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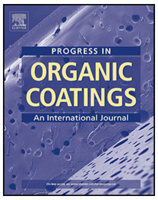

Corrosion resistance and lifetime of polyimide-*b*-polyurea novel copolymer coatings

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ABSTRACT

A novel class of polyurea-*b*-polyimide (PUI) block copolymer coating containing environmentally friendly aromatic polyurea has been successfully synthesized for corrosion protection of aluminum alloy 2024-T3 (Al 2024-T3). The PUI copolymer is able to self-assemble into a supramacromolecule by means of intra and inter-hydrogen bonds (H-bonds). The formation of H-bonds and effect of the later on the crystallinity of the copolymer was studied by using Fourier transform infrared spectroscopy (FTIR) and wide angle X-ray diffraction (WAXD). It was shown that increasing polyurea mole fraction up to 50 mol%, enhanced occurrence of H-bonding induced self-assembly, and resulted in remarkable enhancement in the degree of crystallinity, and corrosion resistance. Corrosion resistance and diffusivity of the copolymer coatings were investigated by electrochemical impedance spectroscopy (EIS), in a 3.5 wt% NaCl solution. The coating lifetime determined by using time-based corrosion resistance, was shown to be about 8 years for the optimized PUI copolymer coating. PUI coating synthesized by using 50 mol% of polyurea has a high contact angle (110°) and remarkably low surface energy of about 25.5 mJ/m^2.

1. Introduction

Corrosion, a very destructive chemical and electrochemical process, is one of the biggest problems encountered in the aerospace, marine and automobile industry and cost the United States an approximated $300 billion annually [1]. Aluminum alloy, Al 2024-T3 is widely used in aerospace due to its high specific strength and light weight [2]. However, it is very sensitive to localized corrosion, due to its heterogeneous microstructure, which leads to a localized galvanic corrosion [3,4]. One way to prevent corrosion in metals is application of polymeric barrier coatings, which insulates the metal from the environment, by preventing attack from electrons and ions. Corrosion occurs when such protective coatings are compromised and electrolyte diffuses through the cracked metal oxide layer. The most effective under-coatings in use today for corrosion protection of Al 2024-T3 are based on chromium containing compounds, which must be replaced because of undesirable environmental and health issues.

Organic polymers such as polyurethane [5], polyaniline [6], polypyrrole and polyimide [7] have emerged as viable candidates for replacement of chromium-containing coatings. Polyimide, a heterocyclic polymer containing imide functional group on the backbone [8], is one of the most valuable high performance polymers because of its outstanding mechanical properties, thermal stability, and high glass-transition temperature (T_g) [9–11]. The presence of a rigid heterocyclic imide functional group and the interaction between the electron rich nitrogen atom and the electron deficient carbonyl group in the polyimide backbone, lead to strong cohesive energy density and high thermomechanical properties [12–14]. However, it is has been shown that polyimide coating is susceptible to moisture absorption, poor adhesion and interfacial failure and moderate lifetime [15]. In order to prepare corrosion resistant polyimide coatings for protection of metals, the drawbacks inherent in polyimide must be overcome. Recently, many approaches have used to enhance the anti-corrosion properties of polyimides. Yu et al. [7] and Jena et al. [16] reported significant improvement in corrosion performance, adhesive strength, as well as thermomechanical properties of polyimide by reinforcement with montmorillonite clay.

In this paper, we report a remarkable improvement in hydrophobicity and surface energy of polyimide coatings by copolymerization of polyimide with rigid poly(4,4′-oxydiphenylene-methylenebisphenylurea). Polyurea was shown by Beemat et al. to enhance anti-corrosion property of epoxy ester-siloxane hybrid coatings [17,18]. The polyurea-*b*-polyimide (PUI) block copolymer synthesized in this study is environmentally friendly and high temperature resistant copolymer. It was prepared by using environmentally friendly 4,4′-oxydianiline and N-methyl-2-pyrrolidinene (low volatile organic compound). It was reported in our pervious paper [19], that the presence of hydrogen-bond donor and hydrogen-bond acceptor atoms in polyimide and polyurea can lead to hydrogen bonding induced

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self-assembly, thereby resulting in ultra-low dielectric constant and dense morphology. This characteristic makes PUI copolymer a good candidate for protection of metals against corrosion. In order to fully explore the corrosion performance of PUI copolymer coatings and fill the gap in the existing knowledge base, PUI copolymers were synthesized and applied onto Al 2024-T3 substrate by solution casting method and tested in a 3.5 wt% NaCl solution. The corrosion resistance of the coated substrate was determined by using electrochemical impedance spectroscopy (EIS).

2. Experimentation

2.1. Materials

Pyromellitic anhydride (PMDA), 4,4′-oxydianiline (ODA), 4,4′-methylenebis(phenyl isocyanate) (MDI), N-methyl-2-pyrrolidinene (NMP) and diiodomethane (99%, contains copper as stabilizer) were purchased from the Sigma–Aldrich Co. (USA). Distilled water was purchased from TEDIA Co. (USA). The substrate used in this study is Al-2024-T3 Q-panels purchased from Q-Labs, Cleveland, OH (USA).

2.2. Synthesis and sample preparation

Anhydride terminated poly(4,4′-oxydiphenylene-pyromellitamic acid), PAA solution was synthesized via condensation polymerization. 15.4824 g of 4,4′-oxydianiline, ODA (0.075 mol) was added into 300 ml of N-methyl-2-pyrrolidinene, NMP with mechanical stirring under nitrogen atmosphere at room temperature. After 30 min of stirring, ODA was completely dissolved in NMP. 17.0334 g of pyromellitic anhydride, PMDA (0.07575 mol) was then added into the solution and cooled into 10 °C by circulating coolant from a refrigerated cooling system. After 2 h of reaction, anhydride terminated PAA solution was obtained. Isocyanate terminated poly(4,4′-oxydiphenylene-methylenebisphenylurea) (PU) solution was also prepared by step-wise polymerization. 25.5495 g of 4,4′-methylenebis(phenyl isocyanate), MDI was added into a 300 ml NMP solution containing 20.6535 g ODA under a nitrogen atmosphere with stirring, and then the mixtures were stirred for 12 h. 48 ml, 96 ml and 192 ml isocyanate terminated PU solutions were added into 128 ml anhydride terminated PAA solution, respectively, to obtain PUI33-EX, PUI50-EX and PUI67-EX copolymers. After 0.5 h of stirring, 0.01 g of ODA was added into mixture solution for further 3 h stirring, followed by thermal curing.

Both PUI copolymer thin films and coatings were obtained by solution casting onto an ethanol cleaned glass plate and 1 in. × 3 in. × 1/8 in. Al 2024-T3 coupons, followed by thermal curing. The step-wise thermal curing scheme used in this study involves heating at 75 °C for 1.5 h, followed by heating at 100 °C for 0.5 h. The curing temperature was then raised and held at 120 °C for 2 h after which it is finally raised and maintained at 150 °C for 5 h. The thickness of cured coatings was maintained within 33 ± 1 μm: 33, 34, 32 and 33 μm for PI, PUI33, PUI50 and PUI67, respectively. By means of a blade, freestanding composite films were obtained by peeling off from the glass plate after thermal curing. PUI copolymer thin films and coatings (on Al 2024-T3 substrates) were obtained after thermal curing.

2.3. Characterization

Nicolet 6700 FT-IR instrument equipped with a Smart Orbit ATR accessory with diamond crystal was used to determine the chemical composition of the samples. ATR was performed over a wavenumber range between 4000 cm^{-1} and 400 cm^{-1}. Wide angle X-ray diffraction (WAXD) was used to study the crystallization and structure of the samples. X-ray diffraction tests were carried out by using a Cu-Kα radiation source at a wavelength of 1.54 Å. WAXD tests were carried out from a diffraction angle, 2-theta, of 5–30°. The cross-sectional morphology of the films was studied by using the Environmental Scanning Electron Microscopy, model FEI XL30 FEG ESEM. ESEM samples were prepared by immersion in liquid nitrogen and then fractured using a pair of tweezers to expose the cross-sectional area. A Polaron SC7640 sputter coater was used to coat the samples with Silver in order to improve their conductivity. Gamry Instrument "Reference 3000" potentiostat, equipped with Gamry framework and Echem Analyst, was used in electrochemical impedance spectroscopy. A cylindrical glass cell with a rubber O-ring of inner area 2.8 cm^2, attached to the grooved bottom of the cylindrical cells and a clamp fixture was used to hold the samples. A saturated calomel electrode (SCE) and a graphite electrode were used as reference and auxiliary electrode, respectively. To simulate sea water conditions, 3.5 wt% NaCl solution was used as the electrolyte and corrosive environment. The potential was applied in a range of ±10 mV from open circuit potential and the frequency was varied from 10^6 to 10^{-2} Hz. The resulting coating resistance, R_c was obtained by using Randles cell model, from "Gamry Echem Analyst" software. The total test period for EIS measurement was 30 weeks, however, the testing was terminated before 30-week test period when the data deviated from the Randles cell model. In order to study the coating performance with respect to exposure time, the bare and coated Al substrate was immersed in a weekly replaced 3.5 wt% NaCl solution. Contact angle measurements were carried out by using a VCA 2000 contact angle analyzer purchased from Advanced Surface Technology, Inc., Billerica, MA. For FTIR, WAXD, EIS and contact angle measurements, three replicate specimens were rested.

3. Results

3.1. Structure studies

3.1.1. FTIR

The FTIR spectra of neat PI, PUI33, PUI50, PUI67 and neat PU are shown in Fig. 1(a). For neat PI, the characteristic asymmetric and symmetric carbonyl stretching of imide ring are observed at 1775.6 (peak a) and 1716 (peak b), respectively. The characteristic absorption peaks of polyurea are carbonyl stretching and secondary amine bending of urea at 1641.2 (peak c) and 1545.6 cm^{-1} (peak d). Increasing polyurea concentration increases the intensity of urea characteristic absorption peaks (peak c and d) and decreases imide characteristic absorption peaks (peak a and b). The red-shift (toward lower wavenumber) in C=O stretching absorption peak of urea (peak c) increases by increasing polyurea mole fraction, and is associated with the blue-shift (toward to high wavenumber) of N—H bending absorption peak (peak d). Luo [20,21], Coleman [22] and Mishra [23] et al. distinguished between free urea C=O and H-bonded urea C=O by using FTIR. In H-bonded urea C=O, disordered H-bonded urea C=O (1660 cm^{-1}) was distinguished from ordered urea C=O (1640 cm^{-1}) by a shift in absorbance to a higher wavenumber. Thus, the red-shift of urea C=O stretching (peak c) and blue-shift of N—H bending (peak d) of urea indicate the occurrence of urea hydrogen bonding and enhanced chain interaction between polyurea blocks. Since the formation of H-bonding between electron-negative carbonyl group C=O and electron-positive hydrogen atom N—H averaged the electron density, the vibration frequency of hydrogen bonding acceptors decreased while the vibration frequency of hydrogen bonding donor increased.