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Styrene N-vinylpyrrolidone metal-nanocomposites as antibacterial coatings against Sulfate Reducing Bacteria

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ABSTRACT

Copolymer of styrene, and vinylpyrrolidone was prepared by various techniques. Different nanometals and nanometal oxides were added into the copolymer as antimicrobial agents against Sulfate Reducing Bacteria (SRB). The nanocomposite chemical structure was confirmed by using FTIR, ^{1}H NMR spectroscopy and thermogravimetric analysis (TGA). The biocidal action of these nanocomposites against the SRB was detected using sulfide determination method in Postgate medium B. The data indicated that the nanocomposites had an inhibitory effect on the growth of SRB and reduced the bacterial corrosion rate of mild steel coupons. The prepared nanocomposites have high inhibition efficiency when applied as coatings and show less efficiency when applied as solids or solution into SRB medium. The copolymer and its nanocomposites effectively reduced the total corrosion rate as determined by total weight loss method.

1. Introduction

Iron materials are corroded in aqueous environments, not only by purely chemical or electrochemical reactions but also by microorganisms or the products of their metabolic activities including enzymes, organic and inorganic acids as well as volatile compounds such as hydrogen sulfide. This process is termed Microbiologically Induced Corrosion (MIC) [1].

The direct cost of the MIC is estimated to be $30–50 billion per year around the world. In the UK, it was suggested that 50% of corrosion failures in pipelines involved MIC [2] and the replacement costs for bio-corroded gas pipes were recently reported to be 250 million per annum [3]. Also, the American industries spend $1.2 billion annually on biocidal chemicals to fight MIC. The MIC may account for 15 to 30% of corrosion related pipeline failures in the natural gas industry as a whole. The petroleum industries in Egypt suffer from MIC. It was estimated that one company (Gulf Suez Petroleum Company, GUPCO) spends more than one million $/year to combat MIC [4].

Bacterial activity, mainly Sulfate Reducing Bacteria (SRB) activity, is responsible for over 75% of the corrosion in productive oil wells and for more than 50% of the buried pipeline and cable failure. It is also deem an agent for extensive corrosion of drilling and pumping machinery and storage tanks [5].

The Sulfate Reducing Bacteria (SRB) represent a large group of anaerobic (oxygen free) organisms which play an important role in many biogeochemical processes. They are widely distributed in the environment particularly in petroleum reservoirs and oil production facilities [6].

The two most common species of these bacteria are *Desulfovibrio desulfuricans* and *Desulfotomaculum nigrificans*. These organisms favor an anaerobic environment.

The presence of SRB in oil environments was readily recognized as responsible for the production of hydrogen sulfide, which is a toxic and corrosive gas responsible for reservoir souring (increase sulfur content) [7] and a variety of other environmental problems which have economic consequences. SRB decreases the quality and value of oil, and natural gas. It causes corrosion of metal surfaces, and contributes to plugging of reservoirs due to the precipitation of metal sulfides in the fluid flow paths [8–10]. As the detrimental effects of SRB in the oil industry are significant, they have been the most commonly studied group in that realm [1].

Considerable efforts have been directed toward controlling SRB growth and corrosion inhibition induced by its activity. Corrosion inhibition is a process to slowdown the corrosion reaction by adding substances in small amounts, to decrease the rate of attack by these bacteria on a metal [11]. A number of methods for controlling SRB sulfide production in different oil and gas facilities have been utilized using the biocides [12].

Although biocide treatments are widely used to decrease biofouling and MIC in steel pipes and in closed systems, the results are far

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from satisfactory. This is because biocides are much less effective against sessile microorganisms with biofilms compared to their effectiveness against planktonic populations. Furthermore, biocide resistance may be developed as its action is reduced by dilution [12]. Molica and Trevis [13] reported that the presence of SRB biofilm (sessile) SRB on metal surface results in a higher corrosion rate compared to the corrosion rate due to planktonic bacteria alone. An important method to control bio-corrosion is by preventing materials from biofilm formation. Currently, the environmental friendly antifouling coating attracts high interest.

The use of polymeric materials with antimicrobial properties gains an increasing interest from both academic and industrial point of view [14]. In addition, antimicrobial polymers usually present longer-term activity. During the last decade there have been notable reviews in the field of polymeric materials with antimicrobial activity, which have considered definite families, aspects and/or applications [15–18].

Antimicrobial polymers which contain silver [19] capture attention because of their novelty as a long-lasting biocidal material with high temperature stability and low volatility [19]. Silver is a metal known for its broad-spectrum antimicrobial activity against Gram-positive and Gram-negative bacteria, fungi, protozoa and certain viruses [20], including antibiotic-resistant strain [21,22]. It has been suggested that impregnation of silver into a coating can be more effective than direct surface coating alone, since surface silver can be readily deactivated by protein anions [21,23]. This impregnation of silver ions (SI) would also be beneficial in protecting the inner and outer metal surfaces against bacterial attachment [24]. Copper has a bacterio-static effect that makes it useful in self-disinfecting paints [25]. ZnO nanoparticles also were reported to act as strong antimicrobial agents [26,27].

Styrene and its copolymers have high tendency for film forming and can be used in many coating applications [28–30]. N-vinylpyrrolidone is known to form complexes with metal and metal oxides. It is extensively used as surface capping agent in the preparation of nanoparticles [31–34] so its incorporation with styrene in a copolymer could be highly beneficial in the proposed antibacterial coatings.

The present paper describes optimized conditions for formation of different metal nanocomposites of styrene co N-vinylpyrrolidone by using Pickering microemulsion polymerization. The resulting nanocomposites will be investigated to control the growth of Sulfate Reducing Bacteria (SRB) and biofilm accumulation in order to reduce corrosion rate.

2. Experimental

2.1. Materials

2.1.1. Chemicals

N-vinylpyrrolidone (VP), styrene (ST) monomers, sodium hydrogen sulfate ($NaHSO_4$) and potassium persulfate ($K_2S_2O_8$) were used as initiator, sodium lauryl sulfate (SLS) was used as surfactant, zinc oxide nanopowder (<100 nm, 99% metal basis), copper (II) oxide nanopowder (<50 nm) and silver oxide (<100 nm, reagent plus, 99%). All chemicals were supplied from Aldrich.

2.1.2. Microorganisms

SRB was isolated from Garden Soil of the National Research Center, Egypt (NRC).

2.1.3. Media

Postgate medium B (Postgate, 1984) is composed of (g/l): KH_2PO_4, 0.5; NH_4Cl, 1.0; $CaSO_4$, 1.0; $MgSO_4 \cdot 7H_2O$, 2.0; sodium lactate, 3.5 g; yeast extract, 1.0; ascorbic acid, 1.0; thioglycolic acid, 0.1; $FeSO_4 \cdot 7H_2O$, 0.5; and tap water, 1 l. The pH value was adjusted to 7–7.5 by 1 N NaOH.

2.1.4. Mild steel coupons (size 1 × 1 cm)

The mild steel was of type DIN 1762 (ASTM 525 A) having the following nominal analysis (% w/w): C, 0.15; Mn, 0.6; Si, 0.3; and Cu, 0.02; however, the actual analysis was made in the Central Metallurgical R&D Institute, CMRDI (Egypt) and revealed the following composition (% w/w: Co, 1.53; Si. 0.205; S, 0.029; C, 0.120; Mn, 0.502; Cr, 0.006; Mo, 0.003; Cu, 0.009; Al, 0.030 and Fe, 97.566). Mild steel coupons were prepared, finished and placed in desiccators until use [35].

2.1.5. Emery papers

Emery papers, numbers 120 type 35 (blue cloth made in Finland), 180, 240 and 320 type PSF HERMES (silicon carbide finishing paper) made in Germany, and 400 and 600 type VSM cp 918 made in Germany, were used for surface polishing of the mild steel coupons.

2.2. Synthesis of (styrene co N-vinylpyrrolidone)

2.2.1. Bulk method

Bulk copolymerization was carried out in sealed glass flask containing monomers (25% styrene and 75% N-vinyl-2-pyrrolidone by weight) and 0.3% benzoyl peroxide as the initiator. The reaction mixture was heated at 80 °C for about 3 h. The resulting solution was poured into a large excess of n-hexane to precipitate the polymer. The precipitated polymer was vacuum filtered, air dried overnight and dried in a vacuum oven at 80 °C for 24 h [36–38].

2.2.2. Solution method

The reaction was carried out in a flask connected with a condenser system. 1/3 molar ratio between (St) and (VP) was placed in 20 ml THF and 0.3% of benzoyl peroxide as an initiator. The reaction was refluxed for 3 h. The resultant solution was poured in large excess of water to precipitate the polymer. The precipitated polymer was vacuum-filtered and washed several times with methanol and water then dried at 65 °C for 10 h till constant weight.

2.2.3. Microwave assisted method

1/3 molar ratio of (St) and (VP) and 0.3% benzoyl peroxide (as initiator) were placed in a sealed flask. The reaction was carried out inside a commercial microwave for 10 min with power 100 W. The resulting polymer was precipitated by pouring the reaction mixture in large excess of water. The precipitated polymer was vacuum-filtered and washed several times with methanol and water then dried at 65 °C for 10 h till constant weight.

2.2.4. Emulsion polymerization

The reaction was carried out in a flask connected to a condenser system. The reaction mixture was 1/3 molar ratio of (St) and (VP), 18 g water, 0.5% initiator (2/1 ratio between $NaHSO_4$ and $K_2S_2O_8$) and 4% surfactant. The reaction was carried out at 100 °C for 3 h. The resultant solution was poured in large excess of methanol to destroy the emulsion and then slowly heated to form large particles that can be filtered. The precipitated polymer was vacuum-filtered and washed several times with methanol and water then dried at 65 °C for 10 h till constant weight.

The polymer nanocomposites were prepared using Pickering emulsion polymerization stabilized by adding inorganic nano-sized particles. Theoretical and experimental researches of Pickering

Table 1
Average molecular weight and yield of the prepared copolymers.

Technique	Mw	Yield
Bulk	28,723	40%
Solution	8411	20%
Microwave	11,582	85%
Emulsion	64,581	50%