Progress in Organic Coatings 64 (2009) 89–97

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Characterization of chemically active antifouling paints using electrochemical impedance spectrometry and erosion tests

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ARTICLE INFO

Article history:
Received 19 February 2008
Accepted 15 July 2008

Keywords:
Permeability
Water sorption
Erosion rate
EIS
Antifouling coatings

ABSTRACT

The water sorption and solubility parameters of chemically active paints were studied by electrochemical impedance spectrometry (EIS) measurements. Erodible acrylic-based coatings containing biocidal tertiary amines were investigated. Results from EIS measurements show that both the water sorption at saturation and the apparent water diffusion coefficient decrease as the alkyl chain length of the biocidal amines increases from 8 to 16 carbon atoms. The increase of the hydrophobic character of the resulting coatings results to a higher resistance to erosion. Erosion tests performed under static and dynamic conditions show that the seawater conditions can markedly affect the performance of chemically active paints.

1. Introduction

Protection against external effects is the most important role played by organic coatings and polymer films. For their barrier function against marine organisms, antifouling coatings are widely used for underwater dynamic structures, such as ships' hulls and static structures like buoys or pontoons. The most successful antifouling paints for several years were triorganotin-based self-polishing antifouling paints. Their efficiency is based on a controlled erosion of the coating attributed to a well-known hydrolysis reaction which occurs in contact with seawater [1,2]. In this case, binders are subjected to alkaline hydrolysis in seawater yielding to a remaining acid-functional polymer, which becomes seawater-soluble and gradually sweeps from the surface of the coating. This chemical reaction, and the water diffusion and solubility determine the leaching rate of tri-butyltin-resulted products and co-biocides, and therefore the antifouling efficiency of the organic coating.

Based on environmental concerns, these tin-based products have been banned and alternative paints have been developed. Different technologies of coatings are reported in the literature coming from research laboratories [3–5] or paint companies [6–8]. In our laboratory, research works are focused on the development and the characterization of erodible (meth)acrylic binders bearing silylated [9,10], titanate [11,12] and ammonium salt moieties [13]. The mechanism of action retained for these resins is mainly based on a chemically controlled erosion of the resulting coating according to Scheme 1.

As the barrier properties towards water are very important because the presence of an aqueous solution in the antifouling paint can activate the dissolution of pigments and the hydrolysis of the binders, water sorption and permeability of liquid water and permeants through protective layers and films is one of the main criteria for assessing the protective effect of antifouling coatings. The water uptake of chemically active paints was reported to be affected by the amount of hydrophilic or hydrolyzable pendant groups onto the polymer backbone [14–16], and by the paint formulation [17]. Experimental techniques such as gravimetric or coulometric measurements are often used in the literature to assess the water uptake of antifouling coatings [16,18]. Electrochemical impedance spectrometry (EIS) measurements are also described as a powerful technique to assess the volume fraction of water in organic coatings immersed in seawater. As few capacitance studies were investigated on chemically active antifouling paints [19], EIS measurements are used here for the screening of pure resins for chemically active paints. The aim of this study is to assess the water uptake characteristics of a range of poly(methacrylic) binders containing tertiary amines as biocides [20], and study the effect of their hydrophobic character on the best performing binder, in terms of both apparent water permeability and erosion properties.

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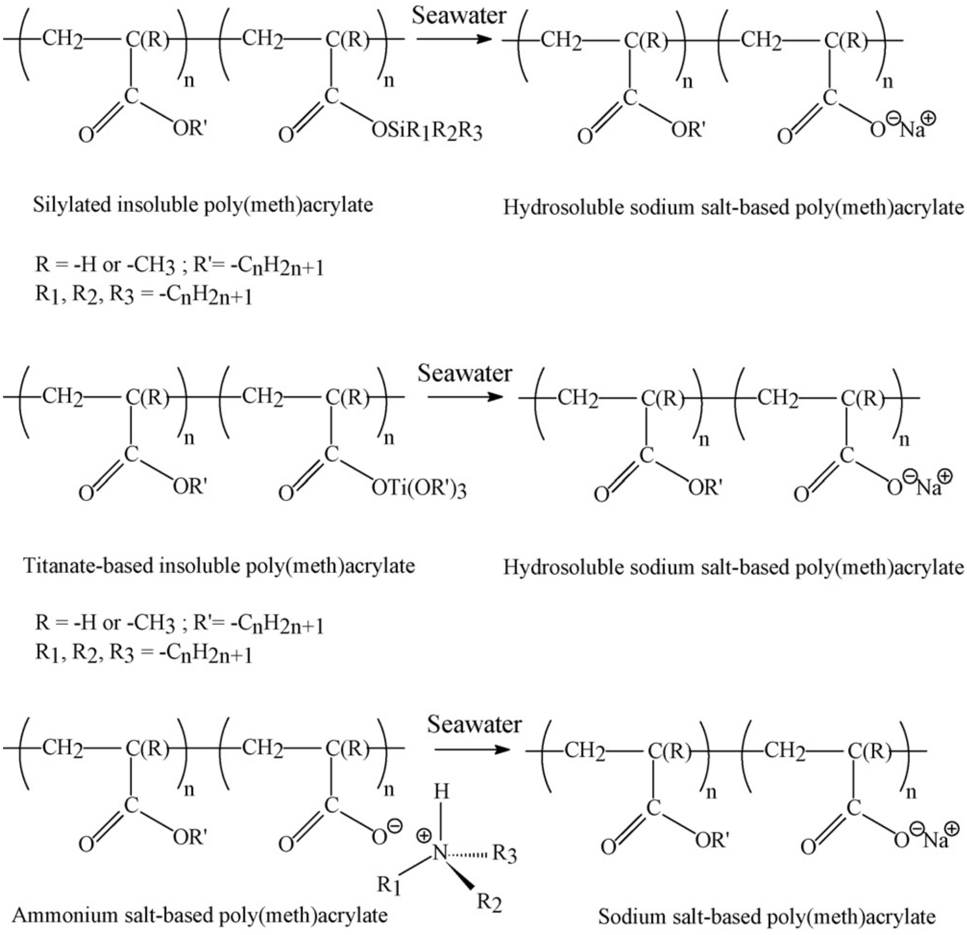
doi:10.1016/j.porgcoat.2008.07.014



Scheme 1. Controlled release mechanism of poly(methacrylic) binders based on an alkaline hydrolysis reaction of ester linkages (a) or on an ionic exchange reaction with ions from seawater (b).

2. Experimental

2.1. Materials

Mixtures of a commercial powdered acrylic resin Elvacite® 2669 (RE1, Lucite International) with dimethyloctylamine, dimethyldodecylamine and dimethylhexadecylamine (Aldrich) were prepared in 1-methoxy-2-propanol (MP). The resin is a terpolymer containing methyl methacrylate monomer units with an acid number of 124 mg KOH/g and with a glass transition temperature of 90 °C. All reagents were used as received. Reaction mixtures were placed into Teflon® moulds to give free films by complete removal of the solvent, designated as FE1CXN/r, where FE1 is used for films obtained directly from the reaction mixture with RE1, CXN the type of the dimethylalkylamine with X the number of carbon atoms within the alkyl chain, and *r* the amine to carboxylic acid group molar ratio. As the reaction between the acrylic resin and the tertiary amines was previously demonstrated to be not quantitative, the resulting films are composed of polymer chains bearing both carboxylic acid and ammonium salt groups and of non-bonded tertiary amine (Table 1) [13].

A tri-butyltin based copolymer containing 68% of methyl methacrylate and 32% of tributyltin methacrylate monomer units was used as reference. Its weight-average molecular weight is 80,000 g mol^{-1} with a glass transition temperature value of 80 °C. Xylene (from Aldrich) is used to dissolve this TBT-reference (REF).

A commercial powdered acrylic resins Elvacite® 2550 (RE2, Lucite International) was used as a retardant resin. This resin is a terpolymer containing butyl methacrylate monomer units with an acid number of 17 mg KOH/g and a glass transition temperature of 50 °C.

Rutile titanium dioxide supplied by Kronos was used as pigments. Zinc pyrithione ZnPy (Progiven) and Seanine® 211 SN (Rohm and Haas) were used as booster biocides in addition to the tertiary

Table 1
Molar proportions of blocked acid groups and weight compositions of coatings obtained from mixtures of tertiary amines and Elvacite® 2669 resin

Sample	% mol. of blocked acid groups	% wt. of resin	% wt. of complexed amine	% wt. of free amine
FE1	0	100	0	0
FE1C8N/1	42	74	11	15
FE1C8N/2	42	59	9	32
FE1C12N/1	41	68	13	19
FE1C12N/2	41	51	10	39
FE1C16N/1	36	63	13	24
FE1C16N/2	36	46	10	44