

Electrochemical impedance Characterization of electroinitiated Acrylic Co-polymers

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Abstract

Electrochemically initiated co-polymerization of acrylonitrile (AN) with acrylic acid (AcA), methyl methacrylate (MMA), diallyl dimethyl ammonium chloride (DADMAC) and propargyl alcohol (PA) was prefer in aqueous solutions on mild steel and stainless steel cathode. The polymerization was carried out under electrolysis and its corrosion protection ability has been studied by impedance technique in aqueous 5% NaCl. The results were compared with uncoated metals, its shows the monomer concentration of the electroinitiated polymerization (EIP) process has some influence on the corrosion resistance of coated metals.

Keywords:

EIP, Acrylonitrile, diallyl dimethyl ammonium chloride, MMA, PA and electrolysis

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1. Introduction

Corrosion is the natural way of destructive disintegration of metals by chemical or electrochemical reaction with environment (1,2). Depending on the nature of the corroding environment and the mechanism of attack, different forms of corrosion exist. Atmospheric, pitting, crevice (3,4), intergranular (5), stress (6) and microbial corrosion are few of most important ones. It is believed that protecting the metal from deterioration could save the loss of materials from metallic corrosion. Obviously, protection method that would give long-term protection to metals is warranted. At this context, it is important to note that long-term protection becomes possible by coating the substrate with other metals or alloys or elastomers or polymers. Among these, coating with polymers has been preferred over the others (1). Lining with polymers has long been recognized as an effective and cheaper means of protecting the steel against corrosion. Tanks, pipings, pumping levers and shipping containers have been lined with polymers and known to be protected in this way. Many of the polymer coatings possess better abrasion resistance and useful properties as coating materials.

Polymers can be conveniently coated on metal surfaces through electroinitiated polymerization (EIP) of monomers at constant potential electrolysis (2). Through this approach, uniform polymeric films could be made on metal surface than by other protective methods. EIP is quite different from electrodeposition and electrocoating. In electrocoating is an already formed polymer is deposited on metal surface by electrophoretic effect. EIP offers special advantages of making uniform and definite thickness of coating by selecting proper experimental conditions.

Polymerization is initiated by electrolysis reported by few investigators (7-10). S.N.Bhadani et.al. (11) studied the electroinitiated polymerization of acrylamide (AA) in an aqueous medium; perchlorate can be used as supporting electrolyte. Acrylonitrile (AN) and methacrylonitrile have been electrocopolymerized on cathode surfaces to produce adherent coatings on metal substrates (12). Likewise, several reports are available on polymerization of different acrylic monomers to obtain protective coatings over different cathode surfaces (13-25). The corrosion resistant property of conducting polymers also employed in electroactive coating on metals investigated by many researchers (26-29).

Coating of polymers with better physical characteristics could be achieved by insolubilising the polymer films during film formation by cross linking with a monomer. Interestingly, use the additional cross linkers resulting the improved insoluble, adherent and corrosion resistant coating on steel surfaces established by T.Grchew et.al. (30), which is employed to obtain the poly (AA-AN) co-polymer in acidic aqueous solution in presence of NN'methylenebisacrylamide (MBA) cross-linker with ZnCl_2 additive. In the presence of ZnCl_2 , electro polymerization of mixture of AA and MBA results a cross linked polymer, possessing the characteristics of corrosion prevention. The electrical properties of the deposited copolymer films have been evaluated by AC impedance measurements (30).

Based on these clues from the literature, a systematic investigation has been made in the present study on generating new copolymer film coatings on metal surfaces by EIP. Several pairs of vinyl and divinyl monomers were used for electrocopolymerization, to obtain new pairs of co polymers as films on metallic substrates (steels) in presence or absence of cross-linker under various polymerization conditions. The corrosion protection of polymeric coatings was evaluated through electrochemical impedance spectroscopy (EIS) and results were compared with uncoated samples.

2. Experimental Details

2.1 Materials:

Acrylonitrile (AN) washed with 5% NaOH followed by 5% H_3PO_4 (11) and dried under anhydrous Na_2SO_4 or CaSO_4 , Methyl methacrylate (MMA) purified (7) by fractional distillation under reduced pressure, Propargyl alcohol (PA) was distilled after the removal of inhibitor, NN'methylenebisacrylamide (MBA) and H_2SO_4 used in this study for electropolymerization.

2.2 Composition of mild steel and stainless steel:

Mild steel (MS) (0.1% C, 0.3% P, 0.2% S, 0.04% Mn and remainder as Fe) and stainless steel (SS) (containing 0.15% C, 16% Cr, 3.5% Ni and remainder as Fe) substrates having the size of 2 x 2.5 x 0.2cm were cut from the rod after making the slices of 1 cm thick used for the deposition of copolymer films by EIP

2.3 Pretreatment of metal surfaces:

In order to achieve adhesive binding of polymeric coating on MS/SS surfaces, adequate pretreatment procedures were employed. The steel alloys were mechanically polished with 1/0, 2/0, 3/0 emery papers successively and then washed thoroughly with running water and rinsed in acetone for 30s. It was degreased with trichloroethylene based on recommended procedure (31) and used for electropolymerization.

2.4 Electrochemical cell for EIP:

In order to obtain the coating on both sides of metal surfaces, Three-compartment electrolytic cell assembly separated by two sintered glass disks was used. SS/MS specimens were used as cathode in central compartment of the electrochemical cell while the other two outer compartments were used for keeping anodes (platinum foils). Monomer solution in the background electrolyte (1M H₂SO₄) was kept in the central compartment since the coating had to be done on the cathode surface.

2.5 Electroinitiated polymerization (EIP) on MS/SS

EIP was carried out (middle compartment) in the presence / absence of MBA in H₂SO₄ medium. In other two outer compartments 1M H₂SO₄ was taken as an electrolyte. The pretreated MS/SS samples were masked with adhesive tape to get an effective working area of 1cm² was used as working electrode. In the conventional Three-electrode assembly having platinum foil as counter electrode and saturated calomel electrode (SCE) was used as reference electrodes respectively. All electrolytic runs were carried out at room temperature. Nitrogen gas was bubbled through the monomer solution (in central compartment) during the process. Electropolymerisation was carried out at a fixed potential (–300mV to –700mV) using Versastat-IITM (EG & G PAR) Potentiostat/Galvanostat (model 6310) instrument.

2.6 Corrosion resistant property evaluation

The steel cathode samples with electropolymerized vinylic coatings were evaluated for their corrosion resistance property in aerated 2M HCl solution using SCE as a reference and platinum electrode as a counter by electrochemical impedance spectroscopy using potentiostat / Galvanostat, (EG & G PAR model 6310) in the frequency region of 100KHz-10Hz at a.c. signals of 5mV/s amplitude at open circuit potential were impressed to the coated steel samples. From the impedance plots, the charge transfer resistance (R_{ct}) and the double layer capacitance (C_{dl}) values were calculated through Boukamp (32) software using the equivalent circuit.

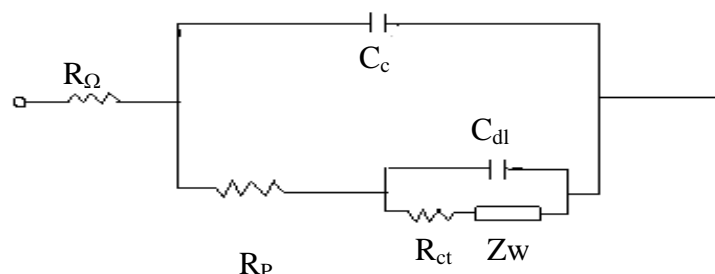


Figure.1 Equivalent electrical circuit of a polymer-coated metal

where R_{Ω} is the solution resistance, R_{ct} is the charge transfer resistance and C_{dl} is the constant phase element of the double layer capacitance. From the impedance data (Nyquist plot) it is possible to calculate capacitance value according to the following relationship.

$$C_{dl} = \frac{1}{[2\pi F_{max} R_{ct}]}$$

where F_{max} is the maximum frequency in Nyquist impedance plot, C_{dl} is the double layer capacitance and R_{ct} is the charge transfer resistance. The impedance data were analyzed by using simple Randel's circuit, since one semi-circle is obtained in the Nyquist plot. Since vinylic clear coating is thinner, so the resistance of the coating is negligible and the impedance behavior represents the charge transfer process of steel substrates. From the measured charge transfer resistance value, the corrosion inhibition efficiency of the coating has been obtained from the relationship,

$$\text{Inhibition efficiency (\%)} = \frac{[R_{t(c)} - R_{t(0)}]}{R_{t(c)}} \times 100$$

where $R_{t(c)}$ and $R_{t(0)}$ are the charge transfer resistance values of the coated and uncoated specimens respectively. The charge transfer resistance (R_t) was derived from the high frequency semicircle of Nyquist plot (33).

3. Results and Discussion

Acrylic coatings were developed on SS and MS surfaces (shown in Table.1) by carrying out EIP used in the mixture of monomers, AN, AcA, DADMAC, PA and MMA, with or without the MBA as cross linker. EIP was performed in aqueous 0.05M H_2SO_4 . The electrolysis was carried out with various concentrations of the monomers and cross-linker, obtained the smooth and adherent polymer coatings on SS/MS surfaces. The polymer coatings were developed under various conditions presented in Table.2. When EIP was performed with mixture of monomers and MBA, the following observations could be noted.

- i) White or yellowish film coating was visible on SS/MS surfaces.
- ii) Coating was adherent on the surface.
- iii) Coating could be seen uniformly on both sides of MS/SS.

3.1 Corrosion efficiency

Organic polymer coatings, formed on metallic substrate show ideal behavior as dielectrics. After exposition to a corrosion agent, organic coatings behave in a different manner due to the appearance of electrolyte activated reaching conductive areas, so called “tracks”, which pass through the coating metal, where electrochemical reactions take place. The interpretation behavior of organic coating on steel and effect of corrosion agent is found by numerous Researchers [20-27]. An equivalent electrical circuit model for the behavior of polymer-coated metal in corrosive environments has been used (Figure.1). The coated metal substrates were exposed in corrosive environment (2M HCl). Electrochemical impedance (EIS) measurements were carried out and recorded the impedance spectra; estimate the corrosion inhibition efficiency (CIE) by the detailed procedure referenced in literature [33].

The impedance parameters such as double layer capacitance (C_{dl}) and charge transfer resistance (R_t) of coatings were estimated from the diameter of the semicircle of Nyquist plot (Fig.1) used to obtain the corrosion inhibition efficiency (CIE) of individual polymer coatings and presented in Table.3. The CIE is an index of makes a comparative extent of corrosion between uncoated SS/MS and polymer coated SS/MS specimens in 2M HCl.

The following different polymeric coatings were coated on SS/MS through EIP and their CIE are measured by EIS and are discussed.

- i) Poly (AN-co-AcA)
- ii) Poly (AN-co-DADMAC)
- iii) Poly (AN-co-PA)
- iv) Poly (AN-co-MMA)
- v) Poly (DADMAC-co-MMA)

3.1.1 Poly (AN-co-AcA) film on MS/SS

The films PCMS1-PCMS11 & PCSS1-PCSS11 made by varying the experimental conditions and the film characterization were also evaluated. EIP was performed on MS and SS as changing the concentrations of AN, AcA and MBA through kinetic approach. In all conditions the coated films are visible and characterized through EIS. The best results of the films are PCMS5 (CIE-95.9%) on mild steel and PCSS6 (CIE-53.9%) on stainless steel substrates, confirmed by their Nyquist plots (shown in figures 1 & 2).

3.1.2 Poly (AN-co-DADMAC) film on MS/SS

By varying the experimental conditions as shown in table.2 coatings PCMS12-PCMS20 & PCSS12-PCSS20 are made and corrosion efficiency of these films were characterized through EIS. All of these results PCMS15 has better (CIE-87.7%) on MS, shown in fig.3 and PCSS16 has better (CIE-67.3%) on SS of poly (AN-co-DADMAC) shown in fig.4. The films under the study showed entirely different behavior than poly (AN-co-AcA) coated films and also the CIE was found to be low in MS substrate. Comparing the CIE of poly (AN-co-AcA) with poly (AN-co-DADMAC) on MS/SS, the AN-AcA polymer film has better corrosion inhibition than AN-DADMAC polymer coated on MS.

But in the case of SS surface AN-DADMAC has better inhibitory action than AN-AcA (shown in table.3). Further, here the cross linker MBA is used, it is provide cross-linked polymer network over the surface on metal and generally the absence of MBA the film was not found to be adherent coating and did not give good response to EIS measurements.

3.1.3 Poly (AN-co-PA) film on MS/SS

Varying experimental conditions, under feed the monomer as well as cross-linker concentrations, the films PCMS21-PCMS29 & PCSS21-PCSS29 were obtained through EIP on MS/SS. The corrosion ability of these films was evaluated through EIS. The CIE of these films were 81.3-95.5%. Compare all these results PCMS21 (CIE-95.5%) and PCSS23 (CIE-65.5%) has better corrosion resistance on MS/SS surfaces respectively. It is also confirmed from their maximum diameter (i.e., maximum R_t) of semicircular plots, shown in figures 5 & 7.

3.1.4 Poly (AN-co-MMA) film on MS/SS

The coated films PCMS30-PCMS37 & PCSS30-PCSS37 made by varying the experimental conditions through EIP and characterized through EIS. The electrolysis were carried out the films made on the surface of MS and SS, when varying the concentrations of monomers AN, MMA and cross-linker MBA. In all the experiments the coatings were characterized and calculated their CIE are 30.7-92.2%. Comparing all these results PCMS30 (CIE-91.2%) on MS and PCSS37 (CIE-77%) on SS are better performance (having maximum R_t) shown in figures 8 & 9.

3.1.5 Poly (DADMAC-co-MMA) film on MS/SS

The next set of experiments the monovinyl monomer AN is replaced by divinyl monomer, MMA making the PCMS38-PCMS45 and PCSS38-PCSS45 with out the use of cross-linker during electrolysis and to identify the corrosion efficiency of these films (in absence of cross-linker) compared with the presence of MBA. The EIP was carried out on MS/SS under electrolysis, when the concentrations of DADMAC and MMA are varied with out the use of cross linker, makes the PCMS38-PCMS45 & PCSS38-PCSS45 films. In all the experiments the films are visible and to evaluate the CIE from R_t values of respective films. Comparing the CIE of deposited polymeric films under different conditions, it can be seen that the PCMS43 (CIE - 81.3 %) and PCSS 40 (CIE-70.4%) having better resistance than other, confirmed by figures 10 & 11.

In addition the CIE of PCSS43 is -1.5% , obtained by varying the concentration of MMA with DADMAC. This coating stimulates the corrosion. But in the case of MS the film having superior corrosion resistance than other due to better adhesion of coating was exhibited on MS over SS surface of the metal.

In the absence of MBA the CIE of PCMS43 are 81.4% , best resistive film obtained in this set of experiments was low compared to the best CIE obtained for using a cross-linker, in the case of poly (AN-co-AcA), poly (AN-co-DADMAC) and poly (AN-co-MMA) and poly (AN-co-PA) are exhibited very near values (i.e. 95.9% & 95.5%) and comparatively better resistance than the other respective polymeric coated surfaces. Resulting, the polymeric films are well adherent to mild steel surfaces than stainless steel during EIP, due to the easiest corrosion of MS. This is confirmed from these CIE values.

In addition, EIS revealed the charge transfer resistance (R_t) and double layer capacitance (C_{dl}) of the protective coatings were decreases and increases respectively an elapsing the exposure time. However, on failure of adhesion or poor adhesion between the coating materials to substrate are also lower resistance and higher capacitance due to the easy penetration of aggressive electrolytes through the protective coatings. In the present work, mixed performance of R_t and C_{dl} of all polymer coatings as increases the monomer and cross linker concentrations were noticed and the values are presented in table.3. All these coatings, were coated on mild steel substrates PCMS37 has higher resistance (252.7ohms/cm^2) and lower capacitance (0.02 mF/cm^2) are exhibited. Polymers coated on stainless steel substrates and characterized through EIS PCSS30 coating has higher resistance (199.0 ohms/cm^2) and lower capacitance (0.03 mF/cm^2) but lower % corrosion efficiency than PCSS12 are exhibited due to the presence of $-\text{OCH}_3$ group of AN co-polymer on both metallic surfaces.

Furthermore, MBA is used as a cross linker to get cross-linked polymer network. These polymer networks have considerably given their performance as corrosion protection. This is proved by the present work, as shown in table.3. The EIP of MMA and DADMAC (during polymerization with out cross linker) and EIP coating is characterized through EIS given comparatively lower resistance and higher capacitance than other systems. In addition the CIE of PCSS43 is -1.5% , obtained by varying the concentration of MMA with DADMAC.

This coating stimulates the corrosion. But in the case of MS the film having superior corrosion resistance than others due to better adhesion of coating was exhibited on MS over SS surface of the metal. All kinds of semicircular Nyquist plots compared with uncoated specimens, establish the improvement of resistance, identified from each Nyquist plots. It shows to achieve the protection ability of polymeric coatings are confirmed.

Nyquist diagrams of all coatings determined for the polymer coated steel panels in the corrosive solution. It can be seen that these diagrams differ from the ideal semicircle because of the superposition of the charge transfer reaction with the diffusion process. The diagrams were fitted by the equivalent circuit of figure.1. All the results obtained for MS/SS surfaces reveals that the polymeric films are well adherent on MS surface than SS due to the easy corrosive nature of MS than SS. Because off, during electro initiation in sulphuric acid medium the mild steel substrates are corrode easier than stainless steel at the same time the polymers are adhered well on mild steel substrates and it also effectively prevent on MS from corrosive medium compared to SS and are effectively proved through EIS.

4. Conclusion

The electrochemical impedance characterization of electro initiated acrylic co-polymers were characterized through impedance spectroscopy under corrosive acid environment, we can drawn as the following conclusions,

- ❖ All the results were revealed that the polymeric films are well adherent on MS surface than SS due to, during electrolysis (carried out in acid medium) the easy corrosive reaction takes place in MS than SS. At the same time the polymers are adhered well on mild steel substrates and it also effectively prevent on MS from corrosive medium compared to SS.
- ❖ AN-co-MMA copolymer coated on stainless steel substrates and characterized through EIS PCSS30 coating has higher resistance and lower capacitance respectively due to the presence of $-OCH_3$ group in it.
- ❖ All these coatings, were coated on mild steel substrates PCMS37 has higher resistance ($252.7\Omega/\text{cm}^2$) and lower capacitance ($0.02\text{ mF}/\text{cm}^2$) are exhibited due to the combination of monomers to generate best variety of AN-MMA copolymer.
- ❖ The cross linker MBA is used in this work, it is provide cross-linked polymer network over the surface of metal and generally the absence of MBA the film was not found to be good adherent coating and did not give good response to EIS.

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Table.1 Variety of electroinitiated polymer coatings on mild steel / stainless steel surfaces by different combination of monomer mixtures

S.No.	Metal surface	Coating with mixture of monomers
1.	Stainless steel	AN, AcA and MBA AN, DADMAC and MBA AN, PA and MBA AN, MMA and MBA DADMAC, MMA
2.	Mild steel	AN, AcA and MBA AN, DADMAC and MBA AN, MMA and MBA AN, MMA and MBA DADMAC, MMA

Table.2 Polymer coatings developed under different conditions on mild steel / stainless steel surfaces.

S.No.	System	Composition maintained in EIP (ml)			Designation	
1.	AN, AcA with MBA	AN	AcA	MBA	Mild steel	Stainless steel
		4.0	8.0	0.5	PCMS1	PCSS1
		4.0	6.0	0.5	PCMS2	PCSS2
		4.0	4.0	0.5	PCMS3	PCSS3
		4.0	2.0	0.5	PCMS4	PCSS4
		8.0	4.0	0.5	PCMS5	PCSS5
		6.0	4.0	0.5	PCMS6	PCSS6
		4.0	4.0	0.5	PCMS7	PCSS7
		2.0	4.0	0.5	PCMS8	PCSS8
		4.0	4.0	0.5	PCMS9	PCSS9
		4.0	4.0	0.4	PCMS10	PCSS10
		4.0	4.0	0.1	PCMS11	PCSS11
2.	AN, DADMAC with MBA	AN	DADMAC	MBA	Mild steel	Stainless steel
		4.0	6.0	0.5	PCMS12	PCSS12
		4.0	4.0	0.5	PCMS13	PCSS13
		4.0	2.0	0.5	PCMS14	PCSS14
		8.0	4.0	0.5	PCMS15	PCSS15
		6.0	4.0	0.5	PCMS16	PCSS16
		4.0	4.0	0.5	PCMS17	PCSS17
		4.0	4.0	0.5	PCMS18	PCSS18
		4.0	4.0	0.4	PCMS19	PCSS19
		4.0	4.0	0.1	PCMS20	PCSS20
3.	AN, PA with MBA	AN	PA	MBA	Mild steel	Stainless steel
		1.0	2.0	0.5	PCMS21	PCSS21
		1.0	1.5	0.5	PCMS22	PCSS22
		1.0	1.0	0.5	PCMS23	PCSS23
		2.0	1.0	0.5	PCMS24	PCSS24
		1.5	1.0	0.5	PCMS25	PCSS25
		1.0	1.0	0.5	PCMS26	PCSS26
		1.0	1.0	0.5	PCMS27	PCSS27
		1.0	1.0	0.3	PCMS28	PCSS28
4.	AN, MMA with MBA	AN	MMA	MBA	Mild steel	Stainless steel
		4.0	3.0	0.5	PCMS30	PCSS30
		4.0	2.5	0.5	PCMS31	PCSS31
		4.0	2.0	0.5	PCMS32	PCSS32
		4.0	1.5	0.5	PCMS33	PCSS33
		5.5	3.0	0.5	PCMS34	PCSS34
		5.0	3.0	0.5	PCMS35	PCSS35
		4.5	3.0	0.5	PCMS36	PCSS36
		4.0	3.0	0.5	PCMS37	PCSS37
5.	MMA , DADMAC Without MBA	MMA	DADMAC		Mild steel	Stainless steel
		4.0	8.0		PCMS38	PCSS38
		4.0	6.0		PCMS39	PCSS39
		4.0	4.0		PCMS40	PCSS40
		4.0	2.0		PCMS41	PCSS41
		8.0	4.0		PCMS42	PCSS42
		6.0	4.0		PCMS43	PCSS43
		4.0	4.0		PCMS44	PCSS44
		2.0	4.0		PCMS45	PCSS45

Table.3 Impedance results of different polymer coatings over MS/SS surfaces

S.No.	System	Designation		Resistance/capacitance/CIE values of coatings					
		MS	SS	mild steel			stainless steel		
				R _t (Ω)	C _{dl} (mF)	CIE (%)	R _t (Ω)	C _{dl} (mF)	CIE (%)
1.	Poly (AN-co-AcA) With MBA	PCMS1	PCSS1	75.3	0.08	93.5	59.8	0.65	52.9
		PCMS2	PCSS2	77.0	0.18	93.8	54.8	0.50	48.6
		PCMS3	PCSS3	107.0	0.06	95.5	53.8	0.50	47.7
		PCMS4	PCSS4	104.0	0.13	95.3	58.5	1.10	51.8
		PCMS5	PCSS5	120.0	0.05	95.9	60.6	0.56	53.5
		PCMS6	PCSS6	56.3	0.34	91.3	61.1	0.78	53.9
		PCMS7	PCSS7	107.0	0.06	95.4	53.8	0.50	47.6
		PCMS8	PCSS8	69.9	0.09	93.0	44.3	0.87	36.5
		PCMS9	PCSS9	107.0	0.06	95.4	53.8	0.05	47.7
		PCMS10	PCSS10	51.3	0.05	90.5	33.1	1.03	14.7
		PCMS11	PCSS11	60.0	0.07	91.8	30.4	1.28	07.5
2.	Poly (AN-co-DADMAC) With MBA	PCMS12	PCSS12	16.8	0.24	71.1	86.2	0.64	67.3
		PCMS13	PCSS13	13.7	0.46	64.5	54.8	1.00	48.6
		PCMS14	PCSS14	28.4	0.22	82.8	45.0	0.86	37.4
		PCMS15	PCSS15	39.8	0.35	87.7	64.7	0.60	56.4
		PCMS16	PCSS16	10.6	0.24	54.4	84.5	0.65	66.6
		PCMS17	PCSS17	13.7	0.46	64.5	54.8	1.00	48.6
		PCMS18	PCSS18	13.7	0.46	64.5	54.8	1.00	48.6
		PCMS19	PCSS19	15.0	0.26	67.6	63.2	0.61	55.4
		PCMS20	PCSS20	20.8	0.20	76.6	--	--	--
3.	Poly (AN-co-PA) With MBA	PCMS21	PCSS21	107.0	0.22	95.5	60.2	1.75	53.2
		PCMS22	PCSS22	87.8	0.27	94.5	41.3	1.16	31.8
		PCMS23	PCSS23	26.0	0.16	81.3	81.6	1.77	65.5
		PCMS24	PCSS24	2.89	0.22	68.6	55.9	1.13	49.6
		PCMS25	PCSS25	63.5	0.26	92.3	49.1	0.70	42.6
		PCMS26	PCSS26	26.0	0.15	81.3	81.6	1.77	65.5
		PCMS27	PCSS27	26.0	0.15	81.3	81.6	1.77	65.5
		PCMS28	PCSS28	70.0	0.14	93.1	57.4	1.63	50.9
		PCMS29	PCSS29	28.5	0.22	82.9	68.0	2.12	58.5
4.	Poly (AN-co-MMA) With MBA	PCMS30	PCSS30	134.3	0.04	96.6	199.0	0.03	59.7
		PCMS31	PCSS31	83.2	0.07	94.5	198.0	0.03	59.5
		PCMS32	PCSS32	66.8	0.09	93.2	191.0	0.03	58.1
		PCMS33	PCSS33	12.7	0.08	64.6	183.0	0.04	56.3
		PCMS34	PCSS34	182.4	0.03	97.5	89.1	0.71	10.1
		PCMS35	PCSS35	227.2	0.03	97.9	99.5	0.64	19.5
		PCMS36	PCSS36	234.4	0.03	98.0	121.0	0.52	34.0
		PCMS37	PCSS37	252.7	0.02	98.2	136.4	0.40	47.3
5.	(MMA-co-DADMAC) with out MBA	PCMS38	PCSS38	26.0	0.24	81.3	61.9	0.77	54.5
		PCMS39	PCSS39	15.9	0.40	69.4	76.2	0.63	63.0
		PCMS40	PCSS40	18.4	0.22	73.4	95.2	0.51	70.4
		PCMS41	PCSS41	18.6	0.21	73.9	41.3	0.94	31.7
		PCMS42	PCSS42	20.4	0.31	76.2	72.6	0.53	61.1
		PCMS43	PCSS43	26.2	0.15	81.4	27.7	1.39	-1.5
		PCMS44	PCSS44	18.4	0.22	73.6	94.3	0.41	70.2
		PCMS45	PCSS45	20.6	0.20	76.3	86.4	0.56	67.4

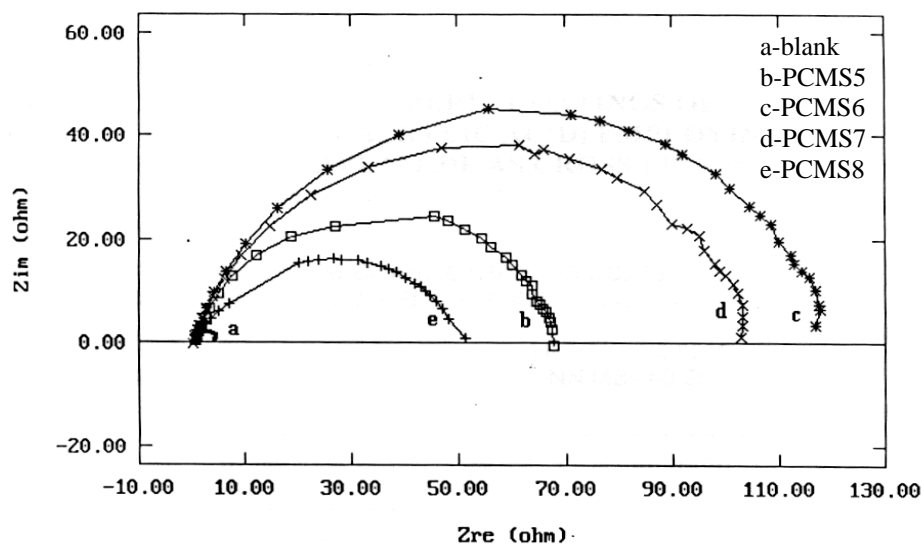


Fig.1. Electrocoating of poly (AN-co-AcA) on mild steel surface
[AN – variation]

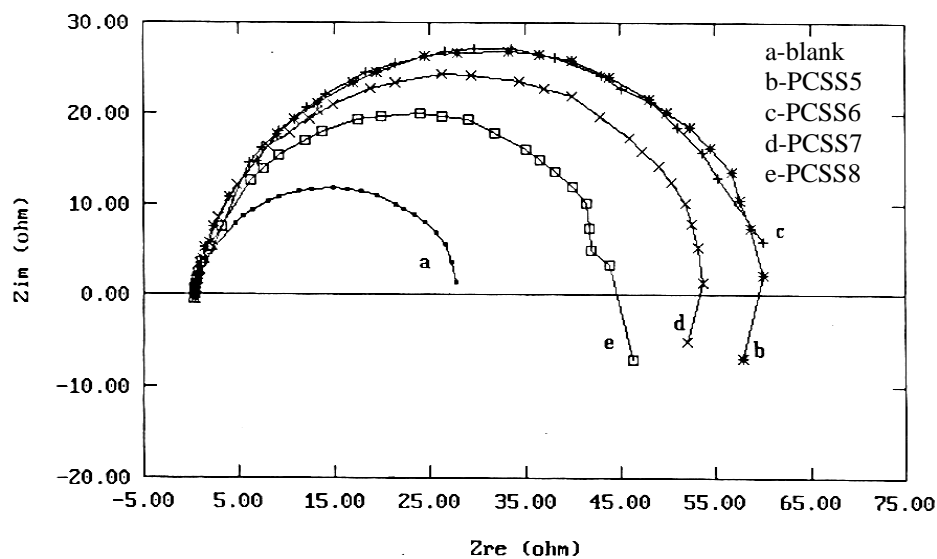


Fig.2. Electrocoating of poly (AN-co-AcA) on stainless steel surface
[AN – variation]

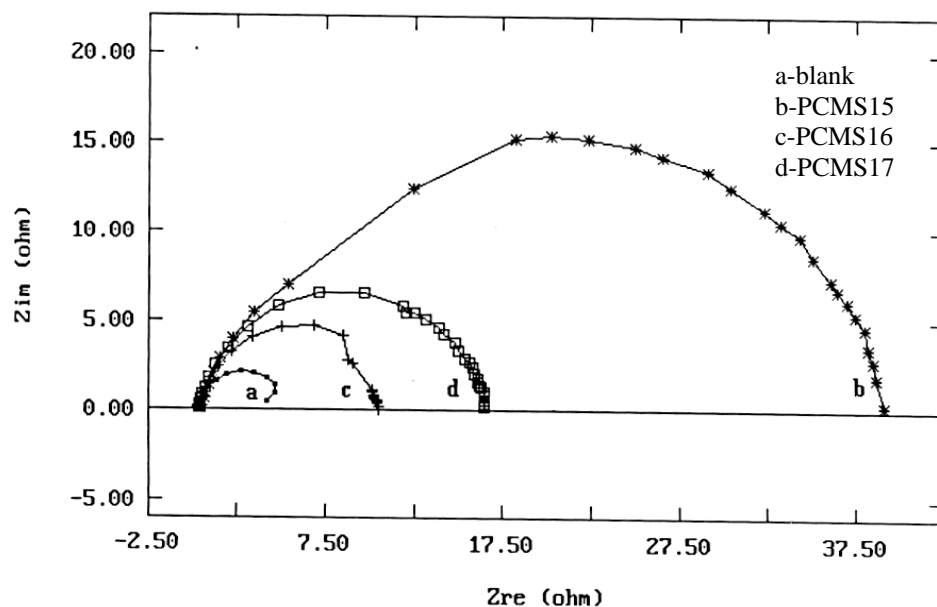


Fig.3. Electrocoating of poly (AN-co-DADMAC) on mild steel surface
[AN – variation]

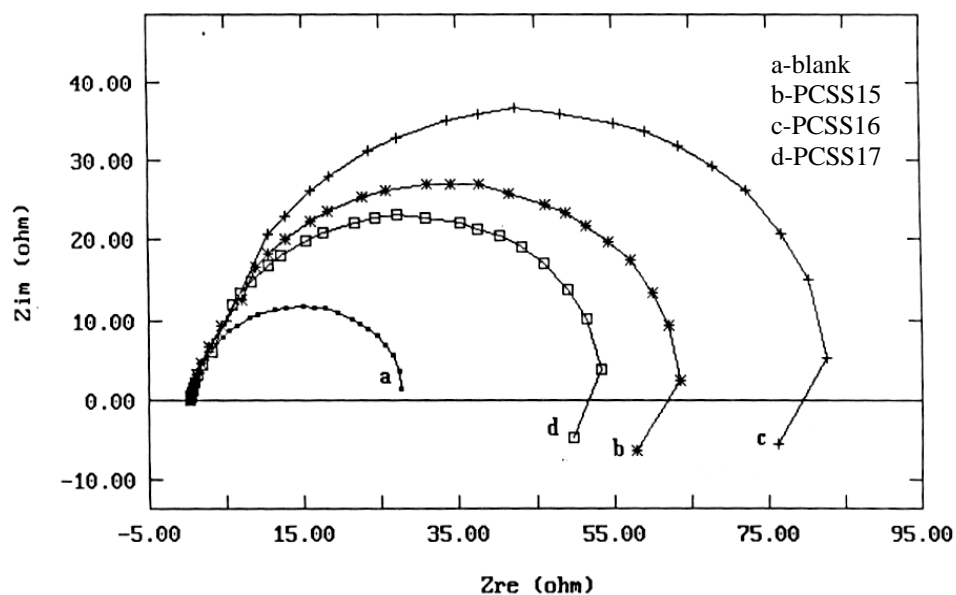


Fig.4. Electrocoating of poly (AN-co-DADMAC) on stainless steel surface
[AN – variation]

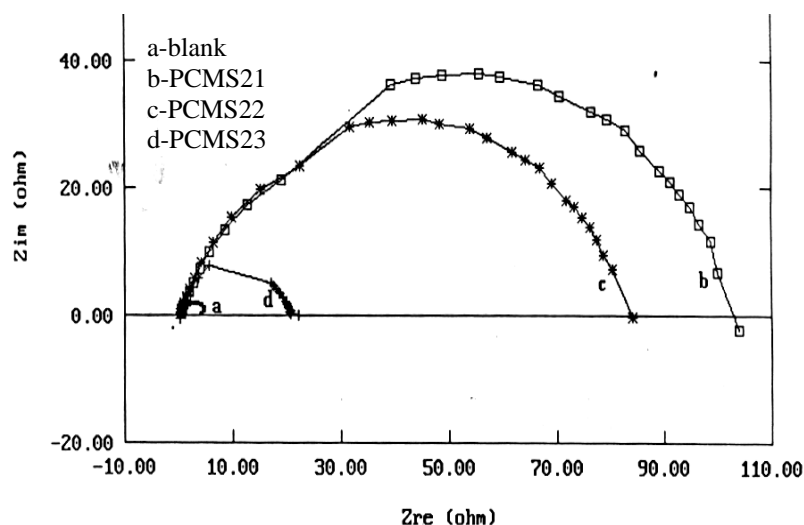


Fig.5. Electrocoating of poly (AN-co-PA) on mild steel surface
[PA – variation]

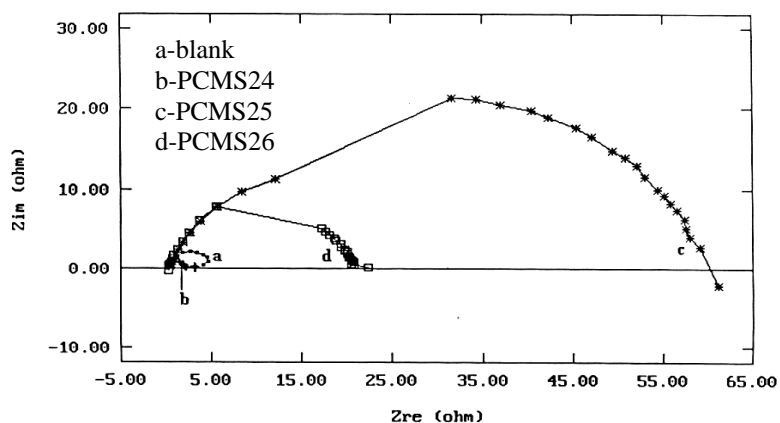


Fig.6. Electrocoating of poly (AN-co-PA) on mild steel surface
[AN – variation]

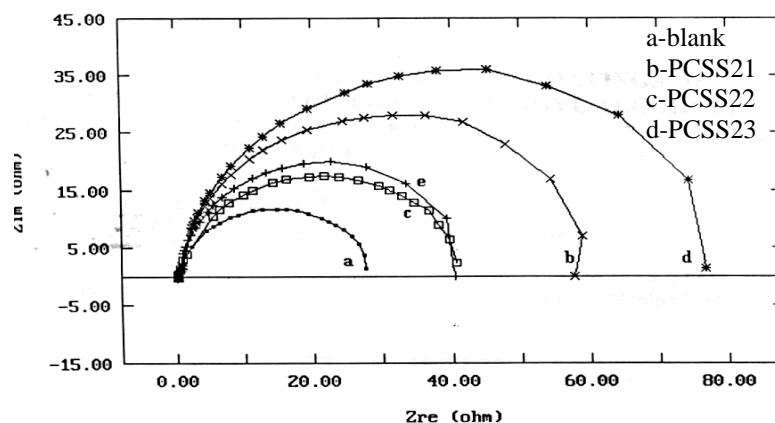


Fig.7. Electrocoating of poly (AN-co-PA) on stainless steel surface
[AN – variation]

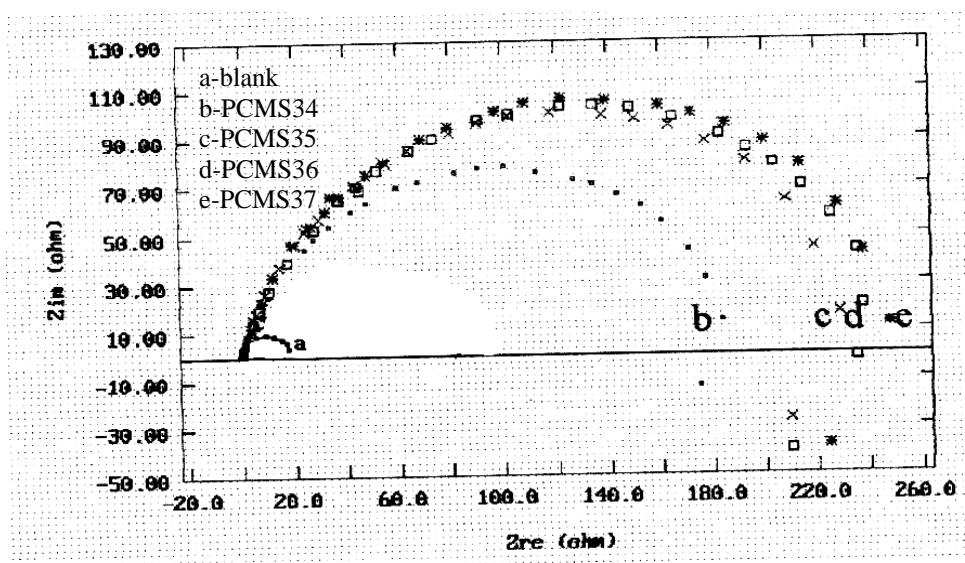


Fig.8. Electrocoating of poly (AN-co-MMA) on mild steel surface
[AN – variation]

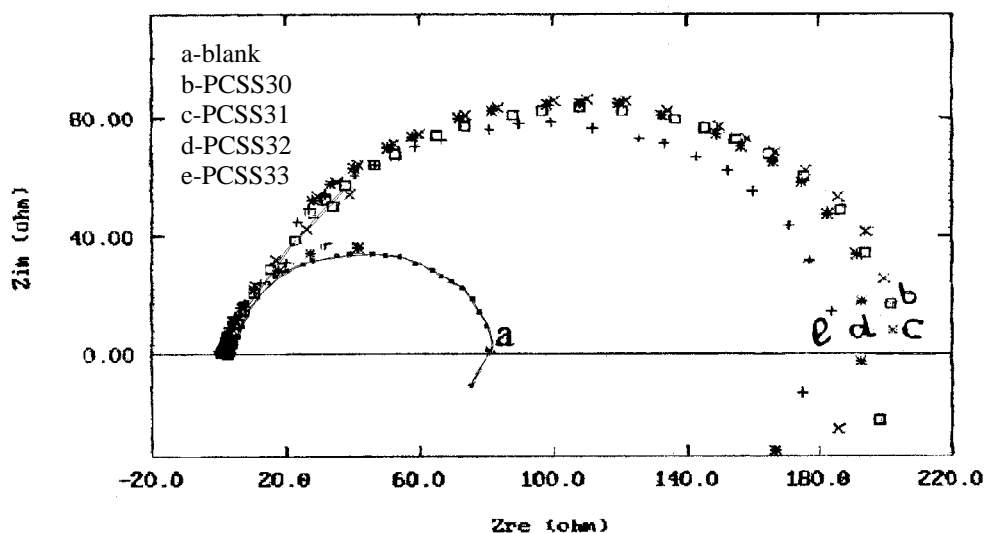


Fig.9. Electrocoating of poly (AN-co-PA) on stainless steel surface
[MMA – variation]

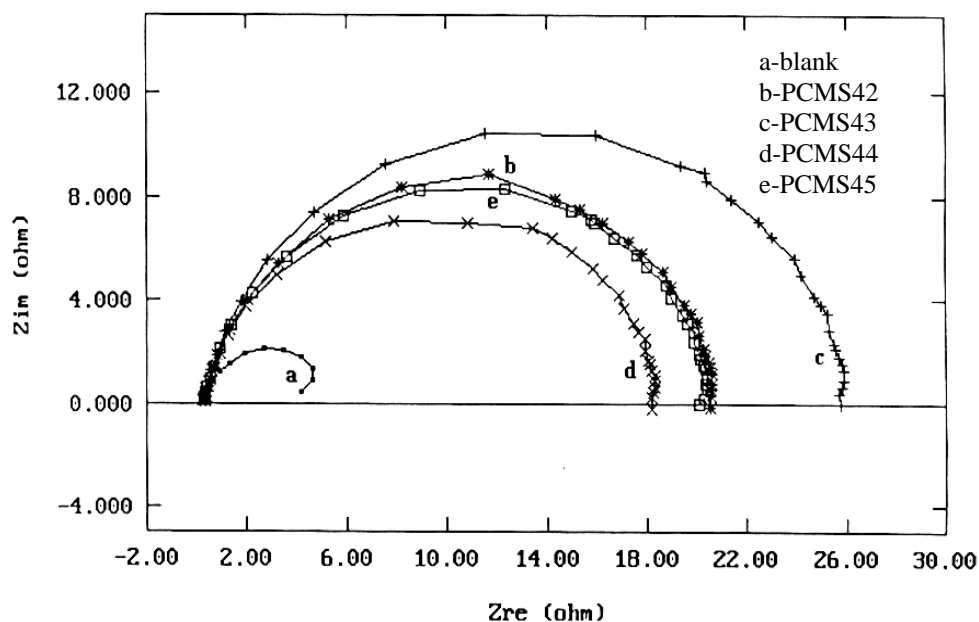


Fig.10. Electrocoating of poly (MMA-co-DADMAC) on mild steel surface
[MMA – variation]

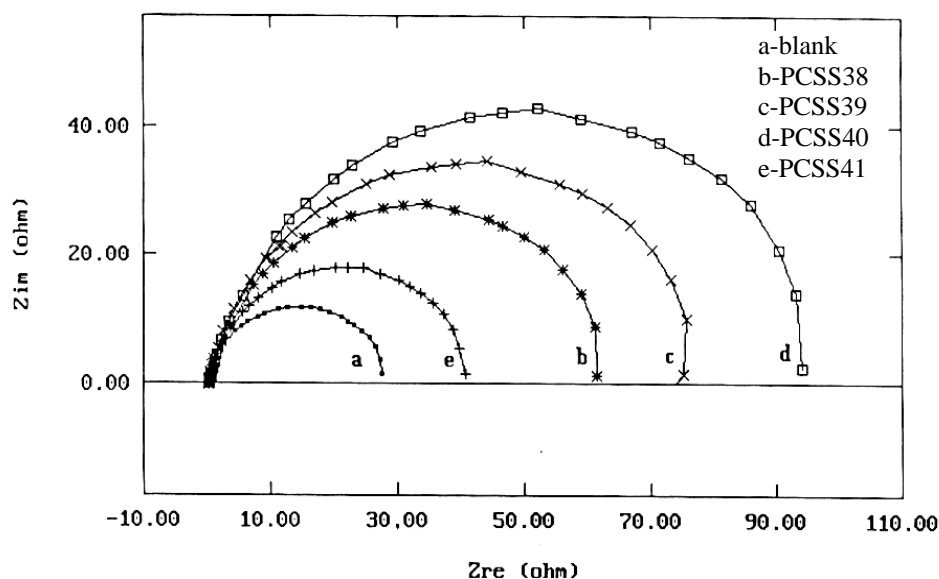


Fig.11. Electrocoating of poly (MMA-co-DADMAC) on stainless steel
surface [DADMAC – variation]

Figure Captions

**Fig.1.Electrocoating of poly (AN-co-AcA) on mild steel surface
[AN – variation]**

**Fig.2.Electrocoating of poly (AN-co-AcA) on stainless steel surface
[AN - variation]**

**Fig.3.Electrocoating of poly (AN-co-DADMAC) on mild steel surface
[AN - variation]**

**Fig.4.Electrocoating of poly (AN-co-DADMAC) on stainless steel surface
[AN - variation]**

**Fig.5.Electrocoating of poly (AN-co-PA) on mild steel surface
[PA - variation]**

**Fig.6.Electrocoating of poly (AN-co-PA) on mild steel surface
[AN - variation]**

**Fig.7.Electrocoating of poly (AN-co-PA) on stainless steel surface
[AN - variation]**

**Fig.8.Electrocoating of poly (AN-co-MMA) on mild steel surface
[AN - variation]**

**Fig.9.Electrocoating of poly (AN-co-PA) on stainless steel surface
[MMA - variation]**

**Fig.10.Electrocoating of poly (MMA-co-DADMAC) on mild steel surface
[MMA - variation]**

**Fig.11. Electrocoating of poly (MMA-co-DADMAC) on stainless steel surface
[DADMAC - variation]**