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Biopolymers nanocomposite for material protection: Enhancement of corrosion protection using waterborne polyurethane nanocomposite coatings

G. Christopher [a], M. Anbu Kulandainathan [b], G. Harichandran [a,*]

[a] Department of Polymer Science, University of Madras, Guindy Campus, Chennai 600 025, India
[b] Electro-organic Division, Central Electrochemical Research Institute, Karaikudi 630006, India

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ABSTRACT

Low volatile organic content based, cost effective and simple procedural nanocomposite coatings were prepared by solution blending technique. Waterborne polyurethane dispersion containing nanoparticles of ZnO, modified with biopolymers were successfully prepared and the resulting nanocomposites were coated on mild steel. The coatings with different loading levels of nano ZnO, which was modified with biopolymers of sodium alginate and lignosulfonate were prepared via ultrasonication method. Surface morphology of these nanomaterials were characterized by scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM); crystallinity by X-ray Diffraction (XRD) analysis. The effect of incorporating surface modified ZnO nanoparticles on the corrosion resistance of waterborne polyurethane coated steel was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy. Also the surface wettability of the composite coating, studied through contact angle suggested that increase in dosages of nanomaterials does not affect the surface wettability of the coating. The results revealed that the increasing percentage of surface modified ZnO in waterborne polyurethane not only promotes the dispersion of the particles but also improves the corrosion performance of nanocomposite coatings. Corrosion results from Tafel plot and impedance analysis showed that the 0.3 wt% loading of ZnO surface modified with lignosulfonate gives better protection than sodium alginate.

1. Introduction

Coating plays an important role for modifying the metal surfaces by its aesthetic and protective purpose which also prevents degradation of substrate by undesirable natural process of corrosion that occurs from chemical reaction with its environment. Corrosion is a continuous process, it can be prevented by various methods like cathodic, anodic and barrier protections [1–3]. Barrier protection reduces the permeability of the corrosive chemicals and hence these are widely used for corrosion protection for metals. It plays as a physical barrier between the metal surface and the aggressive corrosive environment. In organic coatings, many different types of fillers and micro-sized anticorrosive pigments are used, but they come with some undesirable defects like decrease in transparency, flexibility, adhesion and scratch resistance of the coating [4]. One of the approaches to overcome these problems, is to use nano-sized fillers and pigments instead of micro sized one, as they are smaller in size and accommodate a larger specific surface area. The decrease in particle size supports enhancement of barrier and mechanical properties of the coating [5–8]. Apart from the utility of nano-regime in such methods, the amount of materials needed for the coating is also considerably less than the coatings with micron sized particles. Nanoparticles used in organic coatings are SiO_2 [9,10], TiO_2 [11,12], ZnO [13,14], Al_2O_3 [15], Fe_2O_3 [16], $CaCO_3$ [17] and clay [18]. Predominantly, the size, shape and the concentration of these nanomaterials determines the type of coatings they provide.

In last two decades, the area of research mostly focused on the developments of polymer based nanocomposite coatings [19–24], especially in the field of polyurethane anticorrosion coatings which can be markedly improved by incorporating nanoparticles [25,26] into them. Polyurethanes (crosslinking of polyol and polyisocyanate) are the new class of polymers with versatile applications. Recent environmental regulation abides to reduce the usage of

* Corresponding author.
E-mail address: umghari@gmail.com (G. Harichandran).

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volatile organic contents (VOCs). Hence the use of waterborne polyurethane (WPU) can replace conventional organic solvent borne polyurethane, thus reducing its environmental impact considerably. WPU dispersion is a binary colloidal system in which polyurethane particles are well dispersed in a continuous aqueous phase. They are non-toxic and non-polluting in nature. WPUs also finds application in coating, adhesives for textile, paper, wood or glass fibers, and so forth.

WPU finds applications in various fields, but it cannot be the exact alternative for solvent borne coatings in automobile and coating industry, due to its weak thermal, mechanical and barrier properties. This has been overcome by introduction of nanoparticles into the WPU matrix which enhances the said properties. Moreover, coatings made up of waterborne polymer supported with metal oxide nanocomposite, exhibit superior properties such as corrosion protection, resistance for chemicals, abrasion resistance, improved barrier properties and resistance to impact, scratch, etc., [27–31]. Nowadays these coatings are major players in the area of construction, thermal barriers for aerospace applications, automobile, pipeline coatings for marine applications, and decoratives [32–35].

The incorporation of nanoparticles into polymer matrix is difficult as the dispersion formed are not stable and immediately settles down. The large sized agglomerates reduce the barrier protection properties of polymer matrix. Moreover, the lack of functionalization of the nanoparticles and its connection to the polymer, results in a poor performance of the coating. To achieve proper dispersion and avoid drawbacks in nanocomposite coatings, the surface treatment of nanoparticles has been proposed. Dispersing nanomaterials in a polymer medium is a tedious process, now a days various methods have been developed for stabilizing the particles in the matrix, such as, using surface active agents, capping agents, surface modifiers, dopants etc., Many surface modifying agents like long chain fatty acids, various kind of silanes, polymer encapsulation, surfactants etc., were used [4–6,36–41]. But this field needs further innovative work to be done to improve the desired particle dispersion. The coating efficiency can be increased by increasing the anchoring of modified nanoparticles into the polymer. For surface modification of nanoparticles mostly ultrasonication method is used to disperse the nano fillers in polymer medium. Ultra sonication is a greener and economic approach to reduce time and saves energy also it can significantly improve the reaction efficiency in chemical synthesis. This is mainly due to cavitation formation when mechanical vibrations are produced and it can be transmitted into the liquid as ultrasonic waves. This is a useful technique when compared with other techniques in terms of energy conservation and waste minimization. Ultrasonic irradiation can enhance reactions rates and is easy to use. This technique can be extremely efficient and is applicable to a broad range of applications. There have been a few reports addressing the influence of ultrasonic irradiation using surface modification of metal oxide and other nanomaterials [42–48].

The modern approach is the utilization of biopolymers for the preparation of inorganic biopolymer nanocomposites which is extremely important for food and agro-products, due to their excellent properties, such as non-toxicity, biocompatibility, renewability, biodegradability and environmental sensitivity [49–54]. Alginate is a biopolymer, which is present in the cell walls of brown algae as the calcium, magnesium and sodium salts of alginic acid which is not dissolve in water but Sodium Alginate (SA) can dissolve in water [55,56]. Lignosulfonates [LS] are another class of biopolymers and are brown amorphous powder, odorless, and non-hygroscopic in nature. They exist as salts of lignosulfonic acid [57–61]. This is particularly used for inducing powerful surface-active properties and leads to better binding efficiency with the substrates. These biopolymers have excellent adhesion on the substrates and it also combines with nanoparticles. Moreover, it has good control over the nucleation and favor directionally oriented growth of nanoparticles.

Biopolymers are used to blend with waterborne polymers to improve the properties of the host polymer in terms of thermal, mechanical and protection properties. The property enhancement of the bio-based WPU nanocomposites is due to better compatibility between the WPU and biopolymer. WPU-urea/sodium alginate blends improved the water vapour permeability of the coating material and WPU loaded with lignosulfonate and its supramolecular complexes enhanced the mechanical properties were reported [62,63]. In continuation of this research the preparation of enhanced properties of polymer materials achieved by blend with various nanofillers. Biopolymers reinforced nanoparticles are important types of nanofillers that have been successfully used in the functionalization of polymer materials. Recent report on WPU modified with bifunctional nanofillers of carboxylated cellulose nanocrystal composed of silver nanocomposite is improved the mechanical and antimicrobial properties [64]. The introduction of inorganic nanoparticles is brought new functionalities to the host polymer. However, the dispersion of the particles and preventing the formation of aggregates or agglomerates will greatly reduce the applicability. New challenge for this research area is to prepare inorganic nanoparticles without aggregation during their integration into the host polymer.

In this article we present a novel method for surface modification of ZnO by biopolymers through ultrasonication. The composite are dispersed in waterborne polyurethane in various dosages using solution blending technique. The resultant SA and/or LS anchored ZnO nanocomposites are coated on mild steel (MS) and studied for their resistance to corrosion using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

2. Materials and methods

2.1. Raw materials

Waterborne polyurethane dispersion (PU-687) was procured from Piccassian Polymers (Stahl polymers), Argentina and analytical grades of sodium alginate and lignosulfonate were received from S.D. Fine chemicals and Aldrich chemicals respectively.

2.2. Syntheses of nano ZnO and surface modified nano ZnO

ZnO nanoparticles (average particle size 120–135 nm) were prepared using already reported procedure elsewhere [65]. 0.1 M (50 ml) concentration of NaOH solution with a concentration of 0.2 M (100 ml) solution of $Zn(CH_3COO)_2{\cdot}3H_2O$ were added in ethanol. Then mixtures of this solution were sonicated for 30 min (150 W) with Ultrasonics waves (150 W, 20 kHz). Finally, the white precipitate was filtered and washed with methanol. The solid was dried at 60°C for 24 h.

Surface modification of ZnO nanoparticles with biopolymer were carried out using already reported procedure with slight modification, which is briefly described as follows [66]: 0.1 g of prepared ZnO nanoparticles were dispersed in 50 mL of deionized water using a fixed power sonicator (150 W, 20 kHz) for 3 min. This was followed by drop wise addition of ammonia till a pH of 8 was achieved to maintain the alkalinity of the mixture and sonicated for additional 2 min prior to the further experiments. 0.4 g of SA and/or LS was added to water and sonicated for 2 min to dissolve the polymer in 50 ml water in a separate beaker. Then both the solutions were mixed and ultrasonicated. Subsequently, the mixture was dispersed for 15 min (on/off time: 10/5 min) through probe and the beaker were immersed in to water to reduce the temper-