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Epoxy/starch-modified nano-zinc oxide transparent nanocomposite coatings: A showcase of superior curing behavior

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ABSTRACT

A new class of transparent epoxy-based nanocomposite coatings containing starch-modified nano-zinc oxide (ZnO-St) is presented. ZnO nanoparticles physically decorated with starch carbohydrate polymer increased compatibility with epoxy chains and sterically prevented flocculation of ZnO nanoparticles. Surface characteristics of pristine ZnO and ZnO-St are studied by FTIR spectroscopy corroborating self-assembled starch molecules on ZnO surface until reaching a complete coverage. Curing behaviors of epoxy and transparent nanocomposites containing ZnO and ZnO-St are studied by the aid of nonisothermal calorimetric analyses at four heating rates to compare the curing enthalpies, onset temperatures, peak temperatures, and curing intervals of transparent coatings. The ZnO-St, particularly at low heating rate of 5 °C/min, prolonged curing (corresponding to ΔT increase of ca. 166 for epoxy to 200 °C for Zn-St/epoxy), and increased the amount of heat release (in the same order from 328 to 380 J/g) due to epoxide ring opening by starch hydroxyl groups. Such novel class of epoxy/ZnO-St nanocomposite coatings can be applied as top-coats because of their transparency. Additionally, from an environmental/biological standpoint, one should consider that starch is a carbohydrate polymer and ZnO is antibacterial, which may put more stress on the use of transparent nanocomposite coatings developed in this work.

1. Introduction

The use of advanced epoxy-based materials with superior properties has undergone serious developments in recent years and it is estimated to take a particular place in between versatile thermosetting systems such as nanocomposite coatings [1–3]. Having applied as coating, such nanocomposites show significantly different physical, mechanical and thermal properties compared to their conventional counterparts [4,5]. Nano-zinc oxide (ZnO), as one of the multifunctional inorganic nanoparticles, has drawn a great deal of attention due to its prominent physical and chemical properties, such as chemical stability, low dielectric constant, high luminous transmittance, high catalysis activity, effective antibacterial and bactericide, large band gap, very high excitation binding energy, intensive photo-catalytic effect (ultraviolet and infrared absorption), semiconducting characteristics [6–8].

Epoxy-based coatings comprising nano ZnO have been widely used in the quest for protection of metal substrates against environmental corrosions [9,10]. The nanocomposites based on epoxy resins are usually characterized by the ease of curing and/or processing, excellent resistance against moisture, solvent and chemicals as well as outstanding adhesion strength [11–14]. ZnO nanoparticles can also be used as reinforcing phase to improve wear resistant and anti-sliding properties of composites arising from high elastic modulus and strength [15,16]. It is also of vital importance to know that ZnO nanoparticles

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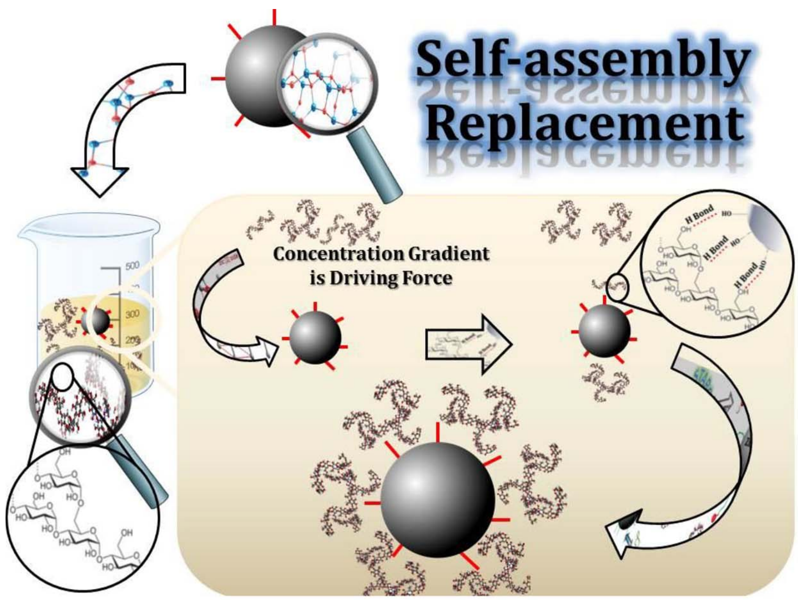
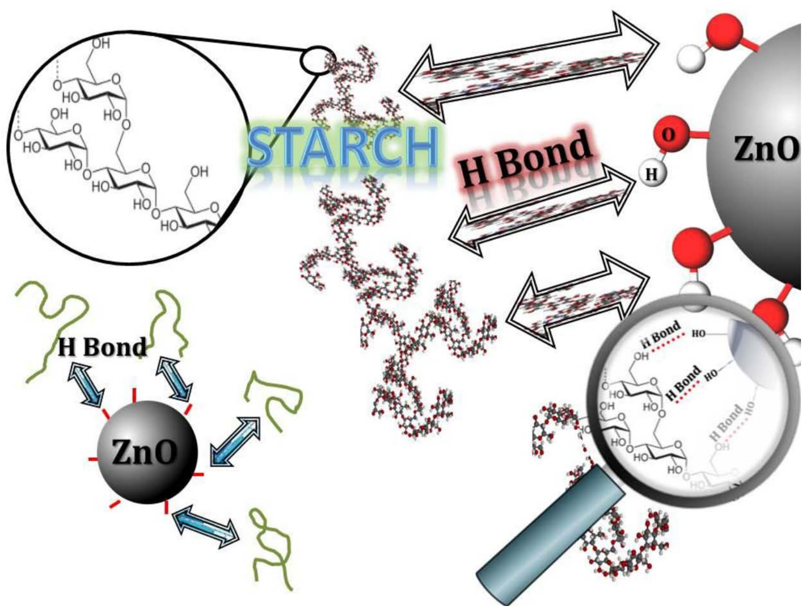


Fig. 1. Illustrative description of Modification of nano ZnO by starch.



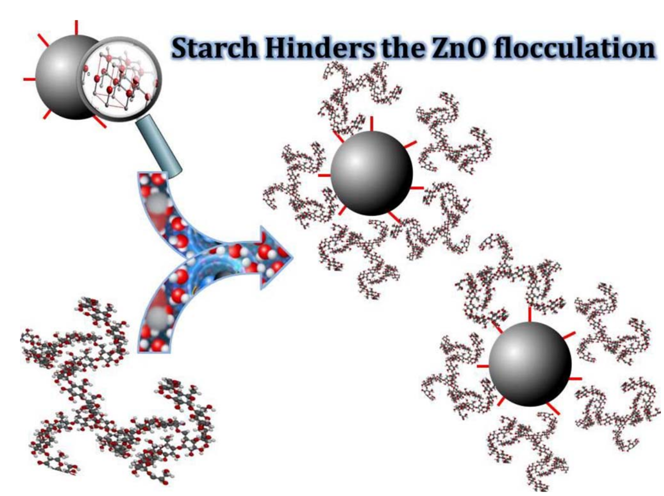


Fig. 2. Schematic demonstration of the chemical structure of the starch-modified nano ZnO.

are nontoxic materials utilized to produce environmentally friendly coatings. Furthermore, it has been found that anticorrosion resistance of the coatings containing this nanoparticle can be superiorly improved [17–19].

However, one must bear in mind that all the above-mentioned advantages will come to reality if only a completed state of dispersion is obtained. It means that ZnO primary particles must be homogeneously distributed and stabilized inside the epoxy matrix. The latter is rare for untreated hydrophilic ZnO particles inside a hydrophobic continuous phase like as epoxy polymers. Surface functionalization of nanoparticles was exploited as the easiest route to conquer such efficacies through modifying the surface physical chemistry properties of filler to increase miscibility between the phases [20,21]. In addition, one can find the best solvent to maintain the dispersing phase inside the matrix to enhance the stability of the dispersion and to prevent the particles to flocculate [22]. By tailoring the functionalities it is possible to simultaneously reach the goals both [23,24].

Starch is a biocompatible macromolecular carbohydrate consisted of large number of glucose units binding together through glycosidic bonds. The structure of this polymer can be divided into two sections of