Water-borne composite coatings using nanoparticles modified with dopamine derivatives

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ABSTRACT

Water-based organic/inorganic composites have gained attention for their use in organic-solvent-free processes, and for being safe and environmentally friendly. In order to improve the mechanical properties of the resin, we modified boehmite nanoparticles (BNPs) and then blended them into a water-based epoxy resin. The BNPs were synthesized via the sol–gel method at a relatively low temperature (80 °C) to achieve a smaller size (13 nm on average), good transparency (over 80%), and be stable enough to be dispersed in water for extended periods of time. The BNP surfaces were then modified with the aqueous modifier dopamine, used here as a human- and eco-friendly water-based coupling agent, in order to prepare water-dispersible nanoparticles, producing dopamine-modified BNPs (DA-BNPs). Dopamine/polydopamine could be effectively coated on the BNP surfaces, allowing them to be uniformly dispersed in water. In order to disperse nanoparticles in alkaline solutions, a charged coupling agent, dopamine sulfonate (DS), was synthesized and used to form DS-modified BNPs (DS-BNPs). The prime nanoparticles were agglomerated in the mixture of water-based epoxy resin, while DS-BNPs were dispersed well in epoxy resin. In pencil hardness tests, DS-BNP/epoxy film displayed a hardness of 3H-4H, much higher than the original polyethylene terephthalate substrate's 1H and prime epoxy coating's 2H. In addition, the transparency was found to be over 80%. Those water-based BNPs could be also dispersed very well in ethylene-vinyl acetate copolymer emulsion. Dopamine and its derivative showed their potential as water-based modifiers to replace some silane-based coupling agents used in fabrication of water-based composites.

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1. Introduction

The composites of polymer matrices are ordinarily derived from polymerizing some monomers with hydrophilic functional groups via solution polymerization, or dispersing polymeric droplets via an emulsifying process. Both of them are dispersed in water and thus we need water-based nanoparticles to be incorporated into waterborne polymer matrixes. Nanoparticles have been found to dope into a polymer substrate to form a highly-dispersive composite displaying special physical properties. In order to increase the organic–inorganic interaction and dispersity, people used to employ a variety of silanes as coupling agents to link all materials inside [1]. However, to use bi-functional silanes in some cases, the inorganic nanoparticles (metal oxides like SiO_2, TiO_2, Al_2O_3, etc.) should be synthesized in a commonly-used sol–gel process prior to being protected with coupling agents. One of the major problems that should be addressed is that the coupling agents have a water-sensitive alkoxysilane or halosilane group which limits the water content in the synthetic process. The use of silane coupling agents is therefore limited in water-based composite materials. Additionally, most coating composites using silicone-containing coupling agents are prepared by adding matured nanoparticles into polymer precursors/ resins, with some organic solvents (alcohols in most cases) for dilution.

Waterborne (or water-based) resins, like water-based epoxy resins, polyurethanes, polyacrylates, silicones, and even fluorinated polymers, are promising due to their eco-friendly coating process without using organic solvents [2]. Those resins are dispersed and prepared in an emulsion form and thus easily spread on substrates. Therefore, nanoparticles well-dispersed in water can be used to fabricate a water-based composite. In order to fabricate an organic/inorganic coating, especially for scratch resistance via hard coating on a surface, some nanoparticles have been incorporated into tough polymer matrixes. For instance, boehmite [3], SiO_2 [4], or TiO_2 [5] can be broadly used as a filler to resist the shear or normal stress propagation and dispersed into photo- or thermo-curable polymer matrixes. The aggregation of nanoparticles generates heterogeneous coating surfaces and a weak stressed domain in the polymer matrix, directly affecting the performance of composites. Therefore, a good coupling agent is required to disperse the nanoparticles in the polymer matrix very well. Recently, a natural and universal glue, dopamine, was found to display adhesive properties in a humid or wetted environment [6–8]. There has been

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increasing research employing the biomimetic concepts to develop surface protection [9], biocompatible coatings [10], adhesives [11], surface modifiers [12], and so on. Dopamine with a catechol structure and a primary amino group at the other end can form polydopamine, which can be firmly coated on a variety of surfaces. The polymerization can spontaneously occur in an alkaline environment of dopamine in an aqueous solution. The polydopamine structures are mainly constituted with covalent-bound polymer chains and supramolecular aggregates of monomers (a combination of charge transfer, π-stacking, and hydrogen bonding interactions) [13]. However, the detailed structure of polydopamine is still under investigation and remains to be discussed. Dopamine can be stable as a monomer in an acidic aqueous solution for a certain period. Therefore, dopamine can be used to cap the nanoparticles and transfer them to an aqueous phase in an acidic aqueous solution, creating a useful method to prepare water-soluble nanoparticles. The preparation employed a surfactant exchange technique by preparing fatty-acid-stabilized iron oxide nanoparticles in an organic phase first and then exchanging with dopamine molecules to surround it with dopamine [14,15]. We further expanded the applications of dopamine to prepare some other water-soluble nanoparticles. Taking advantage of metal oxide synthesis in a mildly acidic aqueous solution, the dopamine could be added to form a dopamine layer on nanoparticle surface with positive charges and disperse the nanoparticles well in the aqueous solution. In the study, we focused on the use of dopamine in a water-based coupling agent and explored its application to prepare water-based composite polymers. Dopamine with a catechol structure can attach on a metal oxide surface, and its amino groups after polymerization can still be active to react with epoxide groups of epoxy resins. Taking advantage of these properties, an eco-friendly way to enhance composite surface strength was developed and the hardness of the coating was also evaluated.

2. Experimental details

2.1. Materials

Aluminum isopropoxide ($Al(O-i-Pr)_3$, >98%) was purchased from ALDRICH, 3-hydroxytyramine hydrochloride ($C_8H_{12}ClNO_2$, 99%) was purchased from ACROS, epoxy resin Epon-82 (a bisphenol-A derivative by Shell Chemical Company) and hardening agent H227 were purchased from Jointmide Co. Ltd., and 1,3-propane sultone ($C_3H_6O_3S$) and ammonium hydroxide (NH_4OH, 28 wt.%) were purchased from SHOWA. All the chemicals were used as purchased.

2.2. Synthesis of boehmite nanoparticles (BNPs)

25 g aluminum isopropoxide ($Al (OCH (CH_3)_2)_3$) and 300 ml de-ionized water were put into a three-necked flask and pre-stirred for 30 min. After adding 2 ml (60 wt.%) HNO_3, the suspension was heated to 80 °C and vigorously stirred for 24 h. The suspension containing boehmite (γ-AlO(OH)) (pH 4) was collected and then evaporated to 20 wt.% solid content suspension.

2.3. Dopamine modified BNPs (DA-BNPs)

20 ml BNP taken from the concentrated suspension was mixed with 0.04 g dopamine (0.002 g/ml in water) in a three-necked flask with N_2 purging. The suspension was stirred for 1 day and then infused with ozone for 6 h of oxidation. The DA-BNPs suspension was poured out for future applications.

2.4. Synthesis of dopamine sulfonate (DS)

Dopamine hydrochloride (1.1376 g, 6 mmol) was dissolved in ethanol 150 ml in a 250 ml three-necked flask. The mixture of 28 wt.% aqueous ammonia (416 μl, 3 mmol) and 1,3-propanesultone (799 mg, 6.5 mmol) was added slowly into the flask. The solution was heated to 50 °C and stirred for 18 h, resulting in the formation of a white precipitate. The mixture was filtered and the white precipitate was washed. The white precipitate was then collected and dried under reduced pressure.

2.5. Dopamine sulfonate modified boehmite nanoparticles (DS-BNPs)

Eight ml of BNPs taken from the concentrated suspension was added in a 50 ml three-necked flask, followed by adding 0.016 g dopamine sulfonate. The mixture was heated to 50 °C and stirred for 12 h. Afterwards, the transparent solution was poured out for the next modification.

2.6. Blending of modified BNPs and water-based epoxy resin

Epon-82 was mixed with H227 with a weight ratio of 2:1 before a certain amount of prime BNPs or modified BNPs was added. The composite suspension was blended for 3 min on a spinning speed of 3200 rpm, giving a composite resin coating with 6.7 wt.% or 9.0 wt.% solid contents.

2.7. Characterization

Modified BNPs were dried and mixed with KBr in a ratio of 1:100 by weight, and the mixture was characterized by an attenuated total reflection Fourier transform infrared (ATR-FTIR) (DIGILAB FTS 3000MX). Its detection incident light was set to 30°, and the wave number range was from 400 cm^{-1} to 4000 cm^{-1}. Modified and unmodified BNPs were dropped on the surface of polypropylene membrane filters
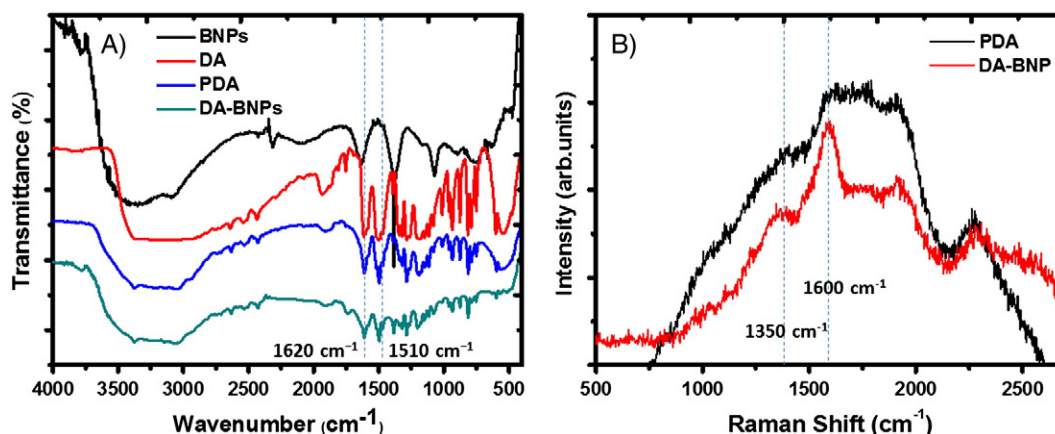

Fig. 1. (A) IR spectra for BNPs, DA, PDA, and DA-BNPs. (B) Raman spectra of PDA and DA-BNPs.