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In-situ generation and application of nanocomposites on steel surface for anti-corrosion coating

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ABSTRACT

Thin organic coatings directly on steel sheets provide excellent barrier protection in saline environment and meet deformability demands, but fail in providing active corrosion protection. We have put an effort to solve this problem by formulating composite coatings using *in-situ* generation of metal oxide nanoparticles (NPs) in the polymer matrix. Here we present a new synthesis method of high performance polyetherimide composite with TiO_2, MgO, and Al_2O_3 nanoparticles and their application for anti-corrosion coatings in saline environment. We observed that *in-situ* synthesis of these metal oxide NPs in the polymer curing process leads to evenly distribution and uniform size of nanoparticles. Thermo-mechanical property was analyzed for these three kinds of free-standing composite film to assess elasto-plastic behaviour and compared to mother polymer film. Results indicated that thermal stability and elastic behaviour of composites film are not affected to the great extent by the presence of NPs. The potentiodynamic and the electrochemical impedance studies on these composite coated steel panels were carried out to identify active–passive behaviour. Results showed active corrosion protection from nanocomposite coating based on TiO_2 and barrier protection was noticed from nanocomposite coating based on MgO and Al_2O_3.

1. Introduction

Polymer nanocomposites have received significant attention from both industries and academia. These composites have shown the combine physico-chemical properties of individual material in the system [1]. Their applications range from aerospace to commonly used materials, and from chemical industries to medical applications [2]. Currently better understanding of the properties of these materials and reliable control over NPs size and distribution enables their large-scale production and hence their cost is going down rapidly with increasing demand.

Nanotechnology and its application is gaining popularity in coating industries, where traditional additives and pigments are being explored to be replaced by nanofillers in the polymer binders. The worst part of a coating is that when it is vulnerable to water and ions. It is well documented in the literature that the rate of diffusion of water and oxygen in the most organic coatings exceeds the diffusion-limited value for oxygen reduction [3]. There is also a challenge to make thin film by using commercially available pigments, additives as they remain aggregated after grinding, and mixing, which alters the appearance and more importantly the coating viscosity and rheological properties [4]. Therefore, these challenges have twisted interest in researchers that thin films can reduce water penetration into coating/substrate interface through designing coatings formulation by generating *in-situ* nano particles. Metal oxide NPs less than 100 nm in dimension are able to reinforce the polymer matrix without disturbing transparency and other important properties of the coatings [5]. *In-situ* generation of polymer nanocomposites represents an alternative to the conventional physical mixing/blending of nano-oxide particles into the polymer matrix. Metal oxide NPs are high potential metal fillers in polymer coating applications [6].

NPs improve the coating's abrasion, scratch resistance, conductivity and also enhance their corrosion resistance. Most commonly used NPs in coatings are Al_2O_3, SiO_2, TiO_2, ZnO, CeO_2, MgO and $CaCO_3$ due to their inherent properties. For example TiO_2 and ZnO NPs are used as UV blocking agents; Al_2O_3 and SiO_2 are used to improve abrasion and scratch resistance, and CeO_2 and MgO NPs are used as anti-corrosion and high temperature oxidation resistant materials. Currently it has shown that polyaniline composites with TiO_2 nanoparticles have better corrosion resistance [7]. Polyaniline due to its *p* nature resists the electron transfer (anodic reaction of

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iron ion formation) and TiO_2 NPs are *n* type and therefore, hinder the hole transfer (hydroxyl ion formation) [8]. SiO_2 polymer composites and Si—O network from silane coupling agents are also used for anti-corrosive coatings, and this is mostly due to increased crosslinking density and reduced pin holes defect in the coatings [9].

In this report we present *in-situ* synthesis and application of TiO_2, MgO, and Al_2O_3 NPs in a polyetherimide (PEI) polymer on a steel sheet. The natures of the composite self-standing films are characterized and results are discussed using FTIR, TGA, DMTA and SEM. Then the active–passive behaviour of composite coated steel substrates is evaluated in saline environment using potentiodynamic and electrochemical impedance spectroscopy (EIS).

2. Experimental

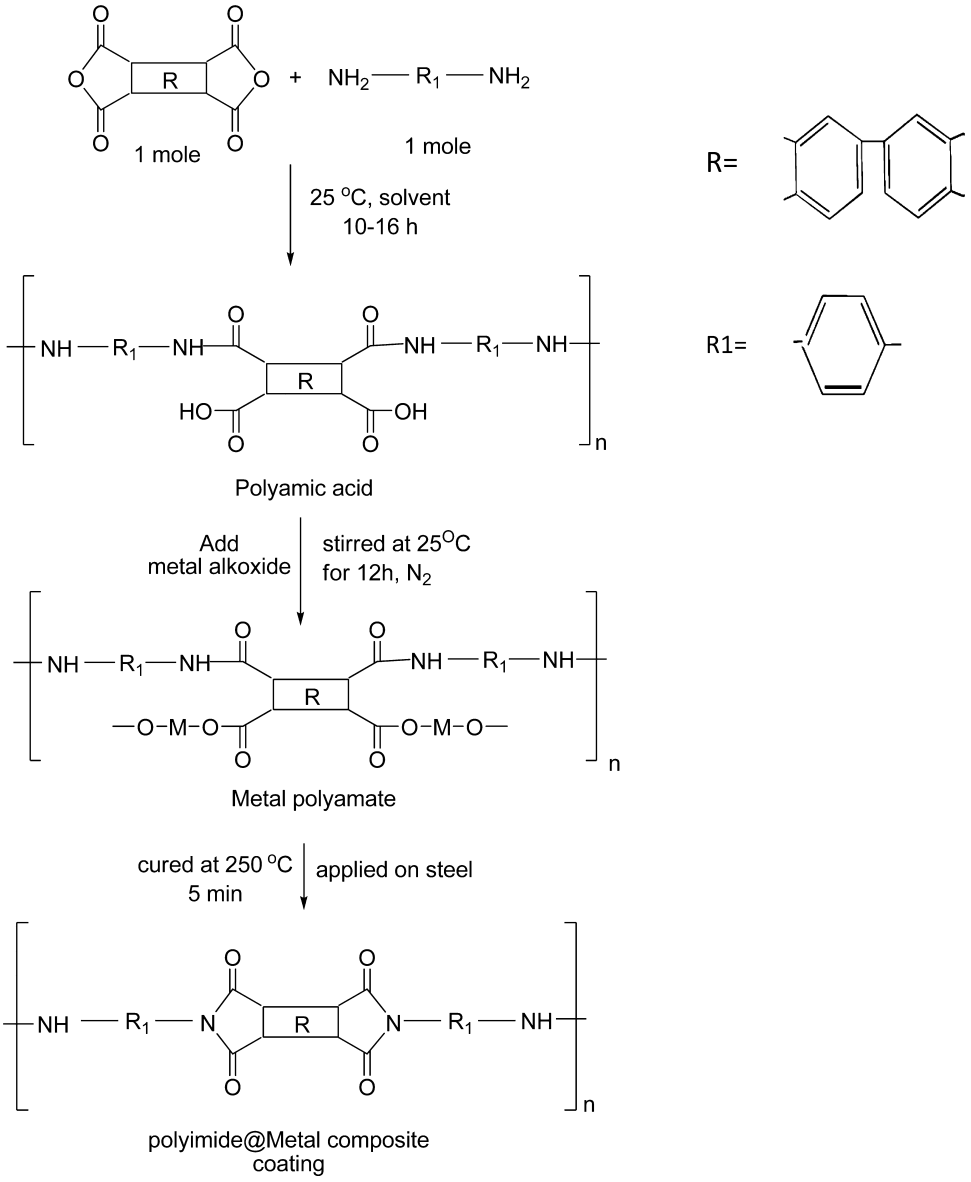
2.1. Materials and instrumentation

2.1.1. PEI film properties film properties

Thermogravimetric analysis (TGA) was conducted with a Perkin Elmer Pyris diamond at a heating rate of 10 °C min^{-1} from 25 °C to 600 °C. We took 13 μg of starting material in all the TGA measurements. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer Pyris sapphire DSC at a heating rate of 20 °C min^{-1} from 25 °C to 280 °C and a cooling rate of 40 °C min^{-1}. Dynamic mechanical thermal analysis (DMTA) was carried out on a Perkin Elmer Pyris diamond DMA at a 1 Hz frequency and a heating rate of 2 °C min^{-1} from 25 °C to 300 °C. All the analyses were performed under nitrogen flow on the freestanding films. These films were casted onto a glass plate and then removed from the plates by immersing them into hot water for about 30 min. FTIR analyses were performed on the films with a Perkin Elmer spectrum 100. All the chemicals were purchased from Aldrich, and solvents were used as supplied.

2.1.2. Steel substrate and corrosion tests

A high strength steel sheet with the dimension of 100 mm × 60 mm × 1.00 mm was used as substrate for the investigation. The chemical composition of the steel in wt% max was: C: 0.052, S:0.003, P:0.011, N:0.035, Mn:1.59, Si:0.10, Ti:0.10, Nb:0.078 and the balance, Fe. The substrate surface was subjected to alkali cleaning and followed by water rinsing and hot air drying



Scheme 1. Synthesis protocol of polyamic acid.