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Corrosion inhibition of mild steel in acidic medium by polyacrylamide grafted Guar gum with various grafting percentage: Effect of intramolecular synergism

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ABSTRACT

Polyacrylamide grafted guar gum (GG-g-PAM) with various grafting levels has been tested as potential green inhibitor against corrosion of mild steel in 1 M HCl. Upto 86% grafting, grafted copolymer maintains inhibition efficiency higher than 90% for about 50 h of exposure. Grafted polysaccharide behaves as mixed type inhibitor and forms an inhibitive layer on the metal surface following Langmuir adsorption isotherm. GG and PAM moieties are found to synergistically influence each other on adsorption and subsequent corrosion inhibition. FTIR spectroscopy reveals the possible binding sites of grafted polymer during adsorption on metal surface.

1. Introduction

Combating metal corrosion in acid medium is a long standing endeavor of scientists and engineers. Application of suitable inorganic and organic inhibitors is one of the most effective remedial measures in this regard. Use of many inorganic inhibitors, particularly those containing phosphate, chromate and other heavy metals are now being gradually restricted by various environmental regulations. Many organic inhibitors are also been reported as toxic and environmentally harmful. As a result, scientists are now examining the other possible avenues, and designing of environmental friendly bio-compatible green corrosion inhibitors has got tremendous impetus. Among many green inhibitors, natural products such as plant extract, amino acids, proteins and bio-polymers have been reported to have the potentiality of efficient corrosion inhibitors [1–16]. Polysaccharides form a special class of bio-polymers. A few polysaccharides have a gelling ability by themselves at low concentration, whereas, a lot of non-gelling polysaccharides are used as a thickener and stabilizer [17]. Apart from this, they are also long been known for various biological activities like, anti-tumour properties, anti-oxidants, and many others [18]. In recent years, some polysaccharides, including gums and chitosan have found a new role as corrosion inhibitors for metals in acidic, alkaline, as well as in saline environment [9–16]. Chemical modification of polysaccharides has resulted into much improvement in their corrosion inhibition efficiency [13–16]. Srivastava et al. have shown the inhibitive effect of polyacrylamide grafted Fenugreek mucilage [13] and Okra mucilage [14] toward corrosion of mild steel in acidic medium. Grafting of acrylonitrile, acrylamide or methyl methylmethacrylate on various gums and other polysaccharides employing conventional chemical method, as well as by microwave assisted synthesis has been reported [19–25]. Grafting of gum by these synthetic polymers normally brings about some modification of the physical properties of gum, like enhancement of hardness, tensile strength and thermal stability [19–25]. Biodegradable characteristic of the parent gum is retained after grafting.

Chemically, guar gum (GG) is a high molecular weight natural polysaccharide consisting of a (1 → 4)-linked β-D-mannopyranose backbone with branch points from their 6-positions linked to α-D-galactose (i.e. 1 → 6-linked-α-D-galactopyranose). There are between 1.5 to 2 mannose residues for every galactose residue [26]. In 1 M H_2SO_4, guar gum has been reported to provide good corrosion inhibition toward C-steel [11]. In this communication, we have focused on the effect of percentage grafting (%G) on the inhibition property by polyacrylamide grafted guar gum (GG-g-PAM) toward corrosion of mild steel in 1 M HCl.

2. Experimental

2.1. Inhibitor preparation and characterization

GG-g-PAM is prepared employing reported procedure (Scheme. 1) [22,23]. A brief description is given here. One g of GG is

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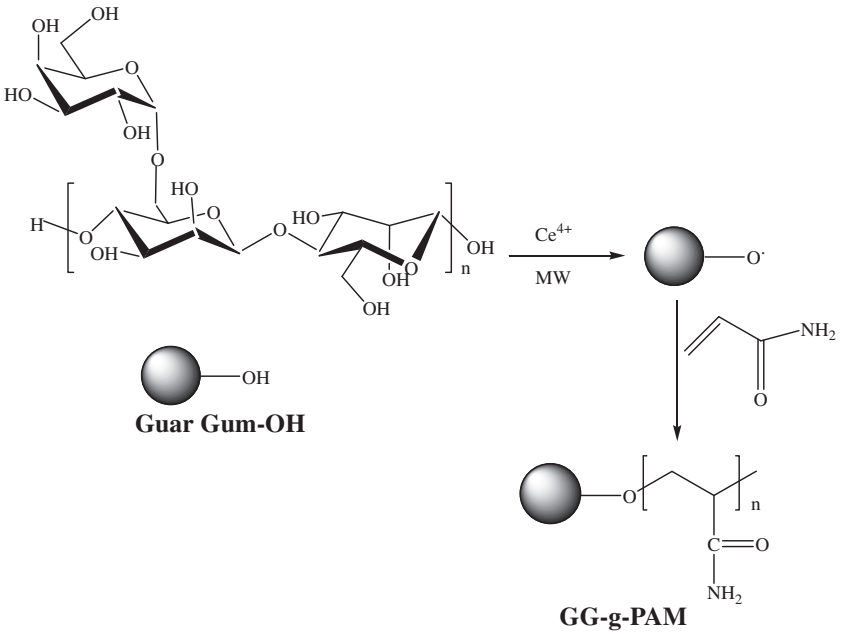

Scheme 1. Mechanistic pathway for synthesis of GG-g-PAM.

dissolved in 40 mL distilled water in a 1000 mL borosil beaker, and is made homogeneous by stirring. 1.5 g of acrylamide (AM), dissolved in 10 mL distilled water is added into the GG solution with constant stirring for 15 min, followed by addition of required amount of ceric ammonium sulfate (CAS). Prior to addition of the initiator (CAS), a few drops of concentrated HCl are added. The solution so obtained is irradiated by a domestic microwave oven (800 W of power) for 3 min. Different concentration of CAS is used to prepare various percentage of grafted GG keeping the other factors same. The gel like mass is then cooled by placing the reaction vessel in cold water, and then poured into excess of acetone with constant stirring. The precipitated grafted copolymer is filtered and washed with acetone and alcohol water mixture. The residue after drying in oven for 2 h at temperature 70–80 °C, is kept in a vacuum desiccator to obtain a constant weight. It is proposed that some of the free —OH groups of mannopyranose backbone convert into —Ȯ radicals by the action of the free radical initiator and the microwave irradiation, which in turn, reacts with the AM monomer resulting into GG-g-PAM (Scheme 1). The percentage grafting (%G, Eq. (1)) as obtained for different concentrations of CAS, are summarized in Table 1 [22,23].

$$\%G = \frac{mass\ of\ the\ grafted\ product - mass\ of\ guar\ gum\ taken}{mass\ of\ guar\ gum\ taken} \times 100 \qquad (1)$$

It is observed that in absence of AM, 0.8 g of GG is recovered from 1 g of GG after performing the whole process. %G for each reaction between GG and AM (entry 2–5 in Table 1) is calculated taking into consideration of the amount of recovered GG (entry 1 in Table 1). It is noteworthy that without any GG, AM does not produce any precipitate of PAM. This is because the maximum concentration of CAS used in this study is low enough to rule out the possibility of formation of any polyacrylamide homopolymer. Grafted polymer is characterized by FTIR (Thermo-Nicolet iS10 IR spectrometer in the range 4000–400 cm^{-1}). The FTIR spectra of GG, PAM and GG-g-PAM are shown in Fig. 1(A–D) and the characteristic frequencies are tabulated in Table 2. All the characteristic absorption bands for GG and PAM are present in the FTIR spectrum of GG-g-PAM, suggesting proper grafting of PAM on the GG backbone [22–25].

As the molecular weight of GG-g-PAM cannot be ascertained accurately due to its inherent molecular complexity and the possibility of partial hydrolysis in acid solution on prolonged exposure, concentration of the inhibitor is expressed in terms of ppm by weight.

2.2. Metal coupons preparation

Test specimens are cut from a commercially available mild steel rod (wt% composition: 0.22 C, 0.31 Si, 0.60 Mn, 0.04 P, 0.06 S and the remainder iron). The cross-sectional surface is ground with different grade emery papers (400, 600, 800, 1200 and 1600), washed with water, rinsed with acetone, again washed thoroughly with doubly distilled water for many times and used as the working electrode in electrochemical measurements.

2.3. Electrochemical measurements

Potentiodynamic polarization and electrochemical impedance measurement are done by conventional three-electrode system (model: Gill AC, ACM Instruments, UK) consisting of mild steel

Table 1
Synthetic details of microwave-assisted grafting.

System	wt. of Guar gum (g)	wt. of Acrylamide (g)	Wt. of CAS (g)	Final wt. of grafted polymer (g)	Times of irradiation (min)	%G
GG	1	–	0.005	0.80	3	0
GG-g-PAM 1	1	1.5	0.005	0.86	3	7.5
GG-g-PAM 2	1	1.5	0.01	1.00	3	25
GG-g-PAM 3	1	1.5	0.05	1.49	3	86
GG-g-PAM 4	1	1.5	0.075	1.55	3	93
GG-g-PAM 5	1	1.5	0.10	1.64	3	105