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Silver-embedded epoxy nanocomposites as organic coatings for steel

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ABSTRACT

A novel hybrid nanomaterial based on silver nanoparticles, AgNPs, supported by 2,4-dihydrazino-6-(methoxypolyethyleneglycol)-1,3,5-triazine (mPEGTH) was prepared using solid phase technique. The synthesis process and the structural properties of the AgNPs were analyzed through X-ray diffraction (XRD), thermogravimetric analysis (TGA), transmittance and scanning electron microscopy (TEM and SEM). The effect of seawater, and pH of solutions on the aggregation and zeta potential of Ag NPs were characterized and identified. The Ag/mPEGTH, hybrid materials produced well dispersion and exhibit a remarkable superiority in enhancing the anticorrosion performance of epoxy coatings and fulfill a significant synergistic effect in anticorrosion and self-healing performance for epoxy composite coatings. The new self-healing mechanism of Ag/mPEGTH nanomaterial for the epoxy coating defects is tentatively proposed and discussed.

1. Introduction

Epoxy resins among several types of organic coatings have been widely used and recommended for several types of substrate such as copper, aluminum and steel due to their excellent adhesion, mechanical properties and anticorrosive performances [1–3]. There are some microcracks produced during the epoxy coatings affected their performances as effective organic coatings and eventually give rise to coating failure [4]. The hybrid epoxy nanocomposites have attracted considerable attention as organic coatings to protect the steel substrate from corrosion due to their ability to control of diffusive and barrier properties of coatings [5–7]. Moreover, the presence of hybrid inorganic nanomaterials in the organic coating reduced the moisture penetration and increased the impact resistance, durability, chemical resistance, substrate adhesion, and surface morphology of organic coatings [8,9]. There are several types of metal oxide nanoparticles such as silica, titania, zirconia, cupper oxides, and iron oxides have been used to improve the coating performances of epoxy [5–7]. The carbon nanomaterials such as graphene, and carbon nanotubes as well as metal such as silver, gold, cupper have been also used to control the mechanical, electrical and weather durability of [10–12]. However, there are still big challenges that affected the applications of the nanomaterials in the field of organic coatings due to their low dispersion efficiencies, agglomeration, leaching out from the coating networks, toxicity and environmental regulations. There are several techniques used to improve the stability, homogeneity, dispersability, sizes and shapes of the nanoparticles such as capping of nanomaterials with organic complexes with active functional group [13]. For these reasons, the modified silver nanoparticles were recommended to apply as filler for epoxy coatings because they are ecofriendly, antibacterial and anticorrosive properties [14–17].

Silver modified nanoparticles are by far the most widely used nanomaterials among the commercially available nano-sized materials due to their excellent antimicrobial characteristics as environmentally friendly materials [18–20]. It was also reported that, the chemical preparation techniques of nanomaterials have been focused on the technique of precursor thermal decomposition and chemical structures of the capping agents used to control the sizes and shapes of nanomaterials [21,22]. The modified polyethylene glycol, polyvinyl alcohol thiol used to protect the silver nanoparticles from oxidation and chemical degradation which increased their stability, antimicrobial activity and resistance silver nanoparticle agglomerations [23–25]. In the present work, the hydroxyl group of methoxypolyethyleneglycol (mPEG) converted into an active group by reacting with another functional group present in 2,4,6-trichlorotriazine (cyanuric chloride) and then the dichloro-derivatives were substituted by dihydrazino groups to

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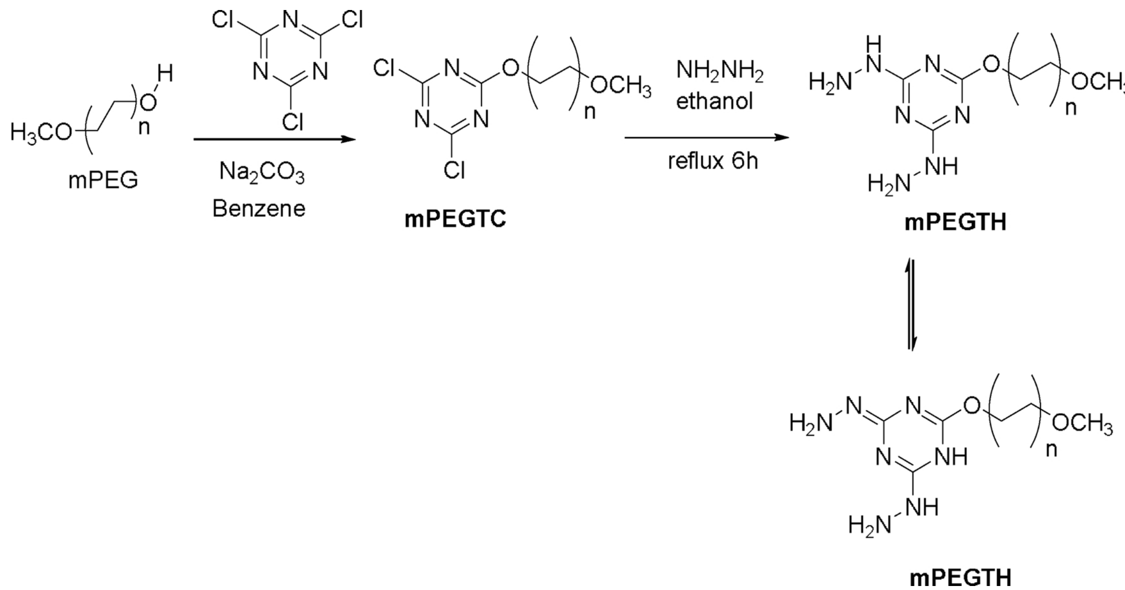

Scheme 1. Synthesis of mPEGTH.

provide an excellent reducing agent to produce effective capping agent. Cyanuric chloride is used in this work due to its commercially availability, low cost, and the ease for stepwise substitution of the three chlorine atoms under temperature control with a variety of nucleophiles [26]. Moreover, the objective of the present work is to advance in the development of novel-capping agents to prepare silver nanoparticles with green solid phase method. Enlightened by the capping and preparation method of silver nanoparticles with the prepared precursor, the silver nanoparticles were prepared by solid phase method to produce uniform and stable silver nanoparticles. Combining the advantages of silver nanoparticles as filler and the prepared capping agent with silver nanoparticles it was expected that these materials would incorporate into polyimide/epoxy resin to increase the epoxy coating performances and to produce epoxy coatings with improved antibacterial properties.

2. Experimental

2.1. Materials

Methoxypolyethylene glycol (mPEG) with molecular weight 5000 and 2, 4, 6-trichloro-1, 3, 5-triazine (cyanuric chloride) were purchased from Sigma-Aldrich, $AgNO_3$ salt were purchased from Merck. All the chemicals used in the study were analytical graded.

2.2. Preparation methods

2.2.1. Synthesis of (mPEGTC)

Methoxypolyethylene glycol (mPEG 5000) (50gm, 10 mmol) was dissolved in anhydrous benzene (200 mL), and the mixture was cold in an ice bath to 15 °C. Solution of cyanuric chloride in benzene (5-fold molar excess, 50 mmol, in 200 mL) slowly added to the mPEG solution; followed by addition of 5 fold molar excess of anhydrous sodium carbonate (50 mmol). The reaction mixture was stirred at room temperature for 24 h, and then the sodium carbonate was removed by filtration. Petroleum ether 40–60 in excess was added to the filtrate and precipitated product (mPEGTC) was collected by filtration, and then redissolved in 100 mL of benzene and precipitated again with petroleum ether 40–60. This process was repeated twice to remove the unreacted cyanuric chloride and afford the pure product as white solid in 82% yield, which used directly to the next step for preparation of the dihydrazino derivatives (mPEGTH)

2.2.2. Synthesis of mPEGTH

Hydrazine hydrate 80% (20 mL) was added at room temperature to a solution of mPEGTC (10gm**)** in ethanol (100 mL). The reaction mixture was refluxed for 6 h and then cooled to room temperature. The excess of solvent and hydrazine hydrate were removed under reduced pressure, and then excess ether was added to afford the product as white solid, which separated by filtration, washed with ether, and then dried under vacuum to render the final modified product mPEGTH in almost quantitative yield (Scheme 1).

2.2.3. Synthesis of Ag NPs using solid phase technique using normal heating or microwave irradiation [27]

The modified polymer (mPEGTH, 0.1gm or 0.2 gm) was mixed well with 0.1 gm of $AgNO_3$ (1:1 and 1:2 wt/wt) at room temperature. In the beginning, the color changed to gray and then black which indicate the reducing of silver ions to silver metal. The solid mixture was heated at 60 °C for 1–2 min using normal heating conditions or for 5–10 sec using microwave condition at 60 °C, 600 W). The AgNPs were suspended in methanol-water mixture 1:1 and then collected using centrifuge (8000 rpm), the collected product was wash with methanol-water mixture and then dried under vacuum.

2.3. Characterization of Ag/Ag_2O NPs epoxy coatings

Fourier transform infrared (FTIR) spectrometer (Nicolet, NEXUS-670) used to confirm the chemical structure of mPEGTH.

UV/vis spectrophotometer (Schimadzu UV-1208 model) used to investigate the surface Plasmon of Ag/Ag_2O NPs.

High-resolution transmission electron microscope instrument (HR-TEM; JEOL JEM-2100 with acceleration voltage of 200 kV) and scanning electron microscope (SEM; JEOL 6510 L A SEM, JEOL, Japan) were used to determine the surface morphology of Ag NPs.

The Ag NPs contents and the thermal stability of mPEGTH were