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Corrosion Characteristics with Polarization Curve of Polymers

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This study was carried out to measure the variations of potential and current density with polymers. The results were particularly examined to identify the influences on potential and rate of various factors including temperature and pH. The Tafel slope for anodic dissolution was determined by the polarization effect depending on these conditions. The optimum conditions were established for each case. The second anodic current density peak and maximum current density were designated as the relative polarization sensitivity(I_f/I_f). The mass transfer coefficient value(α) was determined with the Tafel slope for anodic dissolution based on the polarization effect with optimum conditions.

Key words : cathodic and anodic potential, current density, Tafel, polarization, polarization sensitivity

1. Introduction

In response to the increasing concern over environmental issues[1], the European Commission (EC) and the administrative arm of the European Union(EU) will soon launch a consultation program examining the environmental issues related to PVC(polyvinylchloride). The EC has already adopted a green paper evaluating environmental aspects of PVC with the specific provisos that the consultation is based on science and include aspects related to human health. The paper sets out details of the recent studies the EC has conducted in this area. It also invites discussions on two major areas: the use of additives such as lead, cadmium and phthalates; and the waste management of PVC, including the options of recycling, incineration, and land fill disposal. The aim of this project is to give the EC the scientific basis to develop a comprehensive strategy on PVC in early 2001. The EC emphasizes that PVC to be produced for practical applications will account for about 30% of the total production of plastic in Europe. The green paper is an "unsatisfactory review of the PVC life cycle" according to the assessment of the European Council of Vinyl Manufacturers. Before Shirakwa, MacEiarmid and Heeger made their seminal discovery in 1977, the idea of plastics being able to conduct electricity like metal seemed ludicrous for organic polymers known as insulators. However, these three researchers found that by dropping a known conjugated polymer(poly-acetylene), it could conduct a charge. Since then, scientists have synthesized a number of other conducting polymers as well as a host of related polymers that have semiconducting and light-emitting properties. Accordingly, the development of polymers has led to new types of organic materials that can combine the processing advantages and mechanical properties of plastics with electronic and optical properties of metals and inorganic semiconductors. Furthermore, these materials, in turn, led to the development of organic and polymeric light-emitting diodes, field effect transistors and photovoltaic devices. For example, conducting polymers are being used as anti-static coatings and corrosion inhibitors, and even play "a major role as a radar-absorbing screen coating in stealth bombers", according to the chemistry professor, Andrew B. Holmes, who directs the

Melville Laboratory for polymer synthesis at the University of Cambridge. Professor Holmes told Chemical and Engineer News(C & EN) that a light-emitting conducting polymer is now being included in mobile phone displays. Other applications of conducting polymers that can soon emerge include lightweight batteries for cars, electromagnetic shielding, ultra-thin computer monitors and TV sets, artificial nerves and sensors, according to Darnel H. Busch, president of the American Chemical Society[2]. However, no previous reports exists on the polarization of polymers. Accordingly, this paper is the first attempt to correlate corrosion tests performed using an electrochemical method. Also, this study investigates the detailed influence of temperature and pH.

2. Experimental procedure

The PET(polyethyleneterephthalate) was obtained from the Aldrich Chemical Company, Inc (G.P.C. Chemicals). The electrolytic and polarizing measurements were performed in toluene or dimethylformamide. The supporting electrolyte was either tetrabutyl ammonium perchlorate (TBAP) (G. F. S. Chemicals) or lithiumperchlorate (Aldrich), which were used as received. The supporting electrolyte concentration was typically 0.10 M. The electrode tip of the working electrode system consisted of a $1cm^2$ piece of silver(0.1 mm thickness) as the conducting material, which, together with a silver wire, was sealed perpendicular to the rod(wire) axis for the electrical conduct. The reference electrode was a saturated calomel electrode(Ag/AgCl : Koslow Scientific Company. P/N 1004), and a graphite carbon rod was used as the counter electrode, and the electrolysis cells were of the conventional design.

All experimental solutions for the polarization were typical 0.25 %(w/v) in the redox-active species and deoxygenated by purging with prepurified nitrogen for at least 15 min. All experiments were performed at a scan rate of 7 mV/s by CMS 100 and 105(Gamry Instruments, Inc) with a computer. The pH was measured with a pH meter(Corning 320). The Tafel plots were obtained from the -2.0 to +1.0 V region at a steady state potential. The pH of the solution was controlled by sodium hydroxide or hydrochloric acid. The polymer from Aldrich was used in preparing the nonaqueous solvent(dimethylsulfoxide). All solutions were deairated for 15 min with nitrogen gas and all experiments were carried out at optimum temperature.

3. Result and discussion

3.1. Polarization characteristics

Fig. 1 shows the polyvinylchloride electrolytic

Table 1. Parameter of corrosion effect with temperature and pH condition for polymers

Redox-wave		Temperature(℃)					PH				
		15	25	35	45	55	3.0	5.0	7.0	9.0	11.0
1st-wave	(1)	-0.80	-0.70	-0.70	-0.65	-0.65	-0.50	-0.50	-0.55	-0.50	-0.55
	(2)	-0.80	-0.70	-0.29	-0.24	-0.24	-0.21	-0.14	-0.25	-0.31	-0.39
	(3)	-0.58	-0.58	-0.47	-0.47	-0.47	-0.31	-0.37	-0.37	-0.24	-0.37
	(4)	-0.44	-0.47	-0.41	-0.36	-0.32	-0.48	-0.42	-0.46	-0.46	-0.46
2nd-wave	(1)	0.22	0.11	0.08	0.08	0.28	0.08	0.08	0.12	0.12	0.12
	(2)	-0.60	-0.50	-0.09	-0.02	-0.04	0.00	0.00	0.00	0.00	0.00
	(3)	0.37	0.34	0.32	0.32	0.32	0.37	0.05	0.05	0.26	0.24
	(4)	0.43	0.41	0.40	0.38	0.39	0.00	0.11	0.12	0.14	0.15
3rd-wave	(1)	0.47	0.37	0.33	0.33	0.62	0.50	0.50	0.57	0.55	0.54
	(2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	(3)	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.40	0.00	0.00
	(4)	0.00	0.00	0.00	0.00	0.00	0.43	0.43	0.40	0.44	0.44

Polymers : (1).PVC(polyvinylchloride), (2).PET(polyethyleneterephthalate), (3).PP(polypropylene), (4).PC (polycarbonate)

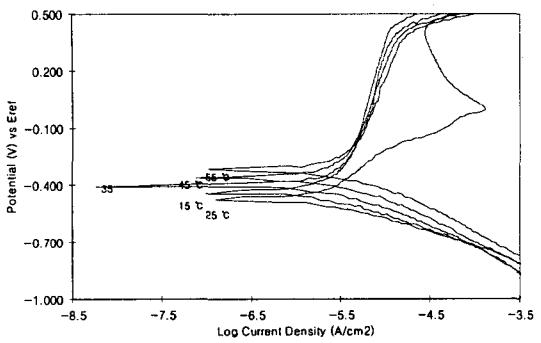

Fig. 1. Polarization curves of PC(polycarbonate) at various Temperatures.

polarization curves in a nonaqueous solvent at 25 ℃. The cathodic and anodic polarization curves for the step potentials and current densities were all measured in an organic solvent. The polarization curves of the polymers were obtained with three step potentials and current densities. The redox potentials of the specimens were measured within the range of + 2.0 V to 2.0 V, vs S.C.E. The results are summarized in Table 1.

3.2. Effect of temperature on redox reaction

Fig. 2 is based on data from the external cathodic and anodic polarization curves, as presented in Fig 1. As shown in Fig. 2 and 3, potential from the 1st and 2nd waves of PET with polymer PVC (polyvinylchloride), PET(polyethylenterephthalate), PP(polypropylene), and PC(polycarbonate)

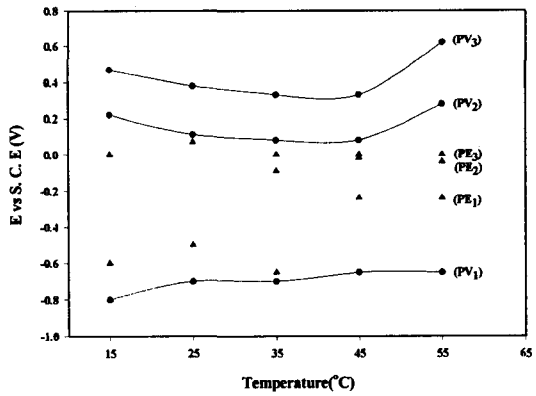

Fig. 2. Variation of potential as a function of temperatures(℃)
(where PV_{1-3}(Polyvinylchloride) waves) : PVC waves ; PE_{1-3} : PET(Polyethyleneterephthalate)waves).

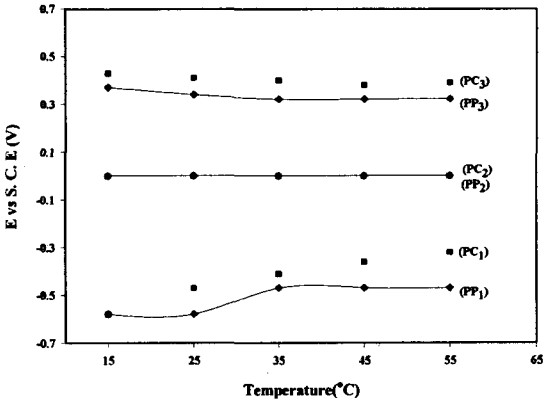

Fig. 3. Variation of potential as a function of temperatures(℃)
PP_{1-3} : polypropylene waves ; PC_{1-3} : ploycarbonate waves.

were exhibited by the cathodic potential, whereas the 2nd and 3rd waves were maintained by the anodic potentials at all temperatures.

Oxidation occurred when the 2nd wave reached 15 ℃(PVC.E = 0.22 V, PP. E = 0.37 V, PC = 0.43 V), 25 ℃(PVC. E = 0.11 V, PP. E = 0.34 V, PC. E = 0.41 V), 35 ℃(PVC. E = 0.08 V, PP. E = 0.32 V, PC. E = 0.40 V), 45 ℃(PVC. E = 0.08 V, PP. E = 0.32 V, PC. E = 0.38 V), 55 ℃(PVC. E = 0.28 V, PP. E = 0.32 V, PC. E = 0.39 V) and when the 3rd wave reached 15 ℃(PVC. E = 0.47 V), 25 ℃(PVC. E = 0.37 V), 35 ℃(PVC. E = 0.33 V), 45 ℃(PVC. E = 0.33 V), and 55 ℃(PVC. E = 0.62 V). Especially, the potential efficiency of the 3rd waves were exhibited by the anodic potentials of only PVC, whereas the PET, PP and PC waves did not occur the redox reaction. The series of polarity tests related to the 2nd waves indicated a lower potential than oxidation from 35 ℃ to 45 ℃(PVC), 35 ℃ to 55 ℃(PP) and 45 ℃ to 55 ℃(PC). Accordingly, the highest efficiency of temperatures occurred rapidly to lower than oxidation potential. Also, the highest efficiency of temperatures was between 35 ℃ and 45 ℃ for PVC.

3.3. Effect of pH on redox reaction

Fig. 4 and Fig. 5 present the variation in the corrosion potential derived from the PVC, PET, PP and PC polarization curves in an electrolytic solution[3]. The effect of pH on the Fig. 4 and Fig. 5 redox potential shifted to a negative potential

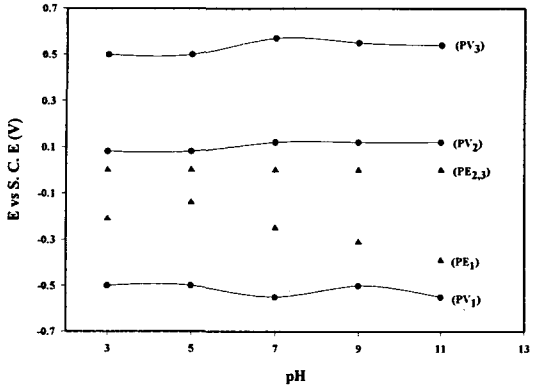

Fig. 4. Dependencies of potential on pH. $PV_{1\text{-}3}$. PVC waves, $PE_{1\text{-}3}$. PET waves.

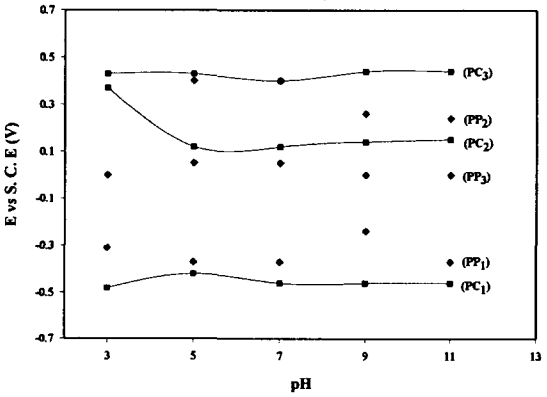

Fig. 5. Dependencies of potential on pH. $PP_{1\text{-}3}$. polypropylene waves, $PC_{1\text{-}3}$. : polycarbonate waves.

with the 1st wave of each pH condition. The curves of the 2nd and 3rd waves occurred while oxygen was being consumed, and the 1st wave of the cathodic reaction consisted of the reduction of hydrogen ions in solution. These oxidation potential values were obtained from 2nd and 3rd waves of each pH conditions. The oxidation potential from the 2nd wave was exhibited at pH of 3.0(PVC (E = 0.08 V), PET(E = 0.00 V), PP(E = 0.37 V) and PC(E = 0.00 V), at pH 5.0(PVC (E = 0.08 V), PET(E = 0.00 V), PP(E = 0.05 V) and PC(E = 0.11 V), at pH 7.0(PVC (E = 0.12 V), PET (E = 0.00 V), PP(E = 0.05 V) and PC(E = 0.12 V), at pH 9.0(PVC (E = 0.12 V), PET(E = 0.00 V), PP(E = 0.26 V) and PC(E = 0.14 V), at pH 11.0(PVC (E = 0.12 V), PET(E = 0.00 V), PP (E = 0.24 V) and PC(E = 0.15 V) and from the 3rd wave was exhibited at pH 3.0(PVC (E = 0.50 V), PET(E = 0.00 V), PP(E = 0.00 V) and PC (E = 0.43 V), at pH 5.0(PVC (E = 0.50 V), PET (E = 0.00 V), PP(E = 0.40 V) and PC(E = 0.43 V), at pH 7.0(PVC (E = 0.57 V), PET(E = 0.00 V), PP(E = 0.40 V) and PC(E = 0.40 V), at pH 9.0(PVC (E = 0.55 V), PET(E = 0.00V), PP(E = 0.00 V) and PC(E = 0.44 V), at pH 11.0(PVC (E = 0.54 V), PET(E = 0.00 V), PP(E = 0.00 V) and PC(E = 0.44 V). Here, negative potential values obtained from the 1st wave were reduction processes. In the meantime, the variation of the oxidation potential from results of the 2nd and 3rd waves was used to establish the efficiency of pH.

A series of oxidation tests from the 2nd and 3rd waves indicated the lowest oxidation potential of polymers at between 3.0 and 5.0 pH(PVC_2 (E = 0.08 V), PVC_3(E = 0.50 V)), and at between 5.0 and 7.0 pH(PP2 (E = 0.05 V), PP_3(E = 0.40 V)) and PC_2((E = 0.11-0.12 V), PC_3 (E = 0.43-0.40 V)) Accordingly, rapidity of oxidation from the 2nd and 3rd waves with all specimens was exhibited at a pH of between 3.0 and 5.0 for PVC, but for PET no oxidation potential was observed from the 2nd wave. However, oxidation for the PP and PC was exhibited at a pH of between 5.0 and 7.0. Therefore, corrosion can be expected in acid rather than alkali solution. Structure of the experimental specimens in Table 1.

PVC : $+CH_2-CHCl+_n$

PET : $+CO-C_6H_4-COO-CH_2-CH_2-O+_n$

P P : $+CH_2-CH(CH_3)+_n$

P C : $+O-C_6H_4-C(CH_3)_2-C_6H_4-OCO+_n$

Here, the efficiency of redox potential was related to the benzene ring in specimens. The redox reaction was rapidly exhibited in the absence of benzene ring. In comparison with PET and PC, the former with one benzene ring exhibited the redox reaction more rapidly than the latter with two benzene rings. For this reason, it was clearly not due to oxidation with oxygen.

3.4. Measurement of resistance and rate

The impedance response is related to the dissociation with the charge transfer process and is given by the product of the interfacial charge transfer resistance. Electrolytic techniques such as linear polarization can be used for the rapid measurement of polarization resistance[4]. Fig. 6 and Fig. 7 are based on data from this experiment. Polarization resistance(RP) and rate(mm/y) can be presented by linear polarization curves[5,6]. The value of resistance($K\Omega cm^2$)[7] and rate(mm/y)[8] were obtained using a Tafel plot and the resistance was obtained from the following equation.

$$R_p = \frac{\Delta E}{\Delta i} = \frac{\beta_A \times \beta_C}{2.30 I_{corr}(\beta_A + \beta_C)}, \quad Rate = \frac{0.13 \times I_{corr} \times E_q \times W}{d},$$

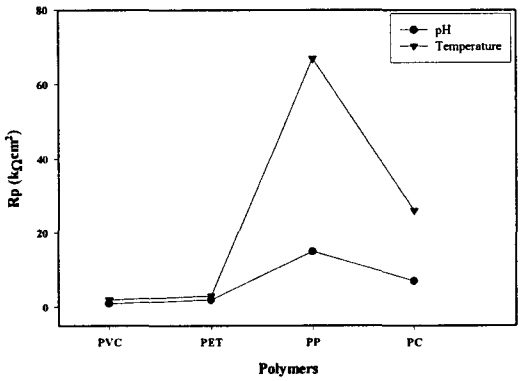

Fig. 6. Variation of resistance for polymers adjusted with optimum temperaturs and pH (temperature : PVC:30 ℃, PET:25 ℃, PP:35 ℃, PC:45 ℃ and pH:PVC=3.0, PET=4.0, PP and PC=5.0).

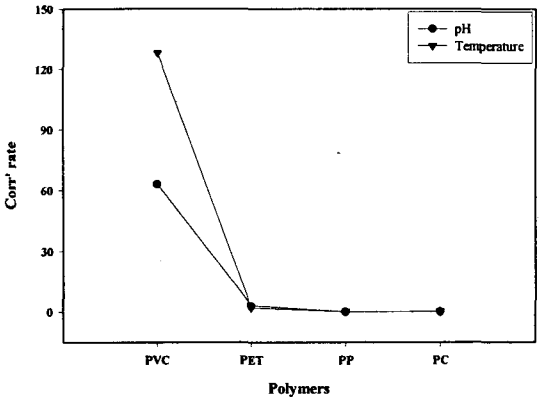

Fig. 7. Variation of corrosion rate for polymers adjusted with optimum temperaturs and pH (temperature : PVC:30 ℃, PET:25 ℃, PP:35 ℃, PC:45 ℃ and pH: PVC=3.0, PET=4.0, PP and PC=5.0).

Where R_p=polarization resistance, ΔE=potential difference, Δi=current difference, β_A=anodic Tafel constant, and β_C=cathodic Tafel constant., I_{corr}=corrosion current, where d = sample density (g/cm^3), and $E_q \times W$=equivalent weight(g).

These values are the slope at E_{oxi} of a plot of I versus E in the region of E_{oxi}. The Tafel method is a useful device for evaluating kinetic parameters. The anodic branch with a slope $(1-\alpha)nF/2.3RT$ was used to obtain the mass transfer coefficients (α). The values(α) obtained, as summarized in Table 2, were higher than 0.50. Accordingly, it is clear that the electrode reaction was reversible under all conditions[9,10]. The Tafel slope for the anodic dissolution was determined by the po-

Table 2. Effect of Various Condition on the Polarization Characteristics for Polymer(PVC (1),PET (2), PP (3), PC (4))

Condition	Parameter					
	Optimum (℃)	potential E(V)	Resistance(Rp) ($K\Omega cm^2$)	rate (mm/y)	Reversibility (α)	Susceptibility (I_f/I_f)
Temperature	(1) 30	0.33	1.56	123.43	0.98	0.82
	(2) 25	0.07	3.05	1.38	0.98	0.41
	(3) 35	0.38	66.7	0.07	0.60	0.65
	(4) 45	0.38	25.6	0.23	0.70	0.74
pH	(1) 3.0	0.50	0.93	63.08	0.97	0.82
	(2) 4.0	-0.14	1.80	2.56	0.97	0.47
	(3) 5.0	0.05	14.90	0.64	0.87	0.75
	(4) 5.0	0.11	7.10	0.69	0.53	0.68

Polymers : (1).PVC(polyvinylchloride), (2).PET(polyethyleneterephthalate), (3).PP(polypropylene), (4).PC (polycarbonate)

larization effects of the pH and temperature. All specimens exhibited a transition in the electrolytes and the slope of linear representing anode dissolution only shifted slightly in the potential direction with different temperatures(15, 25, 35, 45, and 55 ℃). These results are summarized in Table 2.

Table 2 presents the variations in the redox resistance and rate under various conditions. This was determined by the optimum potential effects of pH and temperature. As shown in Table 2, the oxidation rate was the most rapid with the lowest resistance, whereas the various conditions exhibited the slowest oxidation rate with the highest resistance. In contrast, temperature and salt produced a reasonably balanced relationship between resistance and oxidation rate. The optimum condition of resistance and rate was found on the time of exposure[11].

3.5. Effect of reaction sensitivity relative to current density

Fig. 9 presents the variation in the current density ratios with a reverse current(I_r) versus a forward current(I_f) from an anodic polarization curve, as shown in Fig. 8. This was obtained by the polarization curves when measuring with added factors(temperature and pH). The susceptibility was obtained by calculating the ratio of the current density with a reverse current(I_r) to that with a forward current(I_f) from the polarization curves. As shown in Fig. 9, the corrosion susceptibility

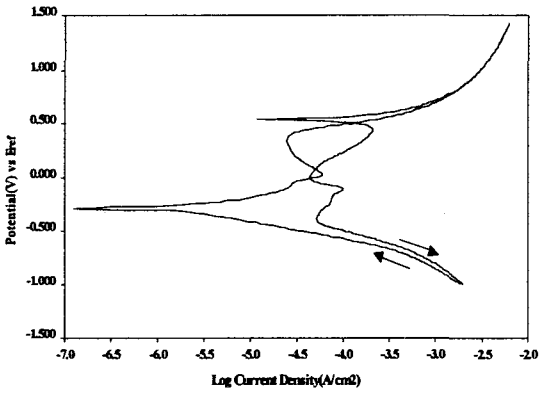

Fig. 8. Current density curve polycarbonate obtained by cyclic polarization curve(forward and reward scan rate : 10 mV/s).

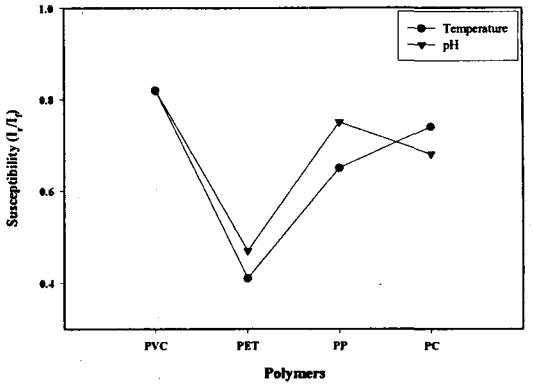

Fig. 9. Sensitivity effects of maximum current density for forward and reward scan at temper(temperature : PVC:30 ℃, PET:25 ℃, PP:35 ℃, PC:45 ℃ and pH:PVC=3.0, PET=4.0, PP and PC=5.0).

was found to be in the following order to PVC > PP > PC > PET of temperature and to PVC > PC > PP > PET of the pH. Since these results cannot be explained as an effect of oxidation, they would appear to result from an increase in the current density owing to another factor. For this reason, it was clearly not owing to reactivity with oxygen.

4. Conclusions

The polarization curves of PET in a nonaqueous solvent showed two or three redox waves. The potential efficiency of the 1st wave exhibited a cathodic reduction potential at all temperatures, whereas the 2nd and 3rd waves were maintained for the anodic oxidation potential.

The optimum temperatures of oxidation were at 30 ℃(PVC), 25 ℃(PET), 35 ℃(PP) and 45 ℃(PC), and the optimum condition of pHs were at 3.0(PVC), 4.0(PET), 5.0(PP and PC). The oxidation of the polymers can be expected in acid solution, and oxidation potential was related to the benzene ring in specimens. oxidation potential was shown to be most rapid with the lowest potential in the absence of a benzene ring. PET with one benzene ring exhibited the redox reaction more rapidly than PC with two benzene rings. The relation of the benzene ring would be appear more rapid with ring one than in the presence of ring two. The relation of the resistance and rate was

the most rapid with the lowest resistance, and it exhibited the slowest oxidation rate with the highest resistance. The electrode reaction was reversible under all conditions.

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