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Amelioration of anticorrosion and hydrophobic properties of epoxy/PDMS composite coatings containing nano ZnO particles

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ABSTRACT

Epoxy-polydimethylsiloxane (PDMS) nanocomposite coatings loaded with different concentrations (ranged from 2 to 8% (w/w)) of ZnO nanoparticles have been successfully achieved by using the solution intercalation method. In this study, it has been aimed to investigate corrosion protection performance and hydrophobic properties of epoxy/PDMS nanocomposites (NC). Fourier transform infrared (FTIR) spectroscopy was utilized in order to study the chemical structure of the developed coatings. The coating surface wettability was studied by contact angle measurements and the dispersion of ZnO nanoparticles was examined via field emission scanning electron microscope (FESEM). The effects of ZnO nanoparticles on the corrosion resistance and the barrier performance were investigated by electrochemical impedance spectroscopy (EIS). Thermal properties were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) From the FTIR spectra it was observed that the incorporation of nano ZnO particles has demonstrated peak shift and change in intensity. The incorporation of nano ZnO particles within the hybrid polymeric matrix had improved the hydrophobicity in terms of contact angle which reached maximum as 128° for NC6 system. NC2 coating had shown higher coating resistance more than 10^9 Ω even after 30 days of exposure in electrolyte medium. The results obtained from TGA and DSC studies demonstrated that introducing PDMS to epoxy resin increased T_g whereas the incorporation of ZnO nanoparticles in the nanocomposite coatings showed reduction in degradation temperature, cross-linking density of the composite by lowering T_g.

1. Introduction

Many decades ago, organic coating has become a very effective method for metal protection. Utilizing these coatings is a smart way to combine the mechanical properties of metals with the surface characteristics of the coatings [1]. However, the performance of the coatings generally depends on their barrier properties and good adhesion to the substrate [2]. The diffusion of oxygen and water molecules toward the metal surface and the permeability of the corrosive species through all polymers due to a free volume micro-voids and strong affinity between water and polar groups of polymers are shortcomings of these coating [3–5].

Polymeric nano-reinforced coatings have attracted extensive research activities as a convenient method for preventing corrosion and fouling of metal surfaces, especially for steel protection. The unique physical, chemical and mechanical properties of the materials in nanoscale domain play an important role in enhancement of the corrosion protection of the bulk-size materials [6]. This good barrier performance will be achieved by the miscibility of nano-sized particles within the polymer matrix, by reducing the porosity and zigzagging the diffusion pathway [7]. Nano-zinc oxide is one of the most commonly used inorganic nanoparticles and it is a multi-purpose nanoparticle used to produce multifunctional nano coatings. It possesses high hardness and low refractive index, hydrophobic enhancement and excellent dispersion with no aggregations [8–10].

In spite of that, microscopic phase separation due to inhomogeneous dispersion of the inorganic nanoparticles within the organic matrix is considered as a major problem. However, aggregation might take place during curing time even with a well dispersion of the particles within the polymer matrix while the blending step. Moreover, increment in viscosity could be observed with the higher percentage of nanoparticles result in a difficulty with coating applications [11]. In present investigation, it is planned to examine the effect of ZnO nano fillers on the wettability, anticorrosion properties, structural investigation and surface morphology of the

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developed silicone modified epoxy nanocomposite coatings (NCs). It is worth to be mentioned that the selection of the mixing rates of the epoxy resin and the poly dimethyl siloxane (PDMS) modifier (90:10 w/w) was done through taking in count the massive research works that have been conducted on such materials by many researchers in the last years [12–15] especially the works that have been done by Ananda Kumar and his research group [16–19].

2. Experimental

2.1. Materials

All chemicals were used as received without any further purification. Epoxy resin (EPIKOTE 828) representing bisphenol A and epichlorohydrin with an equivalent weight of 184–190 and viscosity about 12,000–14,000 cP at 25 °C was supplied from Asachem (Malaysia). Hydroxyl-terminated poly dimethyl siloxane obtained from Sigma–Aldrich (Malaysia) with a viscosity of 750 cSt and density equal to 0.97 g/ml at 25 °C was used as a modifier. 3-Aminopropyltriethoxysilane (KBE-903) from Shin-Etsu Chemical Co. Ltd. (Japan) was used as a cross-linker for epoxy resin and hydroxyl-terminated polydimethylsiloxane and epoxy resin along with dibutyltindilaurate as catalyst that supplied from Sigma–Aldrich (Malaysia). Zinc oxide nanoparticles with a mean diameter of 100 nm and density at 1.7 g/mL at 25 °C, were purchased from Sigma–Aldrich (Malaysia). Polyamide (EPI-CURE 3125) curing agent with an amine value of 330–360 mg/g was supplied by Asachem (Malaysia) and xylene (C_8H_{10}) from Evergreen Engineering & Resources (Malaysia) was utilized as a solvent.

2.2. Specimen preparation and application of coatings

Cold rolled mild steel panels with dimensions of 5 cm × 7.5 cm were used as substrates for this work. Free films were casted on Teflon petri dish. The steel panels were first degreased with solvents to remove impurities and dirt. The specimens were subjected to ASTM D609 standard to achieve Sa 2½ surface profile. Samples were coated by brush method and monitored to have film thickness in the range of 70–80 μm that was measured by using Elcometer 456.

2.3. Preparation of silicone-modified epoxy nanocomposite system

Cured epoxy resin and five sets of NC samples containing 0, 2, 4, 6 and 8 wt% ZnO loadings, abbreviated as Neat epoxy, NC0, NC2, NC4, NC6 and NC8, respectively, were prepared as following through solution intercalation method [20]: the powder ZnO nanoparticles were dissolved in xylene at the weight ratio of 8:2 in order to force the nano-sized particles to swell within the solution. This solution was then subjected to magnetically stirring at a rotation rate of 800 rpm for 30 min following by 15 min of sonicating. After that, 90 g of epoxy resin, 10 g of PDMS, stoichiometric equivalent of 3-aminopropyltriethoxysilane (with respect to OH group of PDMS) and dibutyltindilaurate catalyst were mixed at 80 °C for 20 min with constant stirring. Dissolved nanoparticles were added to the blend and mixed for 20 min at 1000 rpm. 60 min of sonication process was done before the addition of calculated percentage (w/w) of the polyamide. Constant stirring for 5 min followed by subjecting the mixture to vacuum with the assist of vacuum pump to remove the trapped air bubbles and CH_3OH (side product of the reaction of PDMS and 3-APS).

2.4. Characterization techniques

2.4.1. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was carried out to perform qualitative analysis and to trace the cross-linking process. ATR-Nicolet iS10 Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) was used to record FTIR spectra in the transmittance mode. A32-scan data accumulation in the wavenumber range of 400–4000 cm^{-1} at a resolution of 4.0 cm^{-1} was used to obtain all recorded spectra.

2.4.2. Contact angle measurement (CA)

The hydrophobic performance of the nanocomposites was evaluated by employing water contact angle test. The contact angles of five droplets of distilled water at different points of each sample were recorded by using Optical Contact Angle 15EC instrument. 5 μl water droplet was gently deposited on the specimen surface and capturing the image has occurred directly in terms of measuring the static contact angle. The reported contact angle values were the averages of five measurements with less than 2° as a measurement error.

2.4.3. Electrochemical impedance spectroscopy measurement (EIS)

The electrochemical impedance spectroscopy was used in order to investigate the anticorrosion performance of the developed nanocomposite systems. A classical three-electrode cell with 3% NaCl distilled water solution were used for 30 days of immersion. Sample with 3 cm^2 exposed area served as the working electrode, a saturated calomel electrode SCE as the reference electrode and a platinum electrode as the counter electrode were placed in a Faraday Cage to reduce noise during measuring. Gamry PC14G300 potentiostat with a frequency range of 100 kHz to 10 mHz and amplitude of sinusoidal voltage at 10 mV was used to perform the test. All EIS data were analyzed by Gamry Echem Analyst, Version 6.03.

2.4.4. Surface morphological analysis of nanocomposite coatings

Field Emission Scanning Electron Microscopy (FESEM) was used to investigate the surface morphology and the uniform dispersion of the nanoparticles within the polymeric matrix. FEI Quanta 450 FEG with SDD EDS detector at 10 kV as accelerating voltage in presence of low vacuum (LVSEM) was used to characterize the developed nanocomposite coatings.

2.4.5. Thermogravimetric analysis (TGA)

The thermal stability of neat epoxy, silicone modified epoxy and ZnO nanocomposite coating systems was evaluated using TGA technique which was conducted by using Mettler Toledo TGA Q500 from 30 °C to 800 °C at a rate of heating equal to 50 °C/min under nitrogen gas with a flow rate of 60 ml/min. Samples with a mass range between 10 mg and 12 mg were used for TGA measurements. All TGA thermograms were analyzed by TARe software, TA Universal Analysis, Version 4.7A.

2.4.6. Differential scanning calorimetry (DSC)

Glass transition temperatures of the epoxy/PDMS nanocomposites were determined by differential scanning calorimetry. Samples with mass range between 10 mg and 12 mg were tested under nitrogen condition by using TA-Q200 DSC instrument. The temperature range was varied from −50 °C to 180 °C at a heating rate of 10 °C/min. All DSC thermograms were analyzed by TARe software, TA Universal Analysis, Version 4.7A.