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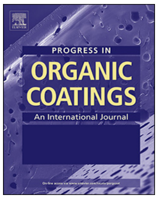

Ceramic hyperbranched alkyd/γ-Al_2O_3 nanorods composite as a surface coating

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ABSTRACT

The work reports engineering an eco-friendly series of ceramic hyperbranched alkyd/γ-Al_2O_3 nanorods composite coatings via solution casting method and auto-oxidation curing mechanism. Sunflower oil based hyperbranched alkyd resin was successfully prepared by using polyesterification method. Controlled synthesis of single crystal γ-Al_2O_3 nanorods with 20 nm average diameter exposed by {400} crystal plane was carried out via hydrothermal and decomposition methods The effects of dispersing different concentrations of one-dimensional ceramic γ-Al_2O_3 nanorod filler in the alkyd matrix were studied. The tailored alkyd/single crystal γ-Al_2O_3 nanocomposites were applied for mechanical and anticorrosive coatings. Coatings' surface and anticorrosive properties were investigated via water contact angle, scanning electron microscopy and salt spray test. Studying the mechanical properties, stability against chemicals and thermal behavior of the ceramic alkyd nanocomposites were also considered. Results approved that the highest improvement was achieved with nanofiller insertion up to 0.5% γ-Al_2O_3 nanorods in the alkyd composites.

1. Introduction

Environmental pollution concerns have driven recent studies toward engineering advanced nanocomposite coatings with low-volatile organic content (VOC) [1,2]. The annual global cost of metal corrosion was estimated to be $900 million in 2015 [3]. Alkyd resins, which represent 50% of the protective resins in the paint industry, hold major advantages such as low-cost, high strength, ease of application and superior adhesion to the substrate [4]. Because of their extraordinary properties such as facile preparation in one-step reaction, hyperbranched alkyd outperforms other dendritic resins [5,6]. Excellent colour retention, durability, weathering resistance, low viscosity and high anticorrosive resistance are among other advantages of hyperbranched alkyd resins [7]. They possess higher strength and drying properties as compared to high solid alkyds [8]. Alkyds are polyester based materials obtained by polyesterification with unsaturated fatty acids of drying oils [9]. The $A_2 + B_3$ approach, i.e. ester linkage formation between a dibasic acid and trifunctional alcohol, is a simple technique for preparing hyperbranched polyesters [10]. Recently, vegetable oils have received great interests because of their renewability and sustainability [11,12]. Sunflower oil (SFO) belongs to Asteraceae family with high amounts of unsaturated long-chain fatty acids [13]. Alkyd coatings based on SFO can reach full cure via oxidative cross-linking and exhibit non-yellowing, high durability, anticorrosion, and weather resistance [14]. Ceramic alkyd nanocomposites based on incorporation of one-dimensional (1D) inorganic nanofillers pave the way for the development of next-generation coatings since they feature lightweight, superior mechanical strength and flexibility. As a ceramic material, γ-Al_2O_3 is perhaps the most important nanofillers and can be applied in composite reinforcement [15]. Low cost, high surface area, thermal and chemical stability and good electrical insulation of γ-Al_2O_3 nanorods can provide wide applicability in coating fields [16]. Controlled synthesis of a single crystal of γ-Al_2O_3 nanorod fillers was obtained by solvothermal method to prepare boehmite (γ-AlOOH) followed by its thermal decomposition [17]. γ-Al_2O_3 nanorods are suitable for functionalized organic and inorganic materials through guest–host chemistry [18]. Nano-alumina was used to improve abrasion resistance of the coating [19]. Studies on the anticorrosive characteristics of Al_2O_3 nanomaterials are currently at the research level. Dhoke et al. [20] reported the formation of alkyd composites with Al_2O_3 nanoparticles for corrosion resistance. Despite those efforts, the novel route to prepare and apply single crystal γ-Al_2O_3 nanorods with uniform size has

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not been reported. Controlling size and morphology of the prepared nanofillers prompted our research to model high strength and anticorrosive ceramic alkyd nanocomposites [21]. Also, ceramic hyperbranched alkyd nanocomposites provide engineered coating with dual advantages of: 1) getting rid of VOC problems and 2) property enhancement.

For the first time, an eco-friendly SFO based alkyd filled with ceramic γ-Al_2O_3 nanorods fillers with promising coating features were introduced in this study. A large scale synthesis method that efficiently controls ceramic nanofillers of single crystal γ-Al_2O_3 nanorods size and shape is reported in this work. The current work highlights the significance of dispersing γ-Al_2O_3 nanorods in determining the improvement in the mechanical, thermal and anticorrosive properties of the nanocomposites. Ecological and economic impacts, ease of fabrication, high mechanical and anticorrosive performance are the prime merits introduced in this work.

2. Experimental

2.1. Chemicals

Aluminium chloride hexahydrate ($AlCl_3{\cdot}6H_2O$, 99%), adipic acid ($(CH_2)_4(COOH)_2$, glycerol ($HOCH_2CHCH_2OH$), dibutyltin oxide ($(C_4H_9)_2SnO$), p-Toluenesulfonic acid (P-TSA, 98.5%), Sodium dodecyl benzene sulfonate (SDBS, 98%), sodium hydroxide, and toluene were supplied from Sigma–Aldrich company and utilized without any purification. SFO and all driers including cobalt octoate ($C_{16}H_{30}CoO_4$), manganese octoate ($Mn[OOCCH(C_2H_5)\text{-}C_4H_9]_2$) and lead octoate $Pb[OOCCH(C_2H_5)C_4H_9]_2$ were obtained from Merck, India and used as received. All solvents are analytical reagent grade and were used as received.

2.2. Preparation of hyperbranched alkyd resin

Hyperbranched polyester was prepared by polycondensation reaction of A_2 (adipic acid) + B_3 (glycerol) monomers in the presence of dibutyl tin oxide catalyst as reported earlier [10,22]. Briefly, in a 250 mL three neck flask flushed with nitrogen, 47.6 g of adipic acid was mixed with 40 g of glycerol ([-OH]/[-COOH] = 2.0) and 0.438 g of dibutyltin oxide (0.5 wt.%), heated to 140 ± 5 °C and stirred for 11 h. The heating was stopped and stirring was continued for cooling down to room temperature (RT). The product was colorless viscous liquid.

Hyperbranched alkyd was obtained by polycondensation reaction of the prepared polyester and SFO fatty acids. The reaction was carried out by using 0.1476 mol of hyperbranched polyester containing hydroxyl groups, 0.03 mol SFO and 0.5% P-TSA catalyst. A three neck flask, thermometer, condenser and nitrogen gas were used for the reaction which was performed at 220 ± 5 °C until the acid value decreased to the desired 10–15 mg KOH/g. Acid value is the mass (mg) of potassium hydroxide (KOH) required to neutralize 1 g of alkyd, and was determined for small amount of samples collected during the reaction.

2.3. Synthesis of single crystal Al_2O_3 nanorods

Single crystal γ-Al_2O_3 nanorods were prepared via a simple hydrothermal method to the synthesis of γ-AlOOH nanostructure followed by thermal decomposition of the prepared γ-AlOOH precursor under air atmosphere [23,24]. In a typical reaction, $AlCl_3{\cdot}6H_2O$ (2.41 g) was dissolved in a 45 mL solution of water and xylene (mixing ration 2:1 by volume) under vigorous magnetic stirring at RT for 15 min 1 g of SDBS was added to the above solution under constant stirring followed by 1 M NaOH solution (25 mL) and suspension solution was obtained. A separating funnel was used without shaking to separate the obtained suspension to form two liquid phases. The upper organic liquid phase was transferred into 50 mL Teflon-lined stainless steel autoclave, which was sealed and heated to 200 °C for 24 h. Then the autoclave was allowed to cool naturally to RT. The product was centrifuged at 5000 rpm for 20 min, washed with a mixture of water and ethanol (50:50 by volume) for several times and dried in vacuum oven at 80 °C for 12 h. A white powder of γ-boehmite nanostructured material was obtained, then put into an alumina crucible in a tube furnace and heated in air to 550 °C for 3 h with a heating rate of 5 °C/min.

2.4. Preparation of coating film and nanocomposites

Carbon steel panels (20 cm × 10 cm × 1 mm) were polished and degreased with SiC paper of standard grit sizes (P180, P320 and P500). The panels were cleaned with ethanol and propanone and dried before film applications. The prepared virgin polymer was applied and cured with common alkyd resin driers via physical and chemical methods called autoxidation. The SFO-based alkyd resin (87 wt.%) was dissolved in 10% mixture of toluene and turpentine (1:1 by volume). A definite amount of the drying agents were added under continuous stirring as follow: cobalt octoate (0.6 wt.% in), calcium octoate (0.6 wt.%) and zirconium octoate (1.8 wt.%) until a homogenous solution was obtained. The mixture was applied to steel surface by spraying and dried at RT. After solvent evaporation, the matrix particles coalesced and the coated film was cured by air oxidation of unsaturated linkages.

The ceramic nanocomposites were prepared by dispersion of different concentrations (0.05 wt.%, 0.1 wt.%, 0.5 wt.%, 1 wt.%, 3 wt.% and 5 wt.%) of γ-Al_2O_3 nanorods in the alkyd matrix by ex-situ method. γ-Al_2O_3 nanorods were sonicated in turpentine by using a tip sonicator (tip diameter of 5 mm, Sonics and Materials Co., USA) for 15 min. The nanofiller dispersion was then added slowly to the alkyd resin under continuous stirring and the mixture was sonicated again for 10 min. The alkyd composite solution was mixed with driers and the mixing ratio was as follow: SFO-based alkyd resin (87% – (0–5 wt.% of γ-Al_2O_3 nanorods)); turpentine (10 wt.%), cobalt octoate (0.6 wt.%), calcium octoate (0.6 wt.%) and zirconium octoate (1.8 wt.%). Zirconium acts synergistically on cobalt and calcium by forming coordinate complexes of zirconium carboxylates and improves the auto-oxidative drying system. The virgin and γ-Al_2O_3 nanorods filled SFO based alkyd samples were cast on steel plates and dried in air for 48 h to form 70 μm thick films.

2.5. Coating formulation

A fabricated coating formulation is as follows: alkyd 76.5%, 0.5% γ-Al_2O_3 nanorods, 10% ferric oxide pigment (95%, SDFCl, India), 0.5% nonionic surfactant to improve latex spreading and color strength in alkyd paint [25], turpentine (10 wt.%) and 3% octoates driers. The film formation and auto-oxidation was carried out as mentioned above.

2.6. Characterization

For the as-synthesized polymer, nanofillers and nanocomposites, FTIR analysis was carried out by a Thermo-Fischer Nicolet™ iS™10 (US) using KBr pelletting. NMR spectra were carried out by using a 300 MHz Varian mercury (300 VX, USA). Trichloromethane was used to dissolve the alkyd and tetramethylsilane was used as internal standard. The thermal stability of the matrix and nanocomposites was assessed by thermogravimetry (TGA) by TA Instruments Q600 (USA). The specimen was scanned at 50 °C–700 °C under nitrogen. Gel permeation chromatography (GPC) was used to determine the molecular weight distribution of the alkyd resin. Crystallinity and purity of γ-Al_2O_3 nanorods composites were assessed by XRD using a PANalytical X'Pert PRO diffractometer (Netherlands). The XRD pattern was obtained by CuKα radiation for 2θ of 5°–80°. Dynamic light scattering was performed on Brookhaven particle size analyzer (90Plus, United States) for γ-Al_2O_3 nanorods were observed by a JEM2100 LaB6 (JEOL, Japan) at 200 kV. Nanorods were ultra-sonicated in ethanol for 10 min, and two drops of the solution were mounted on carbon-coated TEM grid. In order to