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Synthesis of water soluble Polyvinyl alcohol-based Terpolymer and Evaluation of corrosion inhibition property on Mild steel in hydrochloric acid

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Abstract

A grafted terpolymer was synthesized using polyvinyl alcohol, sodium salt of vinyl sulphonic acid and acrylic acid. The synthesis was carried out in an aqueous medium containing 0.5:1:2 of monomer feed ratio comprising polyvinyl alcohol, acrylic acid and sodium salt of vinyl sulphonic acid respectively. The polymerization was monitored at different temperatures and time intervals for determining the optimum reaction conditions. The terpolymer was characterized using FTIR. The corrosion inhibition properties of the terpolymer were studied for mild steel in hydrochloric acid. The effect of change of vinyl sulphonic acid content in the terpolymer composition on the corrosion inhibition was also studied. The anticorrosive properties of the synthesized terpolymer were evaluated by gravimetric method and electrochemical method at room temperature.

Keywords: PVA, Terpolymer, Mild steel, Acid corrosion, polarization studies, impedance spectroscopy

Introduction

Corrosion inhibition of metal is of particular interest for metal industries working in corrosive environment. Hydrochloric acid and sulphuric acid are the preferred mineral acids for pickling, scale removal, and cleaning. As the aggressive anions of acid are coming in direct contact with the metals, this form of corrosion is a serious problem than the general form of corrosion[1]. Apart from the basic properties like hetero atoms, pi-bonds, functional groups, conjugated systems or active centres of the inhibitor which could facilitate the adsorption, the inhibitor must be environmentally-benign as there is an alarming threat for nature and human life by hazardous chemicals.

Polymers are found to be effective inhibitors, because of the superior properties compared to their monomer analogues. The long carbon chain linkages, functional groups and larger size of the polymer moieties aid themselves to anchor strongly on the metal surface. Moreover the cost effectiveness of the polymer inhibitors is a practical advantage to be considered. Synthetic polymers like Polyacrylamide[2], polyacrylic acid[3], polyvinyl alcohol[4], polyethylene glycol[4], polyvinyl pyrrolidone[5]etc., and natural polymers like carboxymethyl cellulose[6], pectin[7], gum Arabic[8], hydroxyl ethyl cellulose[9], amino acids [10] etc., have been reported as prominent corrosion inhibitors in the recent years. To tailor polymers with some special properties, copolymers[11], terpolymers[12,13], quadripolymers[14], grafted polymers[15], and composites[16-18] were synthesized and their corrosion inhibition performance has been evaluated.

In the present work a terpolymer (PVA-g-poly(AA-VSA) has been synthesized by grafting poly(acrylic acid-co-vinyl sulfonate) (poly(AA-VSA) onto the polyvinyl alcohol (PVA) matrix and the inhibition performance was evaluated. The monomers were selected such that there is a combination of two hetero atoms viz. oxygen and sulphur, along with the water soluble polyvinyl alcohol. Polyvinyl alcohol is a universally accepted eco-friendly polymer which facilitated the water solubility of the synthesized terpolymers. Polyvinyl sulphonic acid sodium salt (PVSA) contains negatively charged sulphonic acid groups and is a blood-compatible material used in several medicinal applications[19]. Usually grafting of polyacrylic acid or polyacrylamide onto the polyvinyl alcohol was carried out to produce water-insoluble/stimuli-sensitive hydrogels, and exploited for use in adsorption and drug delivery systems. For the first time we are reporting a water-soluble grafted polymer containing PVA, PAA and PVSA which could be used for corrosion inhibition.

Methodology

Synthesis of the polymer: 0.5 g of PVA having a molecular weight of 1,40,000was dissolved in 40 ml water. To the PVA solution, acrylic acid (1 g) and vinyl sulfonic acid (0.5 g-2.5 g) were added. Then, the whole reaction mixture was flushed with nitrogen for 15 minutes. 5 ml of Sodium lauryl sulphate solution (0.015 g) was added to the reaction mixture. 0.01M of tetraethyl methyl-ethylene diammine (TEMED) and potassium peroxodisulphate (0.273 g) were added consecutively as redox initiator. The polymerization was allowed to proceed for different duration and at various temperatures to obtain the polymer product with requisite water-solubility properties for the current application. The reaction mixture was added to double the volume of acetone and precipitated at pH 12 using ammonia. The polymer product was washed well with acetone-water mixture to remove any homopolymers and unreacted materials. The polymerisation was confirmed using FTIR (figure-1)

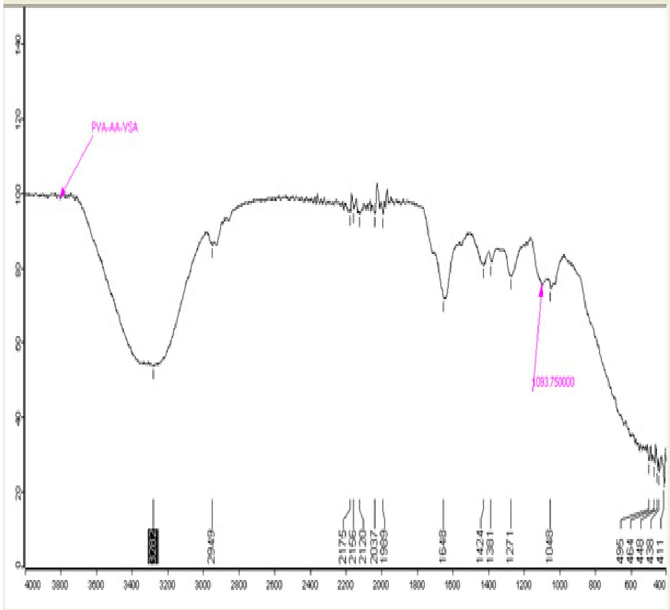

Figure-1
IR Spectrum of PVA-g-poly(AA-VSA)

IR data: 3300-3400 cm^{-1}: Broad peak in this range corresponds to OH-group of PVA. 1650-1890 cm^{-1}: Generally C=O group of acrylic acid appears at 1700 cm^{-1}, and hence shift from this range could be a reason for the graft polymerization of acrylic acid on PVA. The peaks appearing at 2940 cm^{-1} and 1424 cm^{-1} are indicative of CH- and $–CH_2$-stretching vibrations respectively. The medium absorption bands at 1380 cm^{-} corresponds to asymmetric S=O stretching, and at 1270 cm^{-1} may be attributed to the overlapping of symmetric C-O- (of acrylic acid and PVA) and symmetric S=O stretching (of vinyl sulfonic acid) [20]. The medium absorption bands in the region of 1040-1100 in the fingerprint region indicate several modes of absorptions such as C-H deformation, C-O or C-C stretching[21].

Gravimetric studies: Mild steel strips (5 cm X 1 cm X 1 cm) were polished well with different grades of emery paper and used for gravimetric measurements. For weight loss measurements each reaction was carried out in a glass beaker containing 100 ml test solution. Clean and weighed mild steel strips in triplicate were completely immersed in the beaker. The weight loss experiments were performed at room temperature for different immersion periods. The aggressive solutions were prepared using AR grade HCl and distilled water. The inhibitor concentration ranged from 100-500 ppm. At the end of experiments mild steel strips were rinsed with distilled water, dried and weighed. The percentage of inhibition efficiency was calculated using the following equation 1.

$$IE(\%) = \frac{Wo-W}{Wo}\ X\ 100 \rightarrow 1$$

Where W_o and W are the weights of uninhibited and inhibited metals respectively.

Electrochemical measurements: All the electrochemical experiments were carried out using frequency response analyser: Biologic SP-150. The polarisation measurements and electrochemical impedance measurements were carried out using a conventional three electrode assembly containing mild steel (1 cm^2 exposed area), platinum electrode and calomel electrode as working, auxiliary and reference electrodes respectively. During the potentiodynamic polarisation measurements, specimens were polarized in cathodic and anodic directions from -0.1 V to -1 V at a scan rate of 2 mV/sec. The corrosion current densities (I_{corr}) were determined from the intersection point of cathodic and anodic Tafel lines. The IE_{Icorr} is calculated using the following equation 2.

$$IE(\%) = 100\ X\ \left[1 - \frac{Icorr}{I^{\circ}corr}\right] \rightarrow 2$$

I_{corr} and I^{o}_{corr} are corrosion current densities of inhibited and uninhibited solutions respectively.

The polarization resistance R_P was determined from the slopes of the polarization curves of linear polarization region at the vicinity of the corrosion potential. The inhibition efficiency was calculated from R_p using the following equation 3.

$$IE(\%) = \frac{Rp-Rp^{\circ}}{Rp}\ X\ 100 \rightarrow 3$$

Impedance spectra were recorded at corrosion potential in the frequency range 20000 Hz to 0.1 Hz with an AC amplitude of 10 mV. The surface coverage $\boldsymbol{\theta}$was determined using the double layer capacitance values using the following equation 4.

$$\theta = \frac{Cdl^{\circ}-Cdl}{Cdl^{\circ}}\ X\ 100 \rightarrow 4$$

Theinhibtion efficiencies using weight loss, (W), corrosion current (I_{corr}), polarization resistance R_P and surface coverage $\boldsymbol{\theta}$ was calculated using the following equations:

Results and Discussion

Determination of optimum reaction conditions: The reaction progress of the polymerization at various time intervals and temperatures were monitored by measuring the inherent viscosity (table 1) of the polymer solutions using Ubbleholde viscometer.

The inherent viscosity was calculated as described elsewhere[22]. The inherent viscosity gradually increased with time and temperature which is an indication for the polymerization progress. At room temperatureas the time proceeds, the inherent viscosity increased and the respective polymer products were water soluble. At high temperatures and reaction time partially soluble products or hydrogels were obtained as a result of severe crosslinking between the polymer chains. Though, the products obtained at the room temperature were water soluble, a maximum viscosity of the polymerized product was obtained for a reaction period of 4 hours at 45 °C, providing a yield of 80%. Hence the polymerization was carried out for 4 hours at 45 °C to obtain water-soluble products.

Effect of vinyl sulfonic acid on corrosion rate: Once the reaction conditions were determined, the ratio of vinyl sulphonic acid alone was changed from 0, 0.5, 1, 2 and 2.5 with respect to acrylic acid. The effect of changing vinyl sulphonic acid on corrosion rate was studied. Table 2 depicts the corrosion rates when terpolymer containing different amounts of vinyl sulphonic acid was used as inhibitor. The hike in the inhibition efficiency when compared with copolymer PVA-AA exhibits the efficiency of sulphur in preventing metal dissolution. Nevertheless, good product yield and corrosion inhibition efficiency was obtained for the terpolymer synthesized using 1:2 ratio of acrylic acid:vinyl sulphonic acid. When the ratio of VSA is more than 2, the products were oily and sticky. Hence the polymerization was carried out with ratio of 0.5:1:2 of PVA, AA and VSA respectively and used for further studies.

Table-1
Inherent viscosity during the reaction progress

Time (hrs)	**Inherent viscosity (dL/g)**			
	Room temperature	**45°C**	**55°C**	**65°C**
2	**2.65**	**3.75**	**3.49**	**3.75**
4	**3.35**	**4.05**	**4.14**	**Partially soluble**
6	**3.79**	**4.09**	**Partially soluble**	**hydrogel**
8	**3.91**	**Partially soluble**	**hydrogel**	**hydrogel**

Table-2
Corrosion rate and Inhibition efficiency of polymers synthesized with different amounts of vinylsulfonate (Time:3hrs)

Conc (ppm)		**Corrosionrate(mpy)**				**IE(%)**				
	PVA-AA	**Ratio of VSA monomer (g)**				**PVA-AA**	**Ratio of VSA monomer (g)**			
	0	0.5	1	2	2.5	0	0.5	1	2	2.5
100	206.4	165.7	145.4	225.3	165.7	51.1	60.7	65.6	46.6	60.7
200	139.6	158.4	139.6	90.1	110.5	66.9	62.5	66.9	78.6	73.8
300	122.1	141.0	148.3	75.6	101.8	71.1	66.6	64.9	82.1	75.9
400	91.6	120.7	107.6	66.9	90.1	78.3	71.4	74.5	84.2	78.6
500	98.8	74.1	178.8	61.1	93.0	76.6	82.4	57.6	85.5	78.0

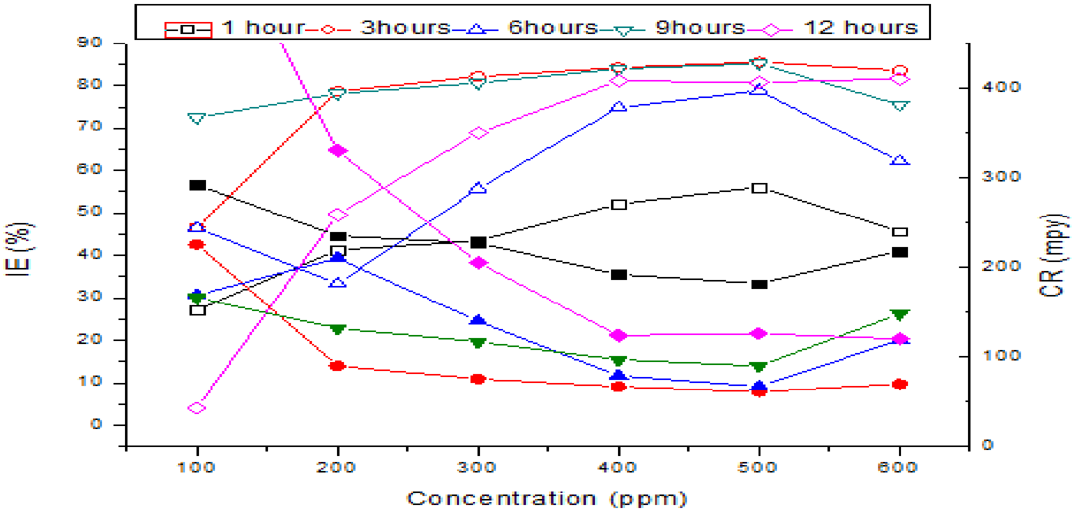

Figure-2
Shows the variation of corrosion rate (CR) and inhibition efficiency (IE) with different concentrations of PVA-g-poly(AA-VSA) at room temperature (CR and IE)

Effect of time on corrosion rate and Inhibition efficiency: Figure-2 Variation of corrosion rate (CR) and inhibition efficiency (IE) with different concentrations of PVA-g-poly (AA-VSA) at room temperatur (CR and IE). It is obvious that inhibitor concentration has a direct proportional effect on the inhibition efficiency and inverse proportional effect on corrosion rate. A maximum inhibition efficiency of was obtained for a concentration of 500 ppm at 3 hours and 9 hours due to adsorption of the inhibitor on the metal surface. At 6 hours and 9 hours, the inhibition efficiency decreases due to desorption of the inhibitor film.

Potentiodynamic polarization studies: Figure-3 is a collection of cathodic and anodic polarisation curves for MS in 1M HCl solution in the presence and absence of the PVA-g-poly(AA-VSA) inhibitor at room temperature. The corresponding electrochemical parameters such as corrosion potential (Ecorr), Corrosion current (Icorr), cathodic Tafel slope (bc), anodic Tafel slope (ba) and corrosion rate (CR) derived by extrapolation of Tafel lines are summarised in table-3.

Inspection of table 3 reveals that there is a definite decrease in corrosion current for inhibited solutions signifying the effective surface coverage of the inhibitor on metal surface. When the concentration of the inhibitor is increased, there is a shift of corrosion potential to noble directions. When the difference in the E_{corr} values between inhibited and uninhibited solutions are more than 85 mV then the inhibitor can be differentiated as cathodic or anodic type[23]. But in this case the difference in E_{corr} values is only less than 12 mV proving that the inhibitor is of mixed-type. The variation of both the Tafel slopes with respect to the uninhibited solution is not very high indicating that the inhibitor has not altered the mechanism of the corrosion inhibition. Increase in the inhibition efficiency with respect to concentration is due to the adsorption of inhibitor on the metal surface. Various type of adsorptions that takes place at metal/solution interface include[24]: i. Electrostatic interactions between charged molecules and charged metal. ii. Interaction of uncharged electron pairs in the molecule with the metal. iii. Interaction of pi electrons with the metal. vi. Combination of 1 and 2.

In this study, the uncharged electron pairs present in the oxygen atom of acrylic acid and polyvinyl alcohol, along with the sulphur atom of sodium vinyl sulfonate could have contributed to the effective adsorption.

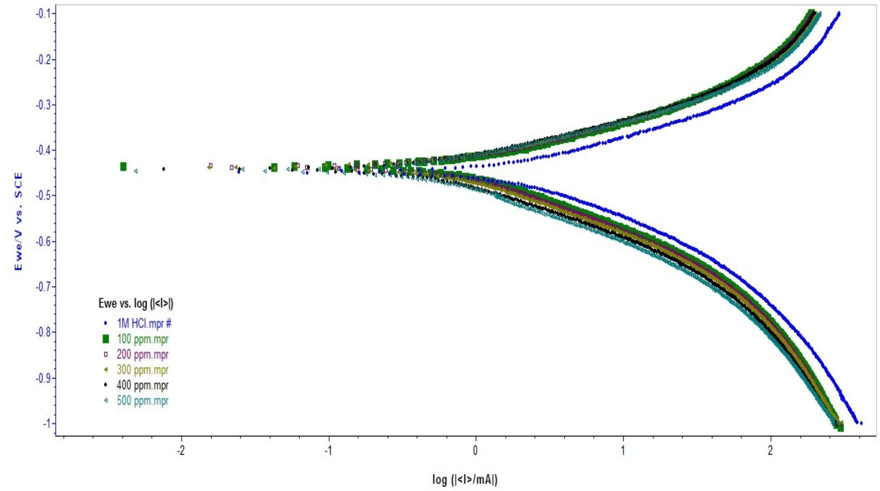

Figure-3
Polarisation curves for MS in 1M HCl solution in the presence and absence of the PVA-g-poly(AA-VSA) inhibitor at room temperature

Table-3
Potentiodynamic polarisation parameters of mild steel in HCL containing various concentrations of PVA terpolymer 2 g VSA

Cncentration(ppm)		**E_{corr} mV**	**I_{corr} μA**	**IE_{Icorr}(%)**	**b_C mV**	**b_a mV**	**Corrosion rate(mpy)**
RT	Blank	-447	2231		151	111	1014.94
	100	-435	1071.00	52.0	144.00	107	487.18
	200	-435	855.00	61.7	136.00	100	389.17
	300	-437	762.00	65.8	133.70	98.2	346.71
	400	-441	613.00	72.5	127.20	95.3	278.91
	500	-445	535.00	76.0	125.60	91.7	243.66

Table-4
Impedance parameters of mild steel in HCL containing various concentrations of PVA terpolymer containing 2 G VSA

Temperature	Concentration (ppm)	R_S ohms	R_{ct}ohms	n	Y_o 10-3 $ohm^{-1}cm^{-2}$	C_{dl}	Surface coverage
RT	Blank	0.7051	37.53	0.741	0.774	2.513	
	100	0.3921	78.16	0.768	0.357	0.976	0.61
	200	0.129	92.84	0.7787	0.362	0.983	0.61
	300	0.423	100.9	0.762	0.305	0.889	0.65
	400	0.3629	106	0.7711	0.293	0.812	0.68
	500	1.313	120.9	0.7711	0.262	0.731	0.71

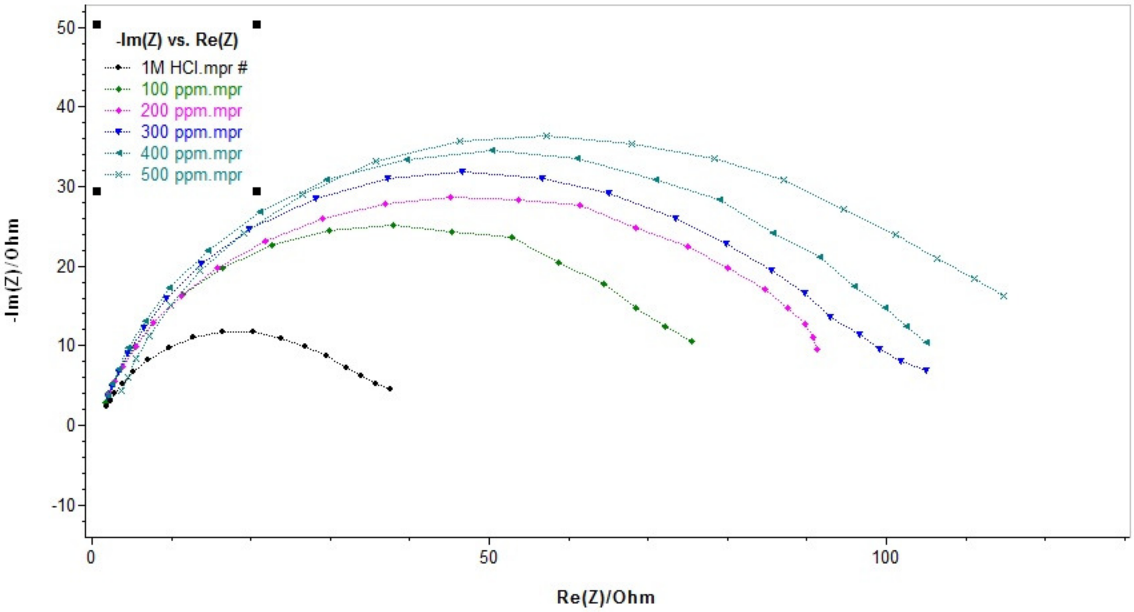

Figure-4
Nyquist plot for MS in 1M HCl solution in the presence and absence of the (PVA-g-poly(AA-VSA) inhibitor at room temperature.

AC Impedance studies: EIS results are more reliable because the measurements were done close to the corrosion potential and is considered as non-destructive test due to small magnitude of the applied potential, i.e. 5 mV. This small perturbation of the corrosion potential minimizes surface modification and errors associated with large deviations from the electrochemical equilibrium[25]. The results derived from the EIS studies for the MS corrosion in the presence and absence of terpolymer PVA-g-poly(AA-VSA) at room temperature is presented in table 4.

Figure- 4 is a Nyquist representation for corrosion of MS in the presence and absence of terpolymer PVA-g-poly (AA-VSA) at room temperature. The considerable increase in impedance with increasing inhibitor concentration could be attributed to the increase in substrate impedance. It can be noticed that the Nyquist plot appear as depressed semicircles onto the real axis as a result of roughness and inhomogeneity of the metal surface[26,27] and is named as 'dispersing effect'[28]. Therefore a capacitance in the circuit should be expressed in terms of a constant phase element (CPE), because the use of CPE is generally required due to the distribution of relaxation time arising as a result of inhomogeneity, roughness, adsorption or diffusion at micro and nano level of the metal surface[29].

Double layer capacitance associated with the CPE element is calculated using the following formula: $CPE_{dl}=(Y_o.Rct^{1-n})^{1/n}$. The charge transfer resistance values increase with increase in inhibitor concentration which can be a result of slower corroding system[30]. A better corrosion protection takes place when the double layer capacitance values are less. In this case there is a decrease in C_{dl} values with increasing inhibitor concentration ensuring the surface coverage of the metal by inhibitor film. The decrease in the C_{dl} values are due to decrease in local dielectric constant or increase in the thickness of the electrical double layer. The decrease in the local dielectric constant takes place because of the replacement of water molecules having high dielectric constant by the inhibitor molecules having lower dielectric constant. The obtained n values are in the range of $0.5 \leq n \geq 1$, which is again an evidence for the surface roughness and other parameters[31].

Conclusion

In order to utilise the sulphur hetero atom from vinyl sulphonic acid and oxygen hetero atom from the acrylic acid, and also to achieve a water-soluble eco-friendly polymer product, a terpolymer was synthesized by copolymerizing and grafting the monomers (AA and VSA) on polyvinyl alcohol. The terpolymer was found to be effective inhibitor when it was synthesized using acrylic acid and vinyl sulfonic acid in 1:2 ratio. When the vinyl sulfonic acid is increased more than the mentioned ratio, the polymer product became sticky and oily. The terpolymer was found to be an effective inhibitor for mild steel in acid medium at room temperature. The inhibitory action is affected by time and concentration. The electrochemical results confirmed the adsorption of inhibitor layer on the mild steel surface and the corrosion inhibition.

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