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Anticorrosion Activities of The Synthesized Poly Acrylic Acid Modified With Dihydroxy Benzene-Redox Polymer

V. Vetriselvi and R. Jaya Santhi*

*PG & Research Department of Chemistry, Auxilium College, Vellore, Tamil Nadu, **INDIA**

Email: shanthiaya02@gmail.com

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ABSTRACT

Poly acrylic acid was synthesized using hydrogen peroxide as an oxidant and it was functionalized with catechol, hydroquinone, a homolytic modification by an oxidative decarboxylation and was characterized using UV and FT-IR. The thermal analysis shows that the poly acrylic acid modified with Hydroquinone was more stable. The percentage of substitution was found to be 74% in PAA/Catechol and 86% for PAA / Hydroquinone. The average molecular weight measured by viscometer was found to be around 5.6×10^5, 8.2×10^5 *g/mol and* 9.5×10^5 *g/mol for PAA, PAA/Catechol and PAA / Hydroquinone. The XRD and SEM studies shows that the PAA modified with Catechol and Hydroquinone moieties are semi crystalline in nature. The PAA modified with Catechol and Hydroquinone inhibits the corrosion reaction of aluminum at pH 10. Polarization measurements showed that the polymers act as mixed-type inhibitors. The inhibition efficiencies of these polymers increase with increasing concentration and molecular weight. The inhibition efficiency was calculated through the polarization method.*

Keywords: Polyacrylic acid, Catechol, Hydroquinone, Redox polymer, Polarization.

INTRODUCTION

Redox polymers are the addition polymers synthesized by polymerizing hydroquinone-quinone derivates which contain vinyl groups. The redox components of the redox polymers can be links of the polymer chains or they can be substituent of the chains [1]. Of the several means of modifying polymers, the chemical transformation remains the leading process consists in functionalizing a pre-made polymer, that is, to anchor functional groups onto it, or to react with the already-existing functional groups of polymer with a molecular reactant. Examples of addition polymers are the redox resins which were investigated by Cassidy and his co-workers [2]. As the hydroquinone-quinone system inhibits polymerization, protecting groups like ether, acetate, benzoate are usually introduced, which can be quantitatively removed after polymerization. Polymers with redox units, being either integral parts of the polymer matrices or attached ones, are distinguished by oxydo-reduction chemistry features. Of the redox entities are organometallics such as metallocenes and organics such as pyridinium salts and hydroquinone/catechol [3,4]. The redox polymers exhibit redox properties, metallic adsorption through their chelating ability, sequestration, the adhesive properties to substrates of different natures antioxidants, electrical conductors, electrode coatings for sensors and corrosion inhibitors, and the properties of dialkoxybenzene-bearing molecules which are electroluminescence, electrical conductivity and optoelectronic property[5,6]. In making the dihydroxybenzene/dialkoxybenzene - containing materials, these properties have been highly coveted. In most cases, the chemical modification of reactive polymers was brought about by the functionalization which is of little interest because it usually afforded crosslinked resins [7,8]. The present study aimed to synthesize and characterize the chemically modified polyacrylic acid (PAA) with catechol/hydroquinone moieties through a homolytic by an oxidative decarboxylation using the conditions of Minisci [9]. The synthesized PAA and its modification with catechol / hydroquinone were studied for their anticorrosion activities against aluminium.

MATERIALS AND METHODS

Materials: The chemicals were purchased from Merck and Aldrich. Acrylic acid was purified by vacuum distillation. The viscometric measurements were performed in dioxane at 30°C using Cannon Ubbelohde capillary viscometer. The average molecular weights (Mw) were estimated by the standard relation of Mark–Houwink–Sakurada[10]. UV–Vis spectra were recorded using a UV–Vis spectrophotometer Systronics 34215. Infrared spectra were taken with a Bruker FT-IR and the X-ray diffraction measurement was carried out using Diffractometer system XPERT-PRO with Cu Kα radiation (λ = 0.154 nm) at the scanning rate of 2°/min. The SEM of polymer samples has been scanned at 12000X magnification by FEI Quanta FEG 200 High Resolution SEM. The thermal studies were recorded on SDT Q600 V8.3 build 101 with the heating rate of 10°C min^{-1} under nitrogen atmosphere. For electrochemical measurements, the aluminium materials were used as cylindrical rods. Prior to each experiment, the surface pretreatment of the working electrode was performed by mechanical polishing (using a polishing machine model Poliment I, Buehler polisher) of the electrode surface with successive grades of emery papers, up to a mirror finish. The electrode was then, rinsed with acetone, distilled water, and finally dipped in the electrolytic cell. A conventional electrochemical cell of capacity 100 cm^3 was used containing three compartments for working, platinum spiral counter and reference electrodes. The reference electrode was normal calomel one used directly in contact with the working solution. The experiments were carried out in aerated stagnant buffer solution of pH 10. The potentiodynamic current–potential curves were recorded by changing the electrode potential automatically from -2.0 to 2.0 V at a scan rate of 0.10 mV s^{-1}. A Potentiostat/Galvanostat (EG&G model 273), lock-in amplifier (model 5210) and a personal computer were used. M352 corrosion software from EG&G Princeton Applied Research were used for the potentiodynamic polarization measurement.

Synthesis and Chemical modification of poly acrylic acid: Poly acrylic acid (PAA) was synthesized via a radical polymerization using hydrogen peroxide [11] as radical initiator and chemically modified using potassium persulphate as an oxidant. The standard procedure with slight modification was adopted in the synthesis and chemical modification of PAA and the percentage of substitution were calculated from the absorbance value through calibration curve [12].

RESULTS AND DISCUSSION

UV and FT-IR spectra: The synthesized poly acrylic acid and the PAA modified with catechol and hydroquinone are subjected to UV and IR studies and the corresponding figures are given in figs. 1 and 2.

The absorption bands at 264 nm is due to carbonyl group which corresponds to the $n \rightarrow \Pi^*$ transition of poly acrylic acid. The absorption band at 288 nm and 293 nm is due to the presence of the catechol and hydroquinone is due to $\Pi \rightarrow \Pi^*$ transition of the aromatic moieties [13].

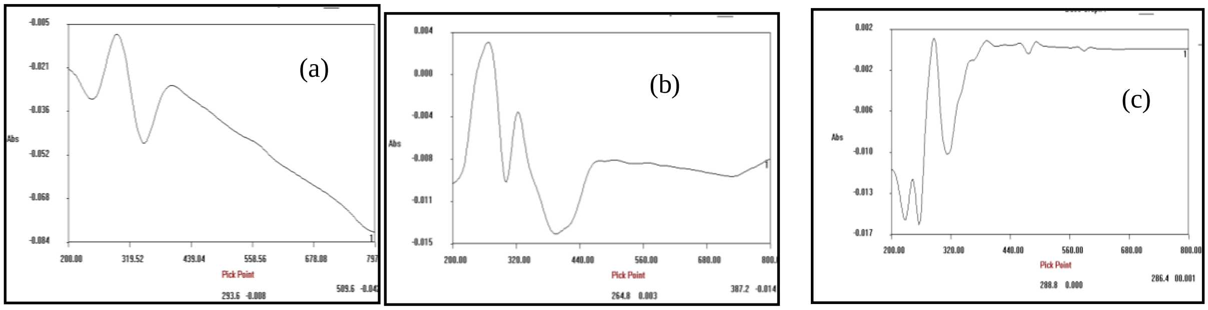


Fig .1 UVspectra of (a) PAA (b) PAA/Catechol (c) PAA/Hydroquinone

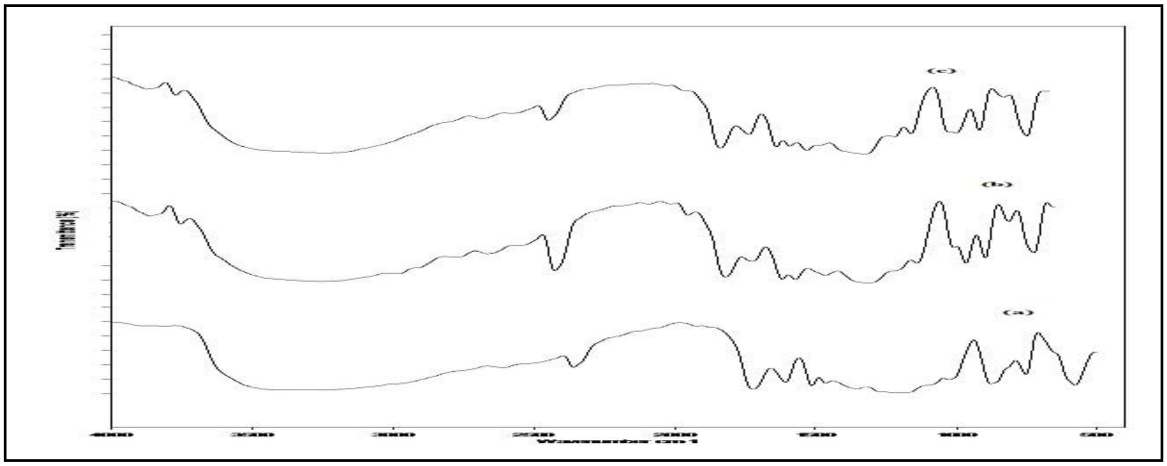


Fig. 2. IR spectra of (a)PAA (b) PAA/Catechol (c) PAA/Hydroquinone

The FT-IR spectra of the PAA and PAA modified with Catechol/Hydroquinone are presented in fig.2. The intensity of the acid O–H stretching band centered around 3500 cm^{-1} in PAA was enhanced due the incorporation of dihydroxybenzene; two hydroxyl groups of the latter replaced by the one hydroxyl group of the carboxylic acid may be due to the substitution of two hydroxyl group of the dihydroxy benzene [14]. A shoulder-looking band around 1300-1400 cm^{-1} is assigned to O–H deformation vibration mode of the dihydroxybenzene. The band between 1625 and 1800 cm^{-1} in PAA is broadened from 1510 to 1800 cm^{-1} indicating the occurrence of substitution of dihydroxybenzene in PAA. The aromatic C=C stretching bands expected at 1580 and 1600 cm^{-1} appeared overlapped and two faint bands are noticed at 821 cm^{-1}and 1271 cm^{-1} is attributed to the angular deformation of C=C and the stretching of C–O, respectively. The presence of band at 876 and 755 confirms the presence of catechol and hydroquinone moieties attached to the PAA chain [15].

Thermo Gravimetric Analysis studies

TGA/DTA of Poly Acrylicacid (PAA): Pure PAA fig. 3(a). shows a three-stage degradation process. A first weight loss of about 6% occurs within the range 100 - 150°C and is related to the formation of intra- and inter-molecular anhydride bonds with a consequent loss of water. A second weight loss of about 26% occurs in the range 200–300°C and is related to the decarboxylation process of the anhydride bonds formed in the previous stage. A third weight loss occurs within the range 650–750°C and is related to the full degradation of the macromolecule [16]. The Tg of the polymer was at 143°C. Above Tg the mobility of PAA increases and the residual acrylic acid monomer will be released. The second endotherm at 300°C corresponds to the release of carbondioxide reflects the the decarboxylation of the anhydride species. The chain scission occurs due to the depolymerization of the acryicacid moieties leads to an oxidation reaction with a large exotherm 450° - 600°C[17].

TGA / DTA of chemically modified PAA: Thermo Gravimetric Analysis of PAA chemically modified with catechol and hydroquinone are given in fig.3(b). The two chemically modified PAA namely PAA/Catechol and PAA/Hydroquinone shows the first degradation peak around 150°C would correspond to the degradation step initiated by radical transfer to the unsaturated chain ends. Possibly, after the H–H scission, some termination occur leading to unsaturated ends which degrades around 270°C. The third decomposition was due to the degradation initiated by the radical transfer to the unsaturated ends formed in the second stage.

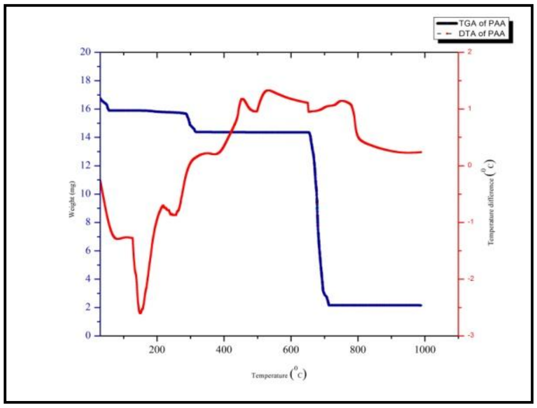


Fig. 3(a). TGA of PAA

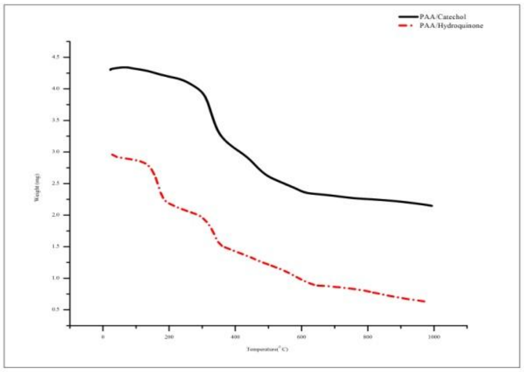


Fig. 3(b). TGA of Chemically modified PAA

Since there is no simultaneous decrease of the second and third transition no coupling took place and the fourth transition occurred at 600°C would correspond to the random scission of the polymeric chains. The side-chain elimination could not be an initiation route for depropagation because of the amount of chars produced [18]. It is noticed for the chemically modified PAA with catechol , the amount of char exceeds to 49% and for PAA/ hydroquinone it 20% and it shows that the PAA/ catechol is more stable than PAA/hydroquinone. The greater percentage of char obtained substantiates that the initial route for depropagation took place without the side chain elimination.

Differential Scanning Calorimetry Studies

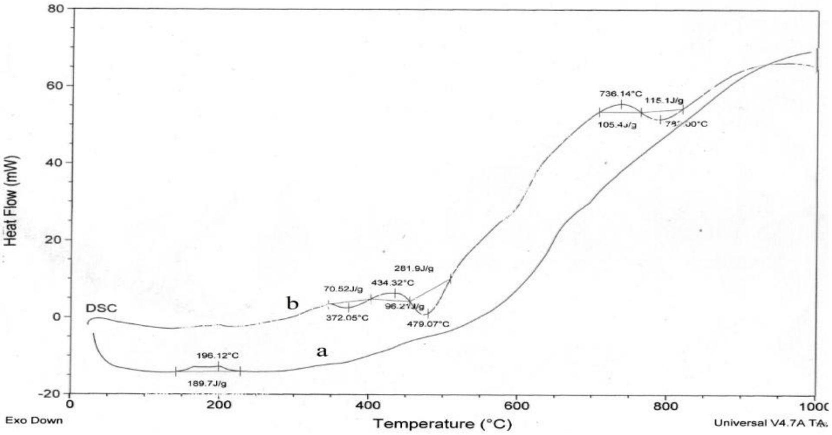


Fig. 4. DSC of (a) PAA/Catechol (b) PAA/Hydroquinone

The different phase temperature was observed from DSC curve (fig.4). The literature value of glass transition temperature of PAA was found to be 143°C. Upon modification with PAA/Catechol and PAA/ Hydroquinone, the T_g of PAA/Hydroquinone decreases gradually with increase in hydroquinone content. It also indicates that original carboxylic acid association could be a main factor to keep a relatively higher T_g in unmodified PAA. Chemically modified PAA with catechol has the Tg of 196°Cwith the ΔH of 189.7 J/g. The T_g of chemically modified PAA with hydroquinone found to have 372°C with the ΔH of 70.52 J/g, The T_c of PAA / hydroquinone was found to be 434°C with the ΔH of 96 J/g, and Tm was 736°C with ΔH of 105.4 J/g . In PAA/Catechol, the absence of endothermic peak after 196°C relates to the lack of melting process of the crystalline fraction which further confirms the presence of strong interactions between the polymeric back bone and the aromatic moiety [19].

Percentage of substitution

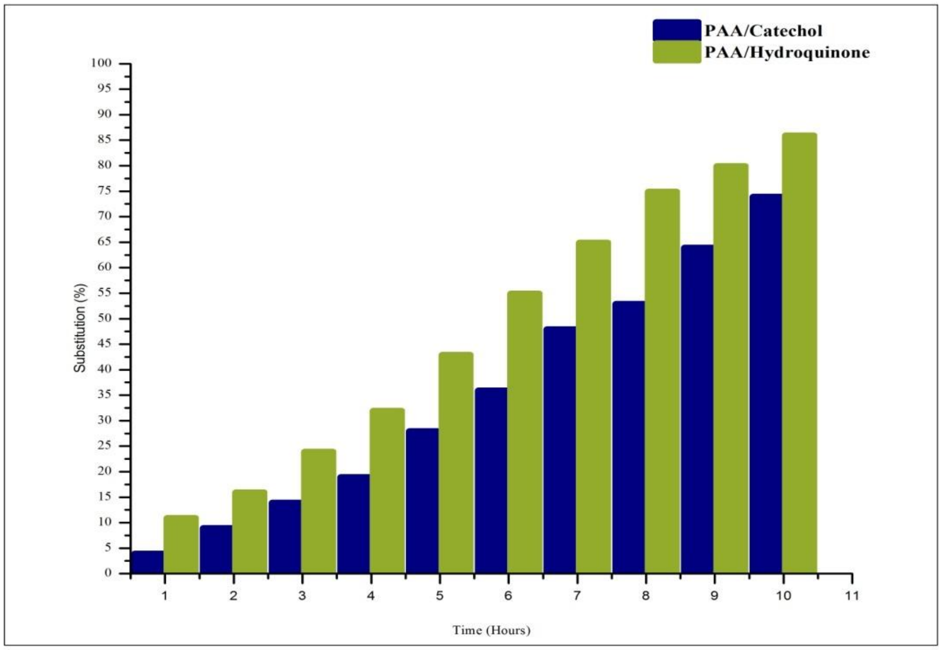


Fig. 5 Effect of time on the percentage of substitution in chemically modified PAA

The degree of substitution of carboxylic groups from the PAA by catechol and hydroquinone was estimated by UV absorbance at different time intervals and the corresponding figures are given in fig.5. The percentage of substitution increased with increase in time. At the end of 10th hour, the degree of substitution was found to be 74% and 86% for modified PAA/Catechol and PAA/Hydroquinone.

Molecular weight: The average molecular weight of PAA, PAA/Catechol and PAA/Hydroquinone was found to be 5.8x10^5 g/mol, 8.2 X10^5 g/mol and 9.5X10^5 with the ή value of 0.58, 0.69 and 0.74 dL g^{-1} respectively. It is observed that as the percentage of substitution increases, the average molecular weight increases linearly from pure PAA to chemically modified PAA. This may be due to the higher branches and longer chain of PAA on the backbone of PAA in the dihydroxy benzene moieties which gets attached leading to higher percentage of substitution [20].

X-Ray Diffraction studies

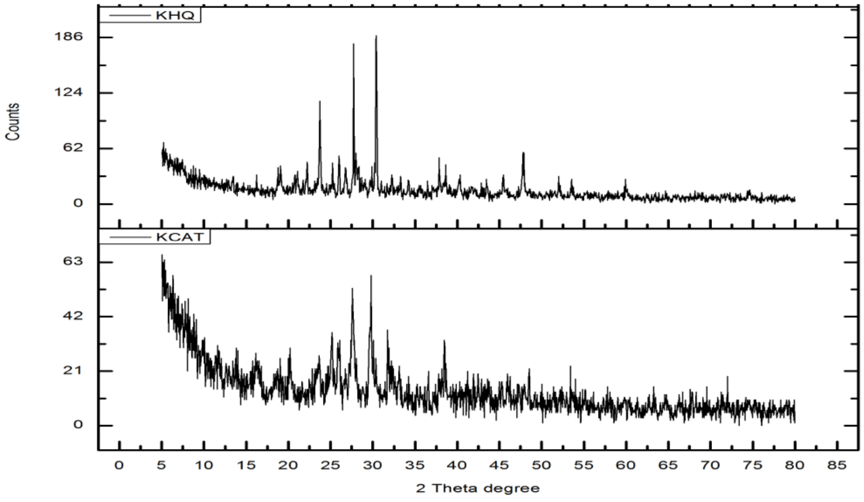
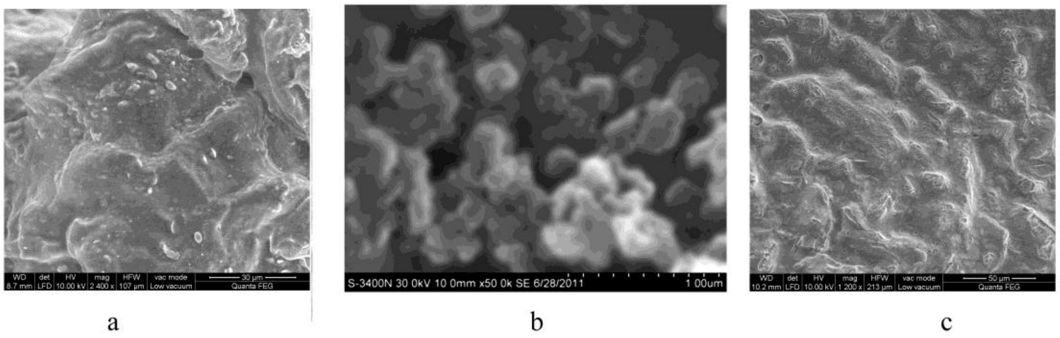


Fig. 6 XRD of PAA and chemically modified Poly Acrylic (a) PAA/CAT (b) PAA/HQ

The XRD spectra of chemically modified PAA are given in fig.6. . The average crystallite size was calculated from the Scherrer's formula[21] The poly acrylic acid is amorphous in nature[22], whereas in the chemically modified PAA/Catechol found to have a small peak at 23.5° with the d-spacing of 3.7821Å, with the crystalline size of 84.3nm. The 100% relative intensity exists at 29.8° and 30.3° with the d spacing of 2.99558Å, 2.94698 Å had the crystalline size of 178.2 nm, 7.04 nm for PAA/Catechol and PAA/Hydroquinone respectively. From the XRD studies it was confirmed that the synthesized chemically modified polymer exhibits semicrystalline nature.

SEM analysis



a b c

Fig. 7 SEM images of of PAA and chemically modified Poly Acrylic Acids (a)PAA (b) PAA/Catechol (c) PAA/Hydroquinone

The SEM of PAA shows a lamellar arrangement with amorphous surface nonporous solid microstructure and for PAA modified with catechol and hydroquinone shows cluster like polymeric arrangement. The SEM micrograph for the polymeric intermediate prepared with chemically modified PAA/Catechol showed polymeric solid structure with big voids and this may be due to the functionalization of catechol into the poly acrylic acid matrix. The polymeric cluster with large number of micro voids exists a porous nature in PAA/ Catechol [23]. The better polymerization in PAA/Hydroquinone is consistence with FT-IR, XRD and the highest percentage substitution UV absorbance studies. The SEM images are illustrated in the fig.7.

APPLICATIONS

Corrosion studies

Corrosion measurements by Polarization Method : The effect of PAA and modified with catechol and hydroquinone concentration on the potentiodynamic anodic and cathodic polarization characteristics of Aluminium in bicarbonate buffer solution (pH 10) at a scan rate of 0.10 mV s^{-1} at 30 °C are given in figs 8a, and b.

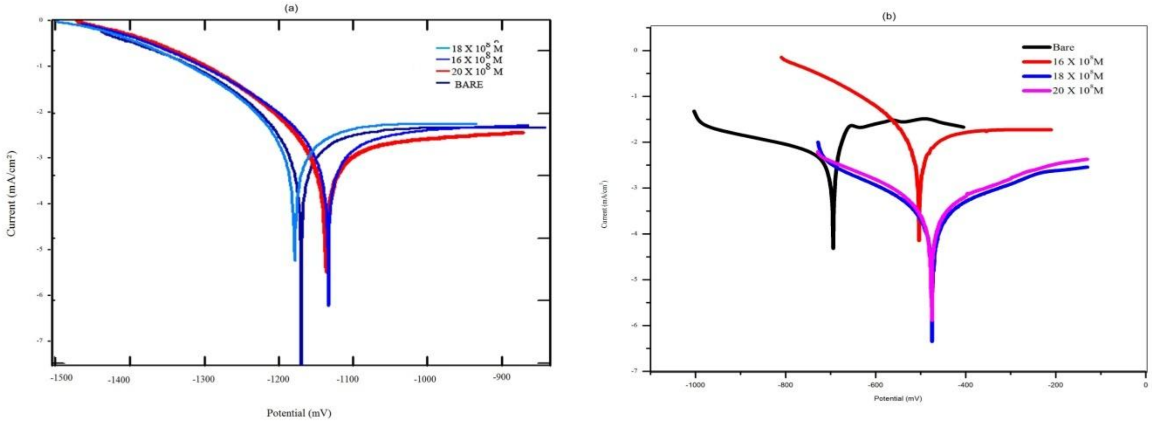


Fig. 8. Potentiodynamic anodic and cathodic polarization curves of in different concentration at 30 °C
a. PAA/Catechol b. PAA/Hydroquinone.

The result clearly show that, the addition of the two polymers, shifts the corrosion potential (Ecorr) slightly in the positive direction and reduces both the anodic and cathodic current densities. The anodic current was, however, reduced, more significantly than the cathodic current. The two inhibitors have significant effects on retarding the cathodic hydrogen evolution reaction and inhibiting the anodic dissolution of aluminium and thus these polymers act as mixed type of inhibitor. The cathodic reaction which occurs when Al corrodes in weakly alkaline solutions has been investigated by Burstein and Liu [24].

Table 1 The electrochemical parameters at different concentration of the inhibitors at 30°C.

Concentration ($X10^8$)/M	E_{corr}/ (SCE)		($j_{corr}X10^3$)/mAcm^{-2}		b_a/mV dec^{-1}		-b_a/mV dec^{-1}	
	PAA/ Catechol	PAA/ Hydroquinone	PAA/ Catechol	PAA/ Hydroquinone	PAA/ Catechol	PAA/ Hydroquinone	PAA/ Catechol	PAA/ Hydroquinone
Bare	-694.52	-1169	0.1544	0.00176	1670.2	52	136.45	67
16	-504.6	-1134.8	0.04256	3.807 $X10^5$	1066.4	71.56	122.41	47.73
18	-475.25	-1130.7	0.02308	4.47$X10^7$	908.54	103.41	144.66	92.54
20	-482.32	-1177.9	0.03567	7.6$X10^6$	4646.4	127.68	147.65	132.81

The electrochemical parameters, j_{corr}, E_{corr}, b_c and b_a associated with polarization measurements of the two polymers at different concentrations were simultaneously determined and listed in Table 1.According to the data, it is obvious that the slopes of the anodic (b_a) and cathodic (b_c) Tafel lines remain almost constant upon the addition of each of these polymers. These results indicate that, these inhibitors act by simple blocking the available surface area for both anodic and cathodic processes.

Table 2 Values of IE% for aluminum in bicarbonate buffer solution (pH=10) containing various concentrations of the three inhibitors at 30°C

Concentration ($X10^8$)M	PAA/Catechol	PAA/Hydroquinone
16	72	28
18	85	99
20	77	84

The inhibition efficiencies at different concentrations of PAA / catechol and PAA / hydroquinone are calculated at pH 10 and listed in Table 2. From the table shown that in all cases, the inhibition efficiency increases with increasing additive concentration. It was clearly the inhibition efficiency is greater in order: PAA/Hydroquinone when compared to PAA/Catechol. The greater percentage of inhibition efficiency was found to be 99% at the concentration of $18X10^8$M for Poly acrylic acid modified with Hydroquinone. The inhibition efficiency is due to high percentage of substitution of the aromatic moieties with increase in molecular weight [24].

CONCLUSIONS

The PAA and the modified PAA were synthesized by oxidative decarboxylation process and they were characterized using different spectroscopic techniques. The thermal study shows that the synthesized polymers were thermally stable even at higher temperature. The inhibition is due to the adsorption of these compounds on the surface of Al. Polarization measurements showed that the two polymers function as a mixed-type inhibitor, The inhibition efficiencies of these polymers increase with increasing their concentration and molecular weight.

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