



# Poly(methacrylic acid)/silver nanoparticles composites: In-situ preparation, characterization and anticorrosion property for mild steel in H<sub>2</sub>SO<sub>4</sub> solution



M.M. Solomon<sup>a</sup>, S.A. Umoren<sup>b,\*</sup>, E.J. Abai<sup>c</sup>

<sup>a</sup> Corrosion Protection and Materials Research Laboratory, Department of Chemistry, Faculty of Science, University of Uyo, Uyo, Nigeria

<sup>b</sup> Centre of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

<sup>c</sup> Department of Science Technology, Akwa Ibom State Polytechnic, Ikot Osurua, Nigeria

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## ABSTRACT

Poly(methacrylic acid)/silver nanoparticles (PMAA/AgNPs) composite was prepared in-situ and characterized by UV–vis spectroscopy, FTIR, TEM, XRD, and EDS. The anticorrosion performance of the composite was investigated by gravimetric, electrochemical, SEM, EDS, and water contact angle measurements. Results obtained show that PMAA/AgNPs act as corrosion inhibitor for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. Inhibition efficiency increased with increase in concentration and temperature. PMAA/AgNPs composite behaved as a mixed-type corrosion inhibitor and adsorption onto the metal surface followed Temkin adsorption isotherm model. Results from all the surface analyses confirm the formation of PMAA/AgNPs protective film on the mild steel surface.

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## 1. Introduction

In recent times, metal nanoparticles particularly silver nanoparticles have become the center of focus because of the uniqueness of their properties which make them promising in areas such as biological sensors, catalysis, drug and gene delivery, optics, energy storage, biomaterials production, and antimicrobial protection [1–3]. These properties depend to a large extent on the size, structure, and distribution of the nanoparticles [4]. Different synthetic methods such as physical and chemical techniques, heat evaporation, electrochemical reduction, and photochemical reduction method are available [5–6] but the chemical method using chemical reducing agents appears to be the simplest and therefore enjoyed the highest patronage [4,7,8]. Common reducing agents used are hydrazine, sodium citrate, *N,N*-dimethylformamide, and sodium borohydride [9–12]. Although these compounds are excellent reducing agents, the high cost and the danger posed to the natural environment by the chemicals used to reduce the corresponding precursor salts to create uniform suspension have come under severe criticism [7,13]. Investigation into finding a cheap and ecologically friendly reducing agent has begun and attention is geared towards naturally occurring compounds. Natural honey is one of the naturally occurring compounds tested and some authors [7,14] have reported

the successful synthesis of nanoparticles compounds using natural honey as the reducing agent. Natural honey, apart from being inexpensive and eco-friendly, has dual functions of acting as a reducing and stabilizing agent during the synthesis process.

Addition of metal corrosion inhibitors to an aggressive environment in which metals are deployed in service has become a common practice due to the fact that metals lost essential properties to corrosion in such environments. Organic compounds containing heteroatoms (O, N, S, & P) are the most utilized as metal corrosion inhibitor. Metal surface protection is brought about by the adsorption of the organic compound through the heteroatom onto the metal surface resulting in the formation of hydrophobic films which barricade the corrosive agents present in the environment from the metal surface. Regrettably, organic compounds are expensive and the synthesis route is very tedious. Polymers have been investigated as metal corrosion inhibitor [15–18] to serve as possible replacement for organic corrosion inhibitors. However, it is found that most polymer materials studied [15,19–22] are moderate corrosion inhibitors. Several attempts such as copolymerizing, addition of substances that exert synergistic effect, cross linking, blending, and most recently incorporation of inorganic substances in nano size into the polymer matrix [23–25] have been made to improve the inhibition ability of polymers. The recent modification attempt (compositing) has been very promising. For instance, Atta et al. [26] evaluated the inhibitive ability of hybrid polymer composites based on silver nanoparticles towards pipeline steel in acid

\* Corresponding author.

E-mail address: [umoren@kfupm.edu.sa](mailto:umoren@kfupm.edu.sa) (S.A. Umoren).

inducing corrosive environment and found that the composite could offer up to 81.16% protection to the metal surface. Atta et al. [12] had earlier found that silver nanoparticles – polyvinyl alcohol composites were an effective corrosion inhibitor for carbon steel surface in HCl environment. Similarly, Sasikumar et al. [4] have reported that CeO<sub>2</sub> nanoparticles – polyaniline composites could serve as inhibitor for mild steel in HCl medium. Nevertheless, synthesis of well-dispersed and active metal nanoparticles composite still remains a challenge as some substances used as base are ineffective in adsorbing on the surface of the nanoparticles [27]. Previous reports [27–29] showed that well-dispersed and highly stabilized nanoparticles composite can be prepared using polymers. The most important feature of the polymer matrix required to prepare composites is the ability to form a metal chelate and its application as an ion stabilizing agent [24]. On this respect, we used poly(methacrylic acid) (PMAA), a cost effective polymer with multiple adsorption centers to prepare silver nanoparticles (AgNPs) composite.

This article reports on the in-situ preparation, characterization, and anticorrosion property of poly(methacrylic acid)/silver nanoparticles composites for mild steel in acid medium. The anticorrosion property of the composite was evaluated using chemical and electrochemical techniques complemented with surface analysis of the corroded steel samples without and with the composite. Hitherto we have reported PMAA to be a moderate inhibitor for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution [21].

## 2. Experimental

### 2.1. Chemicals and materials

Analytical grade AgNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> were procured from Sigma Aldrich. Natural honey (produced by honeybee, *Apis mellifera*) used as the reducing and capping agent in this study was obtained from the Department of Pharmacy, University of Uyo, Nigeria. Mild steel sheet of percentage composition as follows: C, 0.05; Mn, 0.6; P, 0.36; and Si, 0.03 was gotten from Ejison Resources Nigeria Limited, Calabar, Nigeria and the polymer (polymethacrylic acid) with number average molecular weight of 5000 g/mol was a product of Sigma Aldrich.

### 2.2. Preparation of the composite

The composite of PMAA/AgNPs was prepared in-situ by mixing aqueous solutions of the polymethacrylic acid (PMAA) and AgNO<sub>3</sub> solution. A synthetic method previously reported by Haiza et al. [7]. The preparation was actually a three phase synthesis. Firstly, different concentrations (50 ppm, 100 ppm, 500 ppm, 750 ppm, and 1000 ppm) of the PMAA were prepared in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. Secondly, the respective concentration of the polymer solution was used to prepare 0.001 M AgNO<sub>3</sub> solution. Thirdly, to every 100 cm<sup>3</sup> of the respective mixture, 5 cm<sup>3</sup> of natural honey which served as reducing and capping agent was added. The resulting mixtures were allowed to stand at room temperature for four days (96 h). The change in color of the mixture signalled the formation of the composites 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<sup>+</sup> was completely converted to elemental silver (Ag<sup>0</sup>).

### 2.3. Characterization

#### 2.3.1. Uv-visible measurements

The spectral analysis for the development of PMAA/AgNPs composite was 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. Sharp peak in the

range of visible region of the electromagnetic spectrum signals the presence of AgNPs in the composite.

#### 2.3.2. EDS analysis

Test samples were prepared by depositing a drop of colloidal solution on an aluminum grid sample holder and drying at room temperature. Elemental composition of the sample was analyzed with energy dispersive analysis of X-ray spectroscopy (EDS) coupled to the Scanning Electron Microscope (SEM) JEOL JSM-6610 LV.

#### 2.3.3. XRD analysis

PMAA/AgNPs composite solution was centrifuged at 10,000 rpm for 30 min. The solid residues of AgNPs were washed twice with double distilled water and then redissolved in absolute ethanol and evaporated to dryness at 353 K to obtain powder AgNPs used for X-ray powder diffraction measurements. The powder X-ray diffraction (XRD) patterns were recorded on Rigaku Mini-flex II system using nickel filtered Cu K $\alpha$  radiation  $\lambda = 1.5406 \text{ \AA}$  at 40 kV and 30 mA.

#### 2.3.4. TEM analysis

The morphological study of the shape and size of silver nanoparticles in the composite was done with transmission electron microscopy (TEM). The drop of aqueous polymer-silver nanoparticle mixture sample was loaded on carbon-coated copper grid and allowed to dry for an hour. The TEM micrograph images were recorded on JEOL instrument JEM-2100F instrument on carbon coated copper grids with an accelerating voltage of 200 kV.

#### 2.3.5. FTIR analysis

Fourier transformed infrared (FTIR) spectra of PMAA/AgNPs samples were recorded by Fourier transform infrared (Perkin Elmer 16F PC FTIR) spectrometer. The FTIR spectrum ranged from 4000 to 450 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> by making a KBr pellet with the solid residue of PMAA/AgNPs composite obtained by evaporating to dryness the colloidal solution of the prepared composite in a petridish at 323 K.

### 2.4. Corrosion studies

#### 2.4.1. Weight loss experiments

Mild steel specimens in triplicates were suspended freely in glass reaction vessels containing 200 mL of test solutions (0.5 M H<sub>2</sub>SO<sub>4</sub>; 50, 100, 500, 750 & 1000 ppm PMAA/AgNPs) at 303–333 K in a thermostated bath. The specimens were retrieved after 2 h progressively for 10 h, washed in 20% NaOH containing 200 g zinc dust first and then thoroughly under running water with bristle brush, rinsed severally in distilled water, dried with warm air and then re-weighed. The average weight loss, in grams, was taken as the difference in the weight of the mild steel specimens before and after immersion in different test solutions.

The corrosion rate (*CR*) (*mpy*) in the absence and presence of PMAA/AgNPs was calculated using Eq. (1) [21]:

$$CR(\text{mpy}) = \frac{3.45 \times 10^6 \times W}{\rho AT} \quad (1)$$

where *CR* is the corrosion rate, *W* is the average weight loss (g),  $\rho$  is the density of metal specimen (g cm<sup>-3</sup>), *A* is the surface area of the specimen (cm<sup>2</sup>) and *T* is the exposure time (hour). The inhibition efficiency ( $\eta\%$ ) of the composite was calculated from the expression:

$$\eta(\%) = \left(1 - \frac{CR_1}{CR_0}\right) \times 100 \quad (2)$$

where *CR*<sub>0</sub> and *CR*<sub>1</sub> are the weight losses of the coupons in the absence and presence of inhibitor, respectively, in the 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions at the same temperature.

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