Progress in Organic Coatings 88 (2015) 237–244

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Thermomechanical and corrosion inhibition properties of graphene/epoxy ester–siloxane–urea hybrid polymer nanocomposites

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ARTICLE INFO

Article history:
Received 27 October 2014
Received in revised form 25 June 2015
Accepted 8 July 2015
Available online 30 July 2015

Keywords:
Hybrid polymer
Graphene
Composite coatings
Corrosion inhibition
Polarization

ABSTRACT

The effect of graphene on the corrosion inhibition properties of a hybrid epoxy–ester–siloxane–urea polymer was investigated. The weight fraction of graphene was varied from 1 to 2 wt%. Direct current polarization (DCP) and electrochemical impedance spectroscopic (EIS) techniques were used to measure the polarization and coating resistance of the coated aluminum alloy substrate. The grapheme/hybrid polymer composite coatings showed much higher corrosion inhibition property when compared to the neat hybrid polymer coating. An increase in glass transition temperature and rubbery region modulus was also observed for composites containing 1–2 wt.% of graphene. A direct correlation between the rubbery plateau modulus of free standing composite thin films and corrosion resistance of the composite coatings was made, indicating that the corrosion protection mechanism is due to restriction of the polymer chain motion by graphene which causes a decrease in coating permeability.

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1. Introduction

In recent years, there has been a tremendous drive to develop superior polymer coatings with self healing properties for application in highly corrosive environments such as ships, submarines, plant equipment and pipelines. A large number of organic compounds have been investigated as corrosion inhibitors for different types of metals. With increased awareness toward environmental pollution and control, the search for less toxic and environmentally friendly corrosion inhibiting coatings is becoming increasingly important [1–3]. The fabrication of nanostructured polymer composite materials as environmentally friendly anti-corrosion coatings has led to great progress in organic coatings technology and these coatings are being studied as a good replacement for chromate based paintings containing carcinogenic hexavalent chromate ions [4,5] (http://journal.chemistrycentral.com/content/6/1/163-B8).

Epoxy ester resins are known to have good corrosion inhibiting properties and good adhesion to surfaces, however their use as anti-corrosion coatings is limited due to their poor chemical resistance and weak mechanical properties [6]. The mechanical properties of epoxy ester can be improved by the blending or copolymerization with high temperature resistant ploymers such as aromatic polyurea and hydrophobic polymers such as polysiloxanes. Polyurea is used in production of laminates for building and automotive industries. It imparts improved impact and blast resistance to epoxyester while polysiloxanes which have good corrosion inhibition properties due to their hydrophobic nature improve corrosion resistance of epoxyester by limiting the access of water to the metal/hybrid epoxyester coating interface [7–10]. Polymethylhydrosiloxane is the polysiloxane compound of choice, because it is non toxic, stable to air and mositure and has been used as a reducing agent for converting carbonyl compounds to alcohols. It is therefore a suitable candidate for low cost environmentally benign corrosion resistant coatings [11–13]. The focus of this paper is to improve corrosion resistance of hybrid polymer coating containing epoxy ester, polyurea and polysiloxane by incorporation of nanosized graphene sheets. Singh-Beemat and Iroh [6,14,15] reported remarkable improvement in the corrosion resistance of epoxy ester coatings containing 2-D organoclay nanofillers. A remarkable increase in modulus and gas barrier properties of the coatings was also observed after reinforcement with organoclay nanofillers. The improvement in properties is said to be due to the restriction of polymer chain motion in the vicinity of the fillers [6]. Platelike fillers such as “nano-clays” increase the tortuosity of a fluid passing through a reinforced polymer coating or thin film [16–22]. Good interfacial adhesion between the polymer matrix and the 2-D filler is very important and essential for property enhancement and reproducibility. Generally, strong interfacial bonding imparts high modulus, high tensile strength, improved hardness and increased

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http://dx.doi.org/10.1016/j.porgcoat.2015.07.005
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resistance to tear, cracking, fatigue and corrosion. The van der Waals force of attraction between nano-fillers have to be minimal to prevent agglomeration. Agglomeration results in poor physical and mechanical properties of polymer nanocomposites because it leads to stress concentration [23–25] and reduction in strength of composite coatings and films. Uniformly dispersed nanofillers impart improved corrosion inhibition properties to the matrix by ristricting chain mobility and preventing flow of ions to and from the coating interface.

In this study, graphene is used as filler and dispersed in a hybrid polymer matrix consisting of epoxy ester, polysiloxane and polyurea. Graphene is chosen as preferred nano-filler due to its low mass density, high modulus and high strength compared to the layered silicates. Graphene, a two dimensional sheet of sp^2 carbon atoms is considered to be the building block for graphite, carbon nanotubes and bucky balls [26–29]. It possesses a unique combination of properties that are ideal for corrosion inhibition in reinforced polymer coatings, making it suitable for use in microelectronic components including interconnects, aircraft components, and implantable devices. Both single-layer and multilayer graphene films are exceptionally transparent (>90% transmittance for 4-layered graphene) so graphene coatings do not perturb the optical properties of the underlying metal [29]. Graphene based polymer composites have enhanced mechanical properties due to the synergistic combination of high specific surface area and strong nanofiller–matrix adhesion. A recent study shows that graphene-based membranes are impermeable to all gases and liquids making it of great interest in corrosion inhibition of metals [29–35]. Most recently, several researchers have synthesized corrosion protective coatings by depositing untrathin graphene nanosheet. Prasai et al. [29] reported the use of atomically thin layers of graphene as a protective coating that inhibits corrosion of underlying metals. Singh et al. [4] electrophoretically deposited hyrophobic graphene–oxide polymer composite coating on copper. The coating showed very high oxidation and corrosion resistance due to the strong impearmeability of graphene to diffusing ions. Sahu et al. [33] electrodeposited graphene nano-sheets on bare copper substrate with high corrosion inbibition properties and Chang [34] synthesized hydrophobic epoxy/graphene composites as corrosion inhibiting coating for cold-rolled steel.

In this study, we synthesize graphene/epoxy ester–siloxane–urea nanocomposite coatings containing 1–2 wt.% of graphene. Similar study done in the past in Dr. Iroh's research group showed that reinforcement of the hybrid resin system with higher weight fraction of graphene fillers resulted in poor corrosion inhibition properties due to occurrence of agglomeration of nanofillers and the highly conducting nature of the nanocomposites. Optimal low weight fractions of graphene are used in this work to improve the corrosion performance of graphene/hybrid polymer composite coatings. The composite coatings are applied onto aluminum (Al 2024-T3) coupons and the corrosion inhibition property was measured by using electrochemical impedance spectroscopy (EIS) and direct current polarization (DCP) methods. Both electrochemical techniques were used to measure the polarization resistance and corrosion resistance of the coatings. Thermo-mechanical properties of the composites was measured by dynamic mechanical spectroscopy. Results obtained from testing the composites were compared with those for the neat hybrid polymer coating.

2. Experimental

2.1. Materials

Some of the reagents used in this study including 4,4′-oxydianiline, ODA (97% purity), 4,4′-methylenebis (phenyl isocyanate), MDI (98% purity) and N-methyl pyrrolidinone NMP (99% purity) were purchased from Sigma–Aldrich company. Epoxy ester was provided by Cytec surface specialties. Polymethylhydrosiloxane (PMHS) was supplied by Momentive Performance Materials. Graphene sheets of 50–100 nm (thickness) and 7 μm (length) was purchased from Angstrom Materials, Dayton, OH. All the reagents listed above are all analytical grade. De-ionized water was also used in this process.

2.2. Equipments

The dynamic mechanical behavior of the composite films is studied using dynamic mechanical spectrometer (DMS) 6000 from Seiko Instruments Inc. Composite structure was determined by using Thermo scientific Nicolet 6700 Fourier Transform-Infrared (diamond small orbit module). Reference 3000 Potentiostat from Gamry Instruments was used to study corrosion behavior of the coatings by performing direct current polarization (DCP) and electrochemical impedance spectroscopy (EIS) measurements. DCP and EIS measurements were analyzed by using Gamry Echem analyst software

2.3. Synthesis of polyurea

5.0 g of ODA was added to 100 ml of N-methyl-2 pyrrolidone (NMP) in a round three neck flask and stirred for 30 min using a mechanical stirrer in a nitrogen atmosphere, the temperature was maintained at 10 °C. 6.3 g of MDI was added to the solution and stirring was continued for 14 h [6,14,15].

2.4. Preparation of hybrid polymer graphene nanocomposites

The synthesized polyurea was dissolved in NMP and mechanically stirred for half an hour, after which polymethylhydrosiloxane (PMHS) was added to the solution followed by continuous stirring. After 10 min of stirring, epoxy ester (Fig. 1) was added drop wise with continued speed stirring for an additional 2 h. 0.07 g and 0.14 g of grapheme representing 1 and 2 wt.% of graphene was added to the polymer solution and the resultant suspension ultrasonicated for 2 h to ensure homogeneity. The polyurea and PMHS concentrations were maintained constant at 40 wt.% and 20 wt.%, respectively.

2.5. Preparation of films and coatings

Free standing films for dynamic mechanical testing was solution cast in a Teflon mold with cavity dimensions of $(5.1 \times 5.1 \times 6.4)$ mm. Coatings for corrosion testing was prepared by solution drop method onto $(25.4 \times 101.6 \times 3.18)$ mm Al 2024-T3 coupons. The coatings and thin films were cured in an oven in a stepwise manner involving, heating initially at 50 °C and 75 °C for 2 h each, followed by heating at 100 °C for 12 h, and finally heating at 125 °C for 4 h. Stepwise curing is done to reduce flashing and to gradually get rid of by-products and solvents used during polymerization without damaging the samples. If cured in a single step at an elevated temperature, the system could crack due to sudden shock. Thickness of coating and film is 0.13 mm and 0.14 mm respectively. For ease of identification, the samples are labeled 0%-GR, 1%-GR and 2%-GR for the neat hybrid polymer, 1 wt% and 2 wt% samples respectively.

3. Characterization

Dynamic mechanical measurement was performed on composite film by using the dynamic mechanical spectroscopy operated in a tensile mode at a heating rate of 5 °C/min and a frequency of 1 Hz for a temperature range of −50 °C–160 °C. DCP and EIS

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