Effect of polymerized ionic liquid based gel inhibitor on electrochemical performance of self-assembled nanophase coating

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ABSTRACT

The corrosion process is a surface reaction that can be controlled by the addition of corrosion inhibitors, which adsorb on the reacting metal surface. The inhibitors could be applied to a metal surface in many different ways. In this contribution, influence of polymerized ionic liquid (PIL) was examined on inhibition performance of a coating using carbon steel samples. The PIL was loaded in self-assembled nanophase particle (SNAP) coating and the inhibition behaviour was investigated using potentiodynamic polarization, electrochemical impedance spectroscopy and scanning kelvin probe techniques. The inhibition efficiency of the coating increases with the addition of PIL as observed from potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. In addition, scanning kelvin probe (SKP) measurement provides further understanding on the strong interfacial properties of the modified coating compared to that of the SNAP.

1. Introduction

The use of corrosion inhibitors is one of the most effective ways of protecting metal surfaces against corrosion. Their effectiveness is related to the chemical composition, their molecular structures and affinities for adsorption on the metal surface. The organic compounds containing heteroatoms like N, O and S play an important role in inhibition due to the free electron pairs they possess. Also, the electronegative functional groups and π-electrons in conjugated double or triple bonds generally exhibit good inhibitive properties by supplying electrons via π orbitals. When both these features are combined in a single compound, increased inhibition can be observed. Ionic liquids (ILs) are compounds that can possess such combined features in their structure. ILs are known to provide inhibition effect for various metals and alloys forming adsorbed flexible film at interfaces and reducing both interfacial tension and the wetting of aggressive media on the steel surfaces. While significant work has been done with direct delivery of IL from solution, however, the use of such IL inhibitors in polymeric form has the potential to offer a sustainable approach with significant opportunity for effective long term protection of metal. Many ILs and PILs are based on heterocycles containing heteroatoms such as sulphur, phosphorus and nitrogen, which make them highly suitable as corrosion inhibitors to reduce or arrest corrosion [1–4]. PILs possess a large number of functional groups, leading to effective interfacial interaction through complexation with metal or by physical or chemisorption [5].

The performance of such polymeric inhibitors depends on their chemical structure and physico-chemical properties, which are based on factors such as their functional group, the electron density of the donor atom, and also the electronic structure of their heterocycle or aromatic components, which serve as the major active component for any interaction or adsorption with the metal surface. ILs and PILs possess such characteristics which are desirable for a corrosion inhibitor, and therefore offer new opportunities in the field of corrosion inhibition and metal protection due to their structural diversity.

Most commonly used IL is the one with a polymerizable unit on the cation and the key approach to prepare PILs is free radical polymerization of IL monomers, which can be divided to two subclasses: homopolymerization and copolymerization [6–9]. Recently, several novel PIL structures with different properties for different applications have been investigated. Major efforts toward developing novel PILs are focused on using vinylimidazolium based PILs with diverse functional substitutes [10,11]. However, there is very little information available in the literature on imidazolium based PILs for corrosion inhibition application. Thus, imidazolium based ILs and corresponding PILs form the basis of this research work. Several approaches can be used to incorporate the ILs and PILs into the coating, such as electrodeposition, conversion plating solution and dip/spray coating to mitigate material corrosion [12,13]. However, some of these methods may cause damage to the metal substrates themselves depending on the method of application [14]. Therefore, it is crucial to explore new strategies for

incorporating PIL inhibitors into coatings to minimise such risks and also to improve the ease of processing while maximising their anticorrosion potential. In our previous work we reported the potential use of the PIL in the form of nanoparticles as a corrosion inhibitor in an interfacial coating layer [15].

In this work we present the use of unique click chemistry derived polymerisable ionic liquid based gel inhibitors in hybrid film. Thiolene based click chemistry is a powerful platform to combine the sulphur in thiol with the imidazole and nitrogen containing polymerisable IL monomer. PILs were fabricated in gel form using thiol-ene click chemistry [16,17]. A fundamental understanding of structure-property relationship of these PIL gel inhibitor based coatings has been developed using advanced characterization tools, and also their performances as corrosion inhibitors have been evaluated using sol-gel coating. Among the existing coatings, inorganic sol-gel coatings based on self-assembled nanophase particles (SNAP) have been widely used in combination with other functional additives for the protection of aluminium alloys [18,19]. Such inorganic coatings show great potential especially when used as the interfacial layer due to their ability to chemically bond to the metal surface; however, to date there has been little study on the application of SNAP coating for metals that corrode more easily, such as carbon steel. In this regard, this work will focus on the addition of PIL gel particles as inhibitors to improve the corrosion resistance of such SNAP coating on steel surfaces. Unlike aluminium with its native oxide layer, mild carbon steel is more susceptible to corrosion and thus corrosion inhibitors may play a large role in the lifetime of such materials. This study aims to investigate the corrosion inhibition performance of PIL gel particles loaded SNAP coating using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements performed in a 3.5% NaCl solution (to simulate marine environments). Furthermore, scanning kelvin probe (SKP) was also used as a complementary technique to understand the stability and protection properties of the corrosion inhibitors.

2. Experimental

2.1. Materials

3-Glycidoxypropyltrimethoxysilane (GPTMS), (3-mercaptopropyl) trimethoxysilane (MPTS), 3-aminopropyltriethoxysilane, tetraethylorthosilicate (TEOS), acetic acid were all obtained from Sigma-Aldrich and used without further purification. Fluorosurfactant FC-4432 was obtained from 3 M. Double distilled water (DDW) was used for all experiments. PIL based gels were prepared according to the method described in our previous work [16]. Briefly, in a typical synthesis method, a 1:2 mol ratio of pentaerythritol tetrakis(3-mercaptopropionate) (PETKMP) (0.5 mmol, 0.24 g) and DVIMBr (1 mmol, 0.4 g) were dissolved in the minimum volume of methanol (0.2 ml) and small amount of BP (18.2 mg, 5 wt% with respect to monomer concentration). The reaction mixture was stirred for approximately 30 min in 4 ml vial while protecting from light and then ultrasonicated in the ice bath for 10 min with amplitude of 50%. The solution was then degassed in the degassing vacuum chamber while stirring for 1 h. Photopolymerisation was initiated using an UV lamp in a dark hood. The gel beads were disposed drop by drop on a glass slide using a flat end needle (17 gauge, 1.07 mm inner diameter) syringe and beads were formed by exposure to UV light (365 nm wavelength). Transparent gel particles with in average size of 5 mm formed within 5 min. The beads were washed with water and methanol to remove any unreacted monomer; afterwards, they were dried under a high vacuum.

2.2. Preparation of SNAP, SNAP loaded PIL gel inhibitor (SNAP/PIL)

SNAP coating has been used as a matrix to incorporate PIL gel particle as inhibitor. The SNAP solution was prepared with drop-wise addition of 42 ml (0.19 mol) 3-glycidoxypropyltrimethoxysilane

(GPTMS) and 13.4 ml (0.06 mol) tetraethylorthosilicate (TEOS) to 64.8 ml solution of 0.05 M acetic acid in doubly distilled water (DDW) in inert atmosphere. The solution was continuously stirred for 1 h during addition. The TEOS: GPTMS molar ratio used was (1:3 mol ratio) respectively. Hydrolysis and condensation of silanes were conducted at high water/silane ratio of 15. After all the silanes had been added and hydrolysed, the solution was aged in closed container for 3 days under continued stirring at ambient temperature.

PIL gel loaded SNAP coating was prepared with the following method; the coating solutions with total volume of 20 ml were prepared by diluting 7 ml SNAP solution with DDW by a factor of 1.75 with considering the amount of DDW. Then 20 mg (0.2 wt%) finely ground gel particles in micron size (1 μ) were added to the SNAP solution followed by addition of surfactant (3 M FC-4432, 0.04 wt/v%). The mixtures were ultrasonicated at 50% rpm for 5 min to obtain homogenous solutions. At the end (3-amino propyl)triethoxysilane crosslinking agent was added into the solutions and the final mixture was vigorously stirred and applied to cleaned metal substrates by following experimental procedures.

SNAP, PIL gel particle loaded SNAP coatings were applied on steel substrates via the following procedure: The mild steel (Mild Steel CA3SN-G, 0.08% carbon contents, thickness ~ 0.6 mm of 1.7 cm × 1.7 cm) substrates were sequentially polished using abrasive papers with grit numbers 800, 1000 and 1200 prior to cleaning by sequential immersion for 10 min each in acetone, hexane and ethanol solutions to remove surface oils. The substrates were rinsed with distilled water and dried with N_2 purge between each solvent wash and after the final solvent wash. Finally, the dried substrates were treated with alkaline cleaner (0.4 wt% NaOH, pH 13) and rinsed with distilled water and dried. The SNAP coating solutions were prepared by diluting the aged SNAP solution with water by a factor of 1.75 and subsequent addition of crosslinking agent (aminosilane) and surfactant (3 M FC-4432, 0.04 wt/v%). The final mixture was vigorously stirred and applied to cleaned metal substrates by dip coating at a withdrawal speed of 10 cm/min. The coating was made within a time frame of 10–30 min, counting from point of addition of the crosslinking agent. The coated sample was dried at room temperature for 24 h to allow solvent evaporation. The coating was thermally cured at 80 °C, 60% humidity for overnight in humidity oven (ESPEC-model SH-241).

3. Characterization

Electrochemical characterization of the uncoated and the coated samples was carried out using a standard corrosion cell (1 l, Pine Research Instrumentation) with conventional three electrode set-up in non-deaerated 3.5 wt% NaCl solution prepared from analytical grade chemicals (ChemSupply, Australia) and distilled water (Milli Q). A saturated calomel electrode (SCE, Pine Research Instrumentation, +0.24 V vs. Normal Hydrogen Electrode, NHE) was employed as the reference electrode, a graphite rod of 2 mm diameter as counter electrode and the sample under test as the working electrode. All reported potentials in this work (determined using electrochemical techniques) are with reference to SCE. The open circuit potential (OCP) of the specimens was monitored as a function of time and samples were allowed to stabilize at their OCP for 1 h before measurements.

Mild steel coupons (thickness ~ 0.6 mm) of 1.7 cm × 1.7 cm (both coated and uncoated) were used as sample coupons for electrochemical testing. The sample holder is made of Teflon and a platinum sheet and a platinum wire was used for electrical connection. The area exposed to the electrolyte solution is controlled using an inner and outer 'O' rings for an electrode area of 0.785 cm^2. Measurements were done in duplicates. Potentiodynamic polarization experiments were performed at a scan rate of 1 mV s^{-1} in the potential range of ± 300 mV relative to OCP. The Electrochemical Impedance Spectroscopy (EIS) measurements were performed using a Solartron 1260 impedance/gain-phase analyzer in combination with a Solartron 1280 B electrochemical