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Research Article

INVESTIGATION OF A BIOPOLYMER BLEND AS CORROSION INHIBITOR FOR API5LX60 MILD STEEL IN ACID MEDIUM

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Abstract

Acid corrosion is a severe threat to wells and crude oil transportation pipes in the oil and gas industry across the world. Many compounds, including inorganic complexes, organic molecules, and rare earth elements, act as corrosion-preventing agents. However, most of them are not effective environmentally and has low shelf-life. As a result, environmentally friendly, biodegradable, and green corrosion inhibitors have become a need of the hour. This report presents the initial investigation of the corrosion inhibitory property of a biopolymer blend namely Polyvinylalcohol-histidine blend for API5LX60 mild steel in 1N HCl test solution. The blend was synthesized with 95-99% yield and characterized using UV–visible, FTIR, and ^{1}H NMR spectroscopy. Gravimetric Analysis showed 90-95% corrosion inhibition efficiency, which makes it a potential corrosion inhibitor for mild steel.

Keywords: API5LX60 steel; Corrosion inhibitors, Poly(vinylalcohol-histidine); Weight-loss measurement.

Introduction:

Corrosion is a natural process wherein a metal deteriorates on interacting with its surroundings. Like a stealthy cancer, corrosion destroys the surface of metals and alloys in various environments. Acid solutions are more commonly employed in various industries [1-4]. Even at low concentrations, acidic solutions have sufficient strength to produce unintended corrosion in metals and alloys [5-9]. The oil and gas industries also confront a major risk from corrosion brought on by acidic medium in certain areas of their wells and pipelines used to transport crude oil. These pipelines make extensive use of API5LX60 steel because of its easy accessibility and adaptability [10]. Several mitigation techniques are used to prevent corrosion in API5LX60 carbon steel where inhibitor use being the most prominent [10-11]. Organic or inorganic compounds are typically used as industrial corrosion inhibitors. While inorganic compounds function as anodic inhibitors and the metallic atoms encased in the film enhance their corrosion resistance, organic inhibitors impose their inhibition through adsorption [12-16]. However, the majority of these conventional inhibitors pose a risk to both individuals and the environment [17-21]. Therefore, the developments of nontoxic inhibitors that resist corrosion to the greatest extent while having the least negative effects on both humans and the environment have gained more attention [14]. The degree of inhibition is determined by variables such as functional groups, electronic structure, and steric factors. The polymer materials provide multiple adsorption sites for metal surface bonding, resulting in a higher inhibition efficiency compared to their corresponding monomers [12]. Poly(vinyl alcohol) (PVA) is a polyhydroxy water-soluble biodegradable polymer having exceptional film-forming, adhesive, emulsifiability, spinnability, and biocompatibility qualities that makes it a good candidate material for metal corrosion protection. Depending on the metal–acid system, polyvinyl alcohol has been reported to have a 50–70%

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inhibition efficiency against corrosion [22-28]. In recent years, biopolymers have received a lot of attention in corrosion inhibition research as they are easily accessible, biocompatible, non-toxic, cost-effective, and have no side effects [29-34]. Amino acids are also excellent corrosion inhibitors for metals and alloys in a range of electrolytes due to the presence of functional groups, heteroatoms, and numerous bonds in them [12]. This paper reports the initial investigation of the corrosion inhibitory property of a biopolymer blend namely, Polyvinylalcohol-histidine (PVA- histidine) blend for API5LX60 mild steel in 1N HCl test solution. The characterization of the biopolymer blend was performed using UV–visible, FTIR, and ^{1}H NMR spectroscopy. The corrosion inhibition efficiency was measured by employing the Gravimetric weight loss coupons method.

Materials and Methods

Synthesis of Poly(vinyl alcohol- Histidine) Blend

10% PVA solution in 0.5 M oxalic acid was combined with 1% L-histidine solution and the mixture was cooled to 0–5 ^{o}C. 1% ammonium persulphate solution was prepared in 0.5M oxalic acid, and then the freshly prepared ammonium persulphate was added dropwise to the cold mixture with constant stirring. Using a magnetic stirrer, the reaction mixture was mixed well for two hours and then, refrigerated for 48 hours. After 48 hours, ammonia solution was used to make the solution slightly alkaline and the formed polymer blend was precipitated by the addition of acetone. The polymer blend was characterized by UV-visible, FTIR, and ^{1}H NMR analysis.

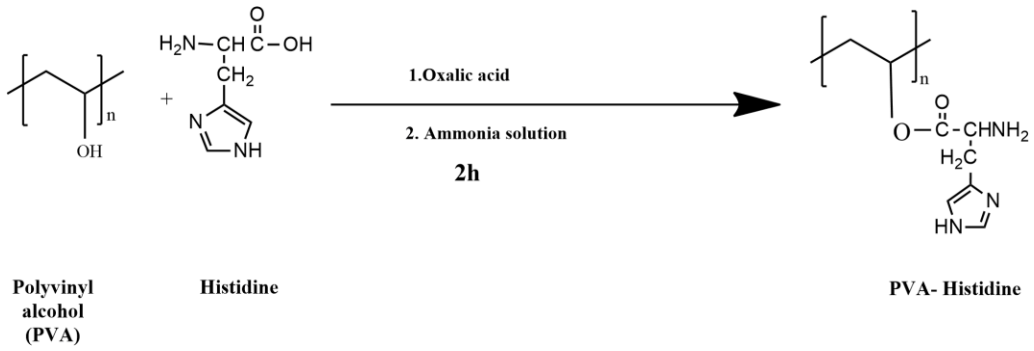


Fig. 1: The PVA- Histidine blend was synthesized, as represented in Scheme 1.

Corrosion Studies

The API5LX60 steel test samples with composition C = 0.28, Mn = 1.4, P = 0.3, S = 0.3, V-Nb = Ti ≤ 15%, were investigated in five inhibitor concentrations (1, 2.5, 5, 7.5, 10 %), prepared in acetone and water. Steel coupons with dimensions of 1.5 cm ×1 cm × 0.6 cm and exposed surface area of 1.5 cm^{2} were used for corrosion inhibitory studies. Steel coupons were polished 5-6 times with emery paper, washed with double distilled water and acetone, and dried at 50- 60 ^{0}C. The 1N HCl test solution was prepared in distilled water. In a stationary state, the polymer blend was examined for its ability to prevent the corrosive attack of HCl solution on API5LX60 carbon steel. Since acids like HCl and H2SO4 are utilized in the oil and gas industry for pickling, cleaning, and other petrochemical processes, it is expected that they come into touch with metal surfaces while they are in a stationary state. Therefore, these corrosion inhibitory experiments were carried out in environments with stationary solutions.

The test steel coupons were immersed in 50 mL uninhibited 1N HCl at 298 K and left for 18 hours prior to the weight loss measurements, and then the samples were coated with different amounts of inhibitor concentrations. % Inhibition efficiencies (IE or η) and corrosion rate (CR) for various inhibitor concentrations were measured using equations (1) and (2) given below [10].

$$\%\eta = \frac{\Delta W}{W} \times 100$$

where, ΔW = W-Wi; W = average weight loss in uninhibited condition, and Wi = average weight loss inhibited condition.

$$\mathrm{CR} = \frac{\mathrm{k} \times \Delta \mathrm{W}}{\mathrm{A} \times \mathrm{t} \times \mathrm{d}}$$

where, K = constant ($8.76X10^4$) in mm/yr; A = Metal sample surface area (in cm^2); t = immersion time (hours); d = density of metal (g/ cm^3); ΔW = weight loss difference of the sample before and after immersion (g).

PEN type pH meter (pH- 009 (I) A) was used for the pH studies of the test solutions. To investigate the UV-visible spectroscopy of the test solutions, a SHIMADZU UV-visible spectrophotometer (Model UV1900) with a wavelength range of 200-800 nm, a medium scan rate, and a light source k of 340.8 nm was used. A digital conductometer (HANNA Instruments) was employed for conductance measurements.

Results and Discussion

Characterizations of PVA - Histidine blend FTIR Spectroscopy

For FTIR analysis, the sample was prepared in liquid form with NaCl disc. The FTIR spectra of PVA-Histidine is depicted in Fig. 2. The FTIR spectrum of the blend showed the characteristic absorption bands for C-N, C-H, N-H, C=O, C=N, and C-O peaks. The peaks at 1080 cm^{-1}, 1500 cm^{-1}, and 1150 cm^{-1} are associated with the C-N, N-H, and C-O bending respectively. Again, the stretching vibrations of C=O, C=N, and N-H are found at 1680 cm^{-1}, 1690 $cm^{-1,}$ and 3300 cm^{-1} correspondingly.

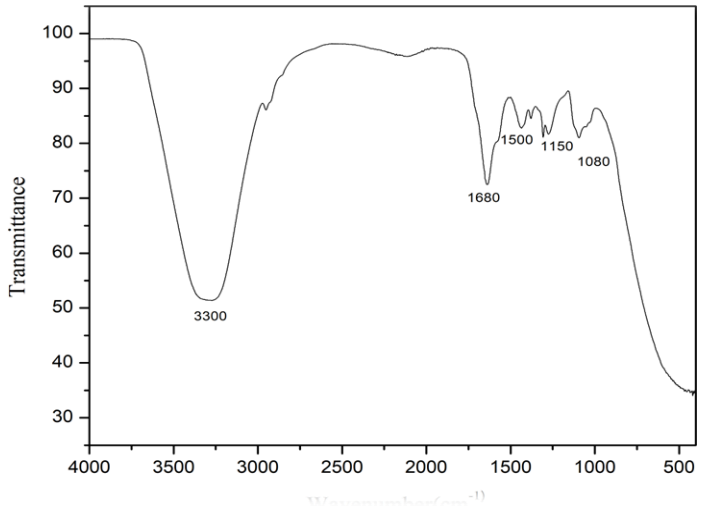
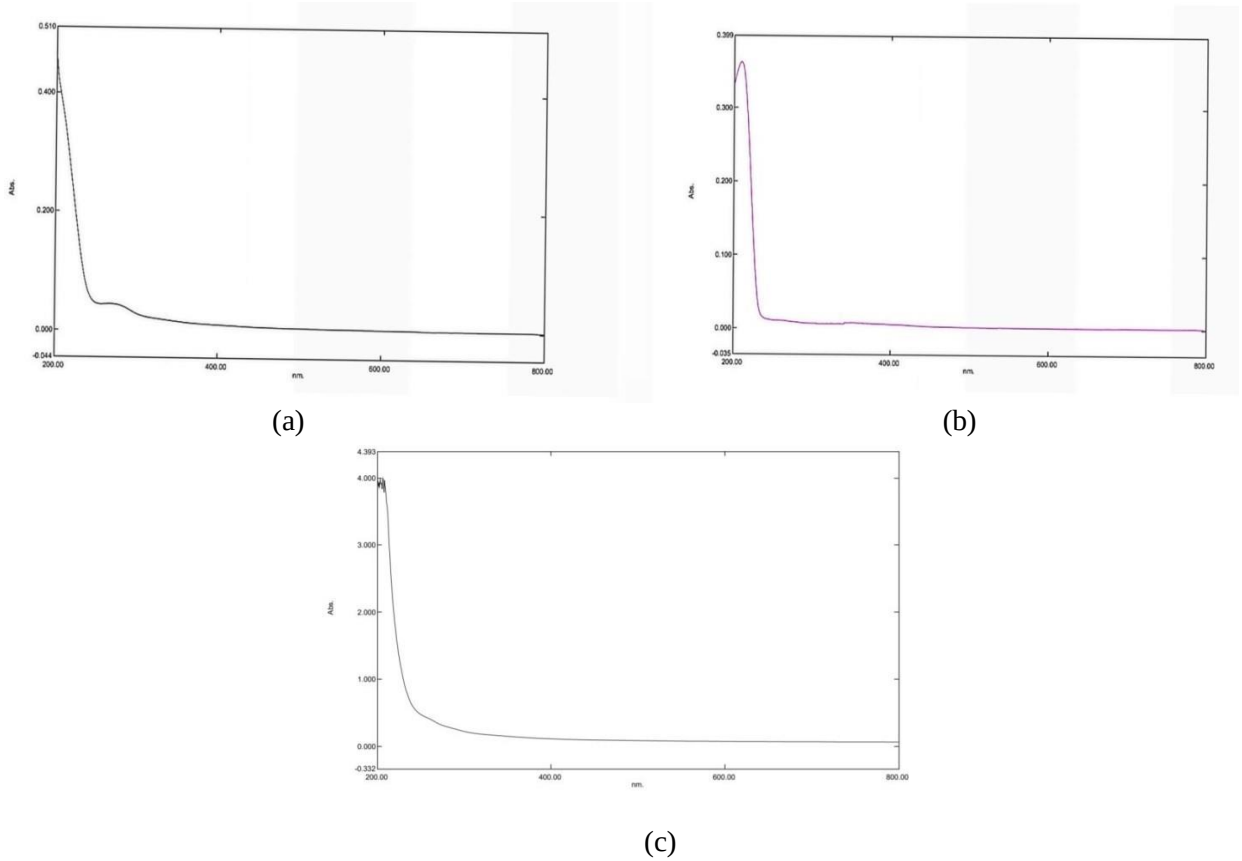


Fig 2: The FTIR spectra of PVA-histidine

UV-Visible Spectroscopy

The UV-visible spectra for the PVA-Histidine blend is different from that of the PVA and histidine spectra, which is prominent from Fig 3 (a), (b) and (c)



(a) (b)

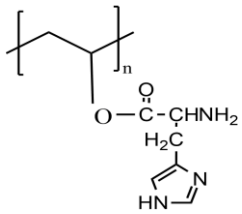
(c)

Fig. 3: UV- Visible spectra for (a) PVA (b) Histidine (c) PVA- Histidine blend

NMR spectroscopy

^{1}H NMR chemical shift values of the PVA- Histidine blend are presented in Table 1, which showed the formation of the C-O bond due to the blending of the PVA and Histidine molecules.

Table 1. Chemical Shift values of the PVA-Histidine blend

Structure	System	Chemical shift (500 MHz, D2O, δ ppm)
	Poly(vinyl alcohol-histidine)	2 (s, 2H); 3.04 (d, 2H); 3.88 (t, 1H); 6.80 (d, 1H); 7.44 (d, 1H); 13.4 (s, 1H); 4.0 (m, 1H); 4.8 (m, 2H)

Gravimetric Weight Loss Measurements

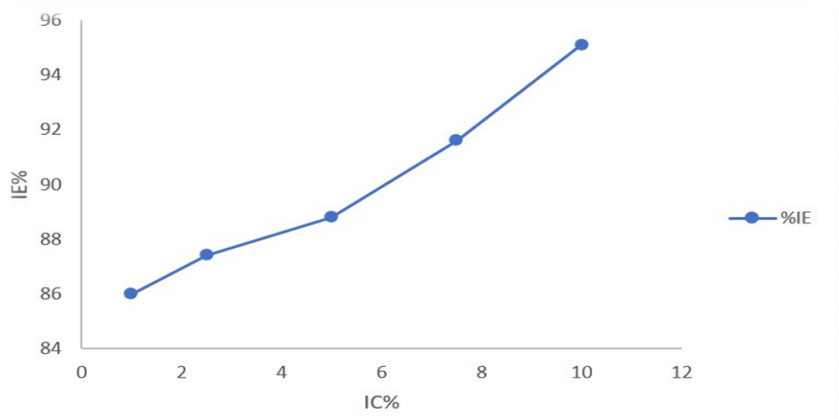
During the corrosion process, mild steel deteriorates, resulting in base metal loss. In order to measure the rate of corrosion, it is a conventional technique to monitor the mass loss of the steel coupons both before and after acid treatment. The weight loss for the API5LX60 steel coupons in 1N HCl was calculated in presence and absence of synthesized inhibitor at concentrations of 1%, 2.5%, 5%, 7.5% and 10% for a 48- hour immersion period. Weight loss results above 10% showed no variation in the % Inhibition Efficiency. Hence, the optimal concentration was stabilized at 10%. The results are

summarized in Table 2, which shows that applying the inhibitor blend considerably lowers the rates of corrosion.

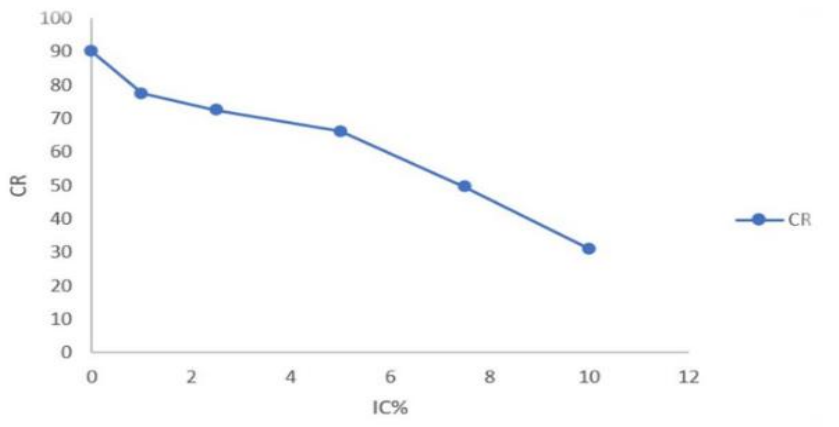
Table 2. Gravimetric analysis results of the corroded test samples.

Inhibitor Concentration (in %)	**Average Weight Loss (in g)**	**Corrosion Rate (mmpy)**	**% Inhibition Efficiency**
Blank	1.43	90.13	-
1	0.20	77.49	86
2.5	0.18	72.46	87.41
5	0.16	66.12	88.8
7.5	0.12	49.59	91.60
10	0.07	30.99	95.10

Further, the results specified that the corrosion rate reduced as the inhibitor concentration (IC) increased. This implies that the polymer blend attaching to the metal surface, reduces the direct contact of metal with the corrosive environment. The inclusion of heteroatoms, bigger molecular size, and linearity in the polymeric chain are responsible for the higher performance of the PVA-histidine blend. Again the % Inhibition efficiency (%IE) seemed to increase with the concentration increase of the PVA-Histidine blend. This change in corrosion rate (CR) and concentration for the inhibitor blend is depicted in Fig. 4(a) and (b).



(a)



(b)

Fig. 4(a): Plot of IE% vs. IC (b) Plot of CR vs. IC

pH, Conductance Determination, and UV–Visible Spectroscopic Studies on test solution

The pH measurement observations in Table 3 exhibited that after dipping of the steel sample coated with inhibitor, the pH of the test samples remains constant. This implies very low dissolution of the inhibitor compound in the HCl solution causing minimal pH variation.

Table 3. pH studies of the test solution

Inhibitor Concentration (%)	pH before immersion of sample	pH after immersion of sample
Blank	1.4	1.5
1	1.4	1.2
2.5	1.4	1.2
5	1.4	1.2
7.5	1.4	1.2
10	1.4	1.2

The Conductance results are showed slight variation with each other, which indicated the least dissolution of inhibitor in the test solutions. The conductance measurement data are tabulated in Table 4.

Table 4. Conductance studies of the test solution

Inhibitor Concentration (%)	Conductance before immersion of sample (mS)	Conductance after immersion of sample (mS)
Blank	1	12.08
1	1	17.1
2.5	1	16.42
5	1	15.67
7.5	1	15.38
10	1	12.68

UV-visible spectroscopy of the test solutions were performed after immersion of the coated samples, which is portrayed Fig. 5 below.

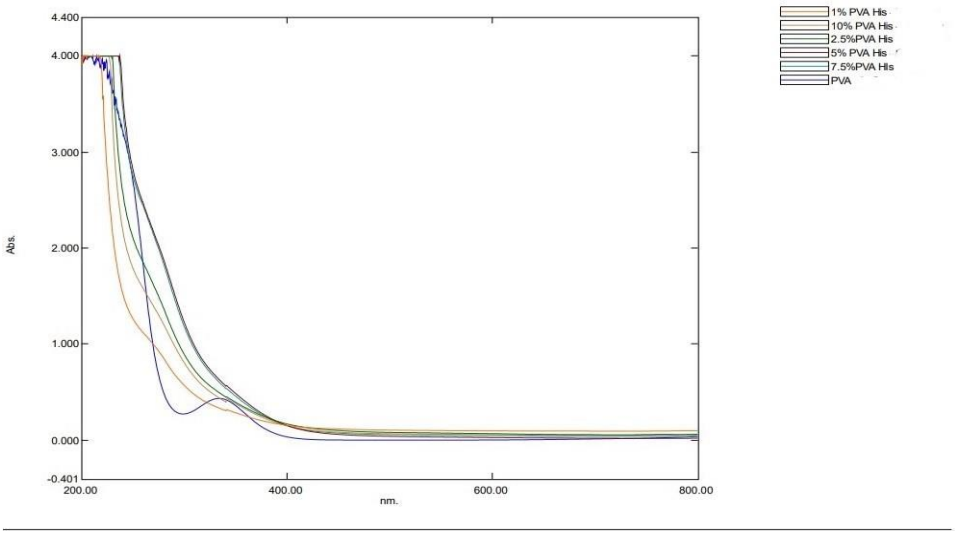


Fig. 5: UV-visible spectra for 1N HCl solution for different inhibitor concentrations

The plot of Absorbance Vs Wavelength affirmed minimal dissolution of the five different inhibitor concentration API5LX60 steel samples in the test solutions which implied the high stability of the blend.

Conclusion

The biocompatible, environmentally benign, and non-toxic qualities of amino acids prompted this study into its use as a corrosion inhibitor in oil wells and transmission pipelines. In this paper, biopolymer blend namely Poly(vinyl alcohol- histidine) was synthesized with good yield and its anticorrosion properties in five different concentrations for API5LX60 steel used in the oil and gas sectors was studied. The highest inhibition efficiency of 95.10% was observed at 10% inhibitor concentration. Inhibition efficiencies were found to increase with increasing inhibitor concentration up to an optimal value i.e. 10%. A decrease in the corrosion rate was also prominent from the Gravimetric Weight loss technique. pH, conductance, and UV–visible spectroscopy analysis of the test solution with and without inhibitor-coated steel revealed inhibitor dissipation in minimal amount in test solutions. Thus, it can be concluded that PVA- Histidine blend is a novel and potential inhibitor to be employed in the oil industry transportation pipelines as green corrosion inhibitor. This study further opens up room for the corrosion studies of other such blends which may spike up the % Inhibition Efficiency to a remarkable level.

Acknowledgement:

NA

Conflict of Interest

The authors declare no conflicting interests.

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