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Investigation and improvement of abrasion resistance, water vapor barrier and anticorrosion properties of mixed clay epoxy nanocomposite coating

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ABSTRACT

Mixture of two different alkyl quaternary ammonium modified clay nanoparticles (aq-CNPs) viz. sepiolite and smectite were used to prepare epoxy/mix-clay nanocomposite coating in various concentrations (0–10%). The combined effect of aq-CNPs has been studied for the first time to understand various coating properties. The water vapor transmission (WVT) barrier, abrasion resistance (Taber) and anticorrosion (salt spray) properties were found improving with increase in the aq-CNPs concentration in epoxy matrix. The morphological (SEM), thermal (DSC), spectroscopic (FTIR), pH and rheological (Brookfield viscosity) studies were done to investigate the insight of properties of epoxy/mix-clay nanocomposite coatings.

1. Introduction

Coating materials filled with inorganic nano particles has been receiving increased research attention during recent decades. Organic inorganic hybrid nanocomposites show enhanced protective properties of the coating such as improvements in mechanical [1], rheological [2], thermal [3] optical [4] electrical [5] and magnetic properties [6]. Polymer clay nanocomposites are new class of material which consists of polymer as matrix and nanoclay as the reinforcement fillers [7]. Initial work of polymer nanocomposites were reported with improved thermal properties, mechanical (strength, modulus, toughness) and physical (barrier, permeability and optical) properties over pure nylon matrix [8]. Clay nano materials have gathered attention recently as interesting filler materials to modify polymers for developing cost-effective high performance protective coatings. The properties of organic modifiers such as polarity, acidity and functionality have much influence on the structure & properties of epoxy clay nanocomposites [9–14]. The individual nanolayers can disperse due to suitable organic modification of clay in the polymer matrix leading to the formation of nanolayer dispersed nanocomposites [15,16]. In this aspect, montmorillonite, sepiolite, palygorskite, pyrophyllites and hectorite etc. [17] are appropriate for inorganic-organic hybrid coatings synthesis.

In this article, we report synthesis and properties of epoxy clay nanocomposite coating where clay-nanoparticles (CNPs) used are combination of two different types viz. sepiolite (80%) and smectite (20%) modified with alkyl quaternary ammonium salt (aq-). This combination and proportion of clays were chosen based on surprisingly high viscosity development inside coating at this combination (US patent # 006036765A, Southern Clay Products), which indicates special spatial arrangements with polymer matrix and may provide interesting results if other coating properties are investigated. It is noteworthy that, combined effect of clay nanoparticles has been investigated for the first time with respect to coatings properties. It was found that the incorporation of aq-CNPs was highly effective to improve the water vapor barrier and improvement in abrasion resistance properties desirable for the protection of metal as coatings.

2. Materials and experiments

2.1. Materials

The alkyl quaternary ammonium clay nanoparticles (aq-CNPs) in the current study is a mixture (approximately 80:20 by weight) of sepiolite and smectite (hectorite, montmorillonite) obtained from BYK-Chemie GmbH, Germany. Bisphenol A based unmodified

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medium viscosity liquid epoxy resin (Araldite GY 250 obtained from Huntsman Corporation) was used as polymer matrix. Other ingredients comprises epoxy curative, based on aliphatic polyamine (Air products) and a silicon based surface wetting additive (BASF Corporation). The epoxy resin, aq-CNPs and surface additives were synthesized as component "A" while polyamine was used as component "B" for the formulation of nanocomposite coating. The clay nanoparticles used in the current study were surface treated with alkyl quaternary ammonium ions (aq-CNPs).

The epoxy resin under study is having epoxide equivalent weight of 190 g/eq and a viscosity of 12,000 cPs, 25 °C. An aliphatic polyamine adduct used as curing agent during current study is modified aliphatic amine with high reactivity having amine value 460 mg KOH/g and viscosity 3000 Cps, 25 °C.

2.2. Synthesis of epoxy clay nanocomposite coating (NCCs)

A 250 mL steel vessel was cleaned and kept for 10 min in oven at 105 °C to remove moisture from the vessel. The vessel was charged with required amount of epoxy resin followed by silicon based wetting additive (0.01% by weight of total epoxy resin) and mixed for 5 min under mechanical stirrer (Dispermill, ATP Engineering B.V.). After mixing of additive, aq-CNPs were charged to have hybrid coating composition. A total of 7 hybrid coatings were synthesized having weight concentrations comprising 0.12%, 0.25%, 0.5%, 0.75%, 1%, 5% and 10%. The material dispersion was done at 1000 rpm by Dispermill machine for 30 min each. The shear force applied by stirrer blade generated heat during dispersion operation (temperature recorded upto 45 °C). Entire operation was performed at laboratory conditions having 23 °C temperature and 50% relative humidity (RH).

2.3. Epoxy nanocomposite coatings (NCCs) properties and concentrations

Different set of properties were studied for various aq-CNPs concentrations based on suitability of coating application and viscosity of the mixed coating. Water vapor transmission (WVT) studies were performed for 0% (neat), 1%, 5% and 10% concentrations. Glass transition temperatures (Tg) were studied for 0%, 0.50%, 0.75% and 1% concentrations. Fourier transform infrared spectroscopy (FTIR) tests were conducted for 0% (neat), 0.5%, 1% and 5% concentrations. Scanning electron microscopy (SEM) were conducted to study the surface morphology at two different specimen viz. 0% (neat) & 1% concentrations. The selection of higher concentrations viz. 5% and 10% were restricted to water vapor transmission (WVT) studies due to limitation of application of coating by spray method due to very high viscosity development at these concentrations. Specimen for WVT were prepared by draw down method. Viscosity study were done at 25 °C for 0.25%, 0.5%, 1% and 5% concentrations while, pH were studied at 0 to 10% concentrations at 27 °C. Due to very high viscosity at these concentrations, test specimen for WVT were prepared draw down methods respectively while all other specimens were prepared by air assisted spray application method.

2.4. Organic–inorganic hybrid nanocomposite specimen preparation

Thin films of epoxy aq-CNPs formulation (component "A") were prepared by spray and drawdown methods for various analyses and testing, after suitably mixing with polyamine adduct curative (component "B"). For salt spray and abrasion resistance studies, it was spray applied onto mild steel metal coupons of 100 mm × 150 mm × 2 mm and 100 mm × 100 mm × 1 mm respectively, at 35 (±2) μ-meter dry film thickness (DFT), using Devilbliss spray gun having 1.4 mm nozzle orifice. Before coating film applications on mild steel coupons, the surfaces were prepared using emery paper of 180# followed by washing with acetone. Free films for water vapor transmission (WVT) study and scanning electron microscopy (SEM) analysis were prepared by draw down method on silicon release paper with calculated amount of material to have 30 μ-meter uniform dry film thicknesses. The applied coatings/films were kept at 23 °C for 168 h. before testing. Draw downed, dried coating films were used for calorimetric and spectroscopic studies.

2.5. Instrumental characterization and performance testing

Water vapor transmission (WVT) for the free films were tested in accordance with ASTM E 96/E96-M-05 water method, the temperature and relative humidity (RH) were kept as 100 ± 1.8 °F (38 ± 1 °C) and 90 ± 2% respectively.

The thermal properties of the films were measured using differential scanning calorimetry (DSC) of TA Instruments, Inc. The weights of the samples were taken 10 milligrams for calorimetric study. The glass transition temperature (Tg) of hybrid nanocomposite samples were measured heating from 25 to 200 °C at a heating rate of 20 °C/min under nitrogen atmosphere at a flow rate of 30 mL/min. The abrasion resistance test was carried out according to ASTM D4060-01 method. Abrasion resistance of the epoxy NCCs with different concentrations were determined by the Taber abrader (make TABER, USA.) instrument using CS-17 wheels, coatings were applied on metal coupons of 100 mm × 100 mm × 1 mm size at 35 (±2) μ-meter thickness. The weights of coated specimens were recorded on four digit electronic balance (Essae, Vibra) before subjecting the specimens for abrasion test. Final weights of the specimens were taken after coating films were rubbed for 1000 cycles, 1 kg weight load at 72 revolution per minute (RPM). Scanning electron microscope (SEM) of JEOL-Tokyo model JSM-6510 LV was used to characterize the surface morphology of epoxy NCCs film. Corrosion resistance of the coated specimens were tested by salt spray resistance method using Q-FOG, Q-Lab corporation salt fog chamber having 5% NaCl concentration, 35 °C, 100% RH, in accordance with ASTM B117. Fourier transform infrared (FTIR) spectroscopic studies were done to investigate the interaction of aq-CNPs with epoxy amine system in different concentrations using Thermoscientific Nicolet i-S10 instrument. Coating applications for various types of specimen preparation under study were done by spray gun (Devilbliss, 1.4 mm nozzle orifice), putty knife applicator and draw down methods. The dry film thicknesses (DFTs) of the coatings were measured by Elcometer – 456 thickness gauge. The pH of the systems were tested by pH meter of Bio Lab instruments and viscosity were tested by Brookfield viscometer, model RVDV-E.

3. Results and discussion

3.1. Differential scanning calorimetry (DSC) analysis

The glass transition temperature (Tg) of neat (0%) epoxy and epoxy NCCs in various concentrations viz. 0.5%, 0.75% and 1% were determined to study thermal behavior of the synthesized coatings. Details of Tg graph obtained are illustrated in Fig. 1. The glass transition temperature (Tg) is found to be shifting gradually towards lower temperatures with increase in concentration of aq-CNPs inside epoxy matrix. The lowering in the glass transition temperature (Tg) of epoxy NCCs can be attributed to the non-cross linked epoxy due to masking of reactive oxirane group by aq-CNPs inside matrix. It is noteworthy that lowering in the glass transition temperature of nanocomposites has been reported earlier in epoxy clay nanocomposites by DSC analysis [18] and by solid state NMR study