Journal of Colloid and Interface Science 462 (2016) 29–41

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

In-situ preparation, characterization and anticorrosion property of polypropylene glycol/silver nanoparticles composite for mild steel corrosion in acid solution

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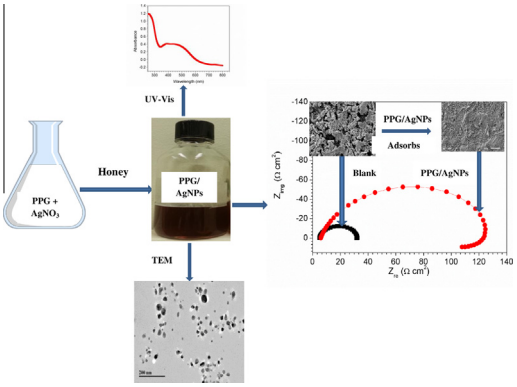
HIGHLIGHTS

- PPG/AgNPs composite was prepared *in-situ* using green approach.
- The composite was characterized using UV–Vis, XRD, TEM and EDS techniques.
- PPG/AgNPs act as effective corrosion inhibitor for mild steel in acid medium.
- Polarization studies indicate that PPG/AgNPs functions as a mixed-type inhibitor.
- Adsorption of PPG/AgNPs composite onto mild steel surface follows Temkin isotherm.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 May 2015
Revised 18 September 2015
Accepted 23 September 2015
Available online 25 September 2015

Keywords:
Silver nanoparticles
Polypropylene glycol
Acid corrosion
Corrosion inhibition
Mild steel
Composites

ABSTRACT

A novel polypropylene glycol/silver nanoparticles (PPG/AgNPs) composite was prepared *in-situ* using natural honey as the reducing and capping agent. Characterization of the composite was done by UV–Vis spectroscopy, FTIR, TEM, XRD, and EDS. The TEM results reveal that the nanoparticles are spherical in shape. XRD and EDS results confirm the presence of elemental silver in the polymer matrix. The influence of the prepared composite on the corrosion inhibition of mild steel in 0.5 M H_2SO_4 solution was studied by weight loss, electrochemical, SEM, EDS, and water contact angle measurements. Results show that PPG/AgNPs is effective inhibitor for mild steel in 0.5 M H_2SO_4 solution and adsorbs onto the metal surface via chemisorption mechanism. Maximum inhibition efficiency of 94% is afforded by the highest studied concentration of PPG/AgNPs at 333 K from weight loss measurements. Potentiodynamic polarization results reveal that the composite acts as a mixed-type corrosion inhibitor. Adsorption of PPG/AgNPs composite onto the mild steel surface follows Temkin adsorption isotherm. The SEM, EDS, and water contact angle images confirm the formation of PPG/AgNPs protective film on the mild steel surface.

1. Introduction

Metals corrosion in aggressive environment deployed in service have been widely studied [1–3]. The reason being that metals gradually lost important properties which warranted their use in the

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http://dx.doi.org/10.1016/j.jcis.2015.09.057
0021-9797/

environment to corrosion resulting in industrial accidents and economy lost. Of all the approaches employed in metal corrosion control, the use of corrosion inhibitors proved most practical and cost effective [4]. Metal corrosion inhibitors are substances which when introduced in small amount to corrosive medium disrupt the metal-corrosive ions reactions. Inorganic (particularly chromates, dichromates, nitrites, nitrates, phosphates, etc.) and organic (mostly those with O, N, S, and P atoms and/or π electrons) compounds have been effective in this regard [5–7] but the toxic nature of most inorganic compounds to the natural ecosystem and the exorbitant prices in addition to the tedious synthetic route of organic compounds have been very worrisome. Polymers, both naturally occurring and synthetic had been tested for metal corrosion inhibition ability [8,9] so as to serve as replacement for the inorganic and organic corrosion inhibitors. Interest in polymers stems from their availability, cost effectiveness, and eco-friendliness in addition to the inherent stability and multiple adsorption centers [10]. Although polymers have shown promising inhibiting effect, insolubility in aqueous solution and desorption at high temperature are the major setbacks [11]. Modification done in recent times had been the incorporation of certain substances capable of enhancing important properties like heat resistance, solubility, mechanical strength, compatibility, etc. into the polymer matrix. The resultant compound is often called a composite.

Composites are materials consisting of two or more chemically distinct constituents on a minute-scale, having a distinct interface separating them, and with properties which cannot be obtained by any constituent working individually [12]. The production of composite materials is either by mixing of components or *in-situ* formation through chemical synthesis although electrochemical method had been used recently [13]. Attention has been given to polymer metal composites in recent times due to their excellent flexibility, high compatibility, and strong adhesive power [14–16]. Specifically, polymer/silver composites have been the most investigated because of their remarkable optical, electronic, catalytic, and antimicrobial characteristics [17,18]. For example, Reda and Al-Ghannam [19] reported that polyaniline/silver (PANI/Ag) nanocomposite prepared using chemical oxidative polymerization of aniline monomer in the presence of nitric acid had the ability to store electric potential energy under the influence of alternative electric field. It had been documented [20] that silver nanoparticles decorated polyaniline/multiwalled carbon nanotubes nanocomposite is a promising candidate for future energy storage system. Also, poly (sodium acrylate) cryogels decorated with silver nanoparticles had been reported [21] to be effective for point-of-use water disinfection. For application as anticorrosion material, metal/polymer composites have shown promising results and are believed to form metal chelate [22] which could barricade metal surfaces from corrosive agents. Atta et al. [23] studied the corrosion inhibition of the poly (ethylene glycol) thiol/Ag nanoparticles composite on carbon steel alloys in aqueous acidic corrosive medium using polarization method and electrochemical impedance spectroscopy techniques. It was found that the composite exhibited excellent inhibiting ability with 90.95% inhibition efficiency afforded by 0.075 mmol/L of the composite. Polarization experiments indicated that the composite acted as mixed type inhibitor. Atta et al. [24] equally used silver nanoparticle (AgNPs) to prepare hybrid polymer based on N-isopropyl acrylamide (NiPAm) and 2-acrylamido-2-methylpropane sulfonic acid (AMPs) and tested the anticorrosion potentials of the hybrid polymer–AgNPs on steel corrosion in HCl environment using electrochemical method. It was found that 250 ppm of AMPs/NiPAm–AgNPs protected the metal surface by 81.46% and behaved as mixed type corrosion inhibitor. Poly 12-(3-amino phenoxy) dodecane-1-thiol surfactant self assembled on silver nanoparticles had been synthesized by Azzam and Abd El-Aal [25] and examined as non-toxic corrosion inhibitor for carbon steel in 1 M HCl solution using weight loss and potentiodynamic polarization techniques. The authors observed that the value of the percentage inhibition efficiency obtained for poly 12-(3-amino phenoxy) dodecane-1-thiol surfactant self assembled on silver nanoparticles was better than that obtained for poly 12-(3-amino phenoxy) dodecane-1-thiol surfactant only. Recently, Solomon and Umoren [26] reported the effectiveness of poly (methacrylic acid)/silver nanoparticles composite (PMAA/AgNPs) as inhibitor for aluminum dissolution in sulfuric acid medium. The authors documented that 1000 ppm PMAA/AgNPs offered protection as high as 85.6% to aluminum surface in sulfuric acid environment and temperature rise had minimal effect on the inhibition efficiency of the composite.

Our aim in the present work is to prepare *in-situ* polypropylene glycol/silver nanoparticles (PPG/AgNPs) composite, characterize and evaluate the inhibition performance of the composite for mild steel corrosion in sulfuric acid solution, using chemical and electrochemical methods of corrosion monitoring complemented with surface analysis techniques.

2. Experimental

2.1. Chemicals and materials

$AgNO_3$ and H_2SO_4 of analytical grade were purchased from Sigma Aldrich. Natural honey (produced by honeybee, *Apis mellifera*) used in this study was obtained from the Department of Pharmacy, University of Uyo, Nigeria. Mild steel sheet of percentage composition as follow: C, 0.05; Mn, 0.6; P, 0.36; and Si, 0.03 was obtained from Ejison Resources Nigeria Limited, Calabar, Nigeria. Polypropylene glycol was a product of Sigma Aldrich with number average molecular weight of 2000 g/mol.

2.2. Preparation of the composite

Composite of PPG/AgNPs was prepared *in-situ* by mixing aqueous solutions of the polypropylene glycol (PPG) and $AgNO_3$ solution. The preparation was done in three phases. Firstly, different concentrations (50 ppm, 100 ppm, 500 ppm, 750 ppm, and 1000 ppm) of the polymer were prepared in 0.5 M H_2SO_4 solution. Secondly, the respective concentration of the polymer solution was used to prepare 1 mM $AgNO_3$ solution. Thirdly, to every 100 cm^3 of the respective mixture, 5 cm^3 of natural honey which served as reducing and capping agents was added. The resulting mixtures were allowed to stand at room temperature for four days (96 h). The change in color of the mixture signaled the formation of the composite and this was confirmed by the addition of NaCl solution to a small portion of the composite solution. The nonformation of white precipitate on addition of NaCl to the mixture suggested that Ag^+ was converted completely to Ag^0.

2.3. Characterization

2.3.1. Uv–visible measurements

Spectral analysis for the development of PPG/AgNPs composite at different reaction conditions such as influence of reductant (honey) concentration, contact time and concentration of polymer were observed using JASCO770-UV–Vis spectrophotometer from 250 to 800 nm using a dual beam operated at a resolution of 1 nm with a scan rate of 200 nm/min at room temperature. The presence of AgNPs in the composite gave sharp peak in the range of visible region of the electromagnetic spectrum.

2.3.2. EDS analysis

Samples were prepared by depositing a drop of colloidal solution on an aluminum grid sample holder and drying at room