll a pigment in the sample represents the quantity of alga and photosynthetic bacterial growth. 10 ml of the scraped biofilm suspension was filtered through a pre-weighed GF/C filter paper (47 mm, 0.22 μm). The filtrates with the filter paper were placed in a screw capped centrifuge tube containing 10 ml of 90% acetone for extracting the chlorophyll a (Holm-Hansen et al., 1977; Bhosle, 2005). The samples were incubated for 12 h at 4 °C in the dark after which the absorbance at 630, 645, 665 and 700 nm were measured using a UV spectrophotometer (Perkin Elmer, Lambda 35, USA).

For the estimation of ATP (indication of the activity of live bacterial cells), the filtrate was taken in 3 ml of 0.02 M Tris (pH 7.5) buffer and boiled for 10 min, to allow for complete extraction of ATP. It is stored at −20 °C until the analysis was carried out as per the method suggested by Hamilton and Holm-Hansen (1967). The amount of ATP was determined based on the firefly bioluminescence reaction (Hamilton and Holm-Hansen, 1967) with a luminometer (Berthold Detection Systems (GmbH) Sirius Luminometer D-75173, Germany). The concentration of ATP was determined from the RLU (Relative Light Units) values with reference to the ATP standard.

Total Viable Count (TVC) was estimated from the scraped biofilm by transferring 100 μl of media into a 1 ml micro-centrifuge tube and was serially diluted. Around 20 μl of the sample was plated on the surface of Zobell marine agar (ZMA) and pseudomonas agar (PS) (Himedia Laboratories Pvt. Ltd Mumbai, India) solid media in sterile petridish and incubated at 37 °C for 24 h (Buck and Cleverdon, 1960; Moat and Foster, 1995). Viable colony counts were obtained by appropriately diluting the samples and visually counting them by using digital colony counter (Scigenics (India) Pvt Ltd, Chennai, India).

The total carbohydrate and protein contents in the biofilm were estimated using phenol–sulphuric acid method using glucose as the standard and Lowry's methods using crystalline bovine serum albumin as the standard respectively (Lowry et al., 1951; Dubois et al., 1956).