

Influence of Corrosion Potential and Current Density on Polarization Curve Variations using Polycarbonate[III]

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In this study, experiments were carried out to measure the variations in the corrosion potential and current density of polarization curves using polycarbonate. The results were particularly examined to identify the influences affecting the corrosion potential including various conditions such as temperature, pH, catalytic enzyme, and salt. The lines representing the active anodic dissolution were only slightly shifted in the potential direction by temperature, pH, enzyme, and salt. The Tafel slope for the anodic dissolution was determined based on the polarization effect with various conditions. The slope of the polarization curves describing the active-to-passive transition region were noticeably shifted in direction. Also, from the variation in the conditions, the optimum conditions were established for the most rapid transformation, including temperature, pH, corrosion rate, and resistance of corrosion potential. The second anodic current density peak and maximum passive current density were designated as the critical corrosion sensitivity (I_p/I_r). The value of I_p/I_r was then used in measuring the extent of the critical corrosion sensitivity of the polycarbonate. The potentiodynamic parameters of the corrosion were obtained using a Tafel plot.

Key words : corrosion potential, anodic current, Tafel, polarization, critical corrosion sensitivity

1. Introduction

Natural polymers are the basis of all life processes, and our current technological society is largely dependent on synthetic polymers(Chang, 1994 ; Brydson, 1995). Undoubtedly the 1970s will be known as the environmental, ecological, or pollution decade, for it was in this decade that environmental pollution first became a popular cause for concern. Much of the material spoken and written about environmental pollution has been presented with great emotion from positions firmly on one side or the other of various issues(Stocker, 1972). However, no previous reports exist on the corrosion of polymers. Accordingly, this paper is the first attempt to correlate corrosion tests executed using an electrochemical method. In addition, this study also investigates the detailed influence of variation factors such as temperature, pH, and casting times with oxygen, along with determining

the corrosion effect of the enzyme(Castro, 1989) and salt.

2. Experimental

The polycarbonate was obtained from the Aldrich Chemical Company Inc(G.P.C Chemicals). The electrochemical and polarizing measurements were performed in chloroform or dimethylformamide. The supporting electrolyte was either tetrabutylammoniumperchlorate(TBAP)(G.F.S.Ch emicals), or lithiumperchlorate(Aldrich), which was used as received. The supporting electrolyte concentration was typically 0.10M. The electrode tip of the working electrode system consisted of a 1cm² piece of silver(thickness 0.1mm) 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), a graphite carbon rod was used as the counter electrode, and the electrolysis cells were of conventional design. All experimental solutions for the electrochemistry were typical 0.25%(w/v) in the redox-active species, and were deoxygenated by purging with prepurified nitrogen for at least 15 min. All experiments were performed at a scan rate of 7 mV/s by CMS100 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 -1.0 to +1.5V region at a steady state potential. The pH of the solution was controlled by sodium hydroxide or hydrochloric acid, which was added to magnesium chloride in order to observe the effects of salt. The enzyme(Citrate lyase : Fluka, grade reagent) was dissolved at a concentration of mg/ml(unit) in a nonaqueous solvent. The polycarbonate(Average Mw. ca 64000) from Aldrich was used in preparing the nonaqueous solvent(CHCl₃ : DMF = 4 : 1). All solutions were deaerated for 10 min' with nitrogen and the experiments were carried out at 25°C.

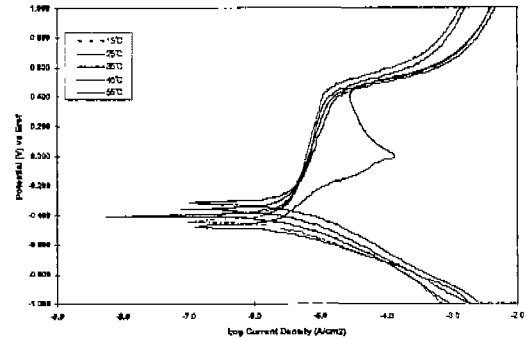


Fig. 1. Polarization curves of polycarbonate(polymer) in nonaqueous solvent.(Contained dissolving oxygen)

3. Results and Discussion

3.1. Electrochemical Polarization Characteristic

Fig. 1 shows the polycarbonate electrochemical polarization curves in a nonaqueous solvent (chloroform and dimethylformamide(4 : 1)) at 25°C. Cathodic and anodic polarization curves

for all the two step potentials and current densities were measured in an organic solvent. The corrosion potentials of the two specimens were measured within the range of +1.0V to -1.0V, vs S.C.E. The polycarbonate steady state corrosion potentials were obtained at -0.33V and +0.38V. These results are summarized in Table 1.

3.2. Effect of Temperature on Corrosion

Fig. 2 was drawn with data from the external cathodic and anodic polarization curves, as presented in Fig. 1. As shown in Fig. 2, with polycarbonate, the potential efficiency of the 1st wave was exhibited by the cathodic potential whereas the 2nd wave was maintained by the anodic potential at all temperatures. Oxidation occurred

Table 1. Parameter of corrosion effect with various conditions.

Parameter Redox Steps	Corrosion Polarizing E(V)	P. C										P. C + 0.1M MgCl ₂									
		(°C)					pH					(°C)					pH				
		15	25	35	45	55	3.0	5.0	7.0	9.0	11.0	15	25	35	45	55	3.0	5.0	7.0	9.0	11.0
1st-wave	-0.33	-0.44	-0.47	-0.41	-0.36	-0.32	-0.48	-0.42	-0.46	-0.46	-0.46	-0.48	-0.51	-0.50	-0.47	-0.43	-0.51	-0.51	-0.51	-0.50	-0.41
2nd-wave	0.38	0.43	0.41	0.40	0.38	0.39	0.00	0.11	0.12	0.14	0.15	0.04	0.00	-0.18	0.00	0.01	0.00	0.01	0.03	0.02	0.05
3rd-wave	0.43	0.43	0.40	0.44	0.44	1.34	1.26	1.16	1.01	0.90	0.91	0.90	1.09	0.95	0.91

Parameter Redox Steps	P. C + 9 Unit/ml Citrate										P. C + O ₂				
	(°C)					pH					(°C)				
	15	25	35	45	55	3.0	5.0	7.0	9.0	11.0	20	40	60	80	100
1st-wave	-0.45	-0.48	-0.47	-0.37	-0.33	-0.38	-0.43	-0.45	-0.41	-0.42	-0.42	-0.39	-0.39	-0.42	-0.40
2nd-wave	0.00	-0.22	-0.22	0.00	0.07	0.00	0.13	0.16	0.15	0.15	0.44	0.46	0.23	0.46	0.28
3rd-wave	0.40	0.41	0.39	0.38	0.38	0.41	0.36	0.39	0.43	0.42

P. C : Polycarbonate Unit : μmol

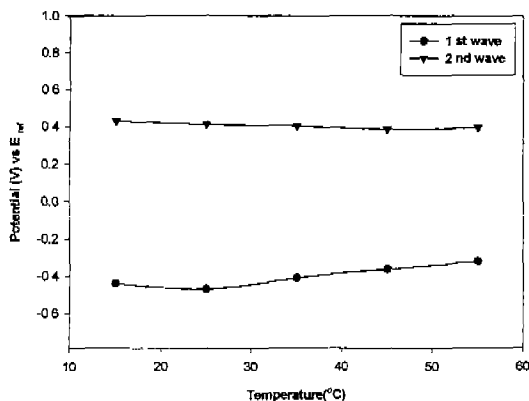


Fig. 2. Variation of temperature and corrosion potential.

when the 2nd wave reached 15 °C ($E = 0.43$ V), 25 °C ($E = 0.41$ V), 35 °C ($E = 0.40$ V), 45 °C ($E = 0.38$ V), and 55 °C ($E = 0.39$ V), respectively. The series of corrosion tests related to the 2nd wave indicated a higher potential than oxidation from 15 to 35 °C, and corrosion occurred at a potential lower than $E = 0.38$ V at temperatures between 45 and 55 °C. Accordingly, the most efficient corrosion temperature was between 45 to 55 °C.

3.3. Effect of pH on corrosion

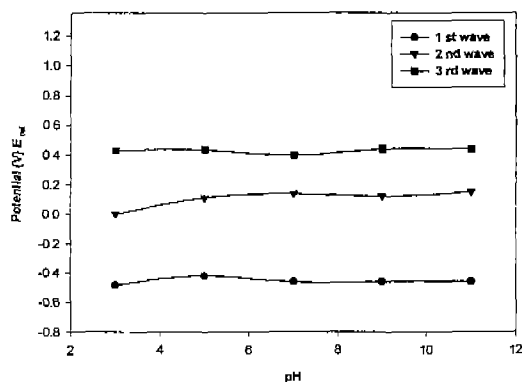


Fig. 3. Variation of corrosion potential on pH efficiency.

Fig. 3 presents the variation in the corrosion potential derived from the polycarbonate polarization curve in an electrolytic solution (Temmmali, 1972 ; Antonian, 1998). The effect of pH on the polycarbonate corrosion potential shifted from a positive to a negative potential with the first 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 to hydrogen in air. Accordingly, the rapidity of the oxidation from the second and third waves exhibited a pH of 5.0 ($E = 0.11$ V), ($E = 0.43$ V) and 7.0 ($E = 0.12$ V), ($E = 0.40$ V), respectively. Therefore, it would appear that pH had an effect on corrosion at pH 5.0 and 7.0.

3.4. Measurement of resistance

3.4.1. Relationship between resistance and temperature

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. Electrochemical techniques such as linear polarization can be used for the rapid measurement of polarization resistance (Goodson, 1986). Polarization resistance (R_p) and rate (mph) can be presented by linear polarization curves. The value of the corrosion resistance (R_p) and rate (mph) were obtained using a Tafel plot. These values are the slope at E_{corr} of a plot of I versus E in the region of E_{corr} . The Tafel method is a useful device for evaluating kinetic parameters. The Tafel slope for anodic dissolution was determined by the polarization effects of pH and temperature. The linear slopes of the polarization curves describing the active-to-passive transition region shifted noticeably in the noble direction. All specimens exhibited an active-to-passive transition in the electrolytes and the linear representing active anode dissolution only shifted slightly in the potential direction at different temperatures (15, 25, 45, and 55 °C). These results are summarized in Table 2.

Fig. 4 presents the variations in the corrosion resistance and rate at various temperatures. As shown in Fig. 4, only slight differences appeared in these resistances and rates from 15 until 25 °C and 45 until 55 °C. The highest resistance was exhibited at 35 °C when the rate was the lowest. Therefore, the optimum temperature condition would appear to be at 35 °C. This can be explained by the reduction in the absence of oxidation and break down (Wheeler, 1979).

Table 2. Effects of various condition on the electrochemical characteristics.

Parameters		Best Condition (°C, pH)	Corrosion Potential (V ; 2nd)	Resistance(R _p) (K Ω cm ²)	Corrosion sensitivity (I _r /I _i)	Reversibility (α)
Sample solu'	Temp'	45°C	0.38	25.3	0.74	0.70
	pH	5.0	0.11	7.1	0.68	0.53
Sample solu'+ MgCl ₂	Temp'	55°C	0.01	45.5	0.71	0.77
	pH	5.0	0.01	42.7	0.60	0.66
Sample solu'+ Citrate	Temp'	55°C	0.07	13.3	0.74	1.00
	pH	5.0	0.13	14.5	0.60	0.60
Sample solu'+ Oxygen	25°C	60min'	0.23	11.6	0.79	1.00
	(pH7~9)	100min'	0.28	57.3	0.80	0.50

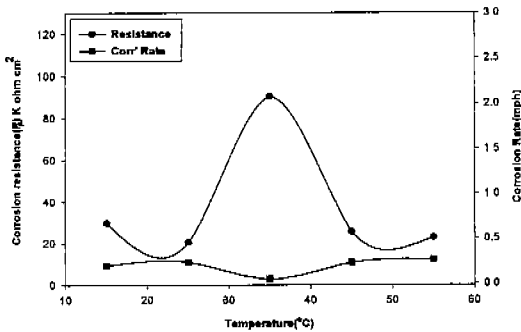


Fig. 4. Variation of resistance(R_p) and corrosion rate (mph) relative to the temperature.

3.4.2. Resistance effect of pH

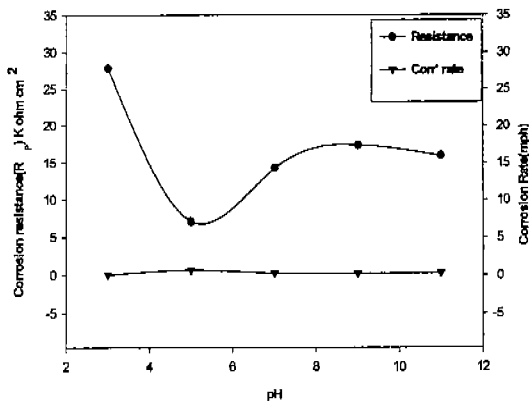


Fig. 5. Variation of resistance(R_p) and corrosion rate (mph) relative to the pH.

Fig. 5 presents the variation in the corrosion resistance and corrosion rate with an adjusted pH.

The resistance(R_p) values increased to a maximum at pH 3.0, decreased at pH 5.0, and then increased again slightly at pH 7.0. Accordingly, the minimum corrosion resistance was found at pH 5.0. The impedance response is related to the dissociation with the charge transfer processes and is given by the product of the interfacial charge transfer resistance. These result revealed that the corrosion rates decreased at pH 3.0 and mostly increased at pH 5.0. However, thereafter, it gradually decreased at pH 7.0, 9.0, and 11.0. This corrosion phenomenon results from the sufficient supply of hydrogen ions leading to a hydrogen reduction reaction as well as the presence of chloride ions which lead to pitting(Do, 1992 ; John, 1986).

3.5. Electrochemical Polarization Characteristics of Added Salt

3.5.1. Optimum Temperature for Corrosion Potential with Salt

As shown in Fig. 6, corrosion tests were carried out to qualitatively determine the effect of various temperatures on the corrosion of polycarbonate in a 0.1M MgCl₂ solution. It was found that the corrosion potentials could be evaluated as positive potentials. However, in the mean time, the variation of the corrosion potential from the 2nd and 3rd waves exhibited an optimum temperature for the rapid onset of corrosion between 45°C(0.00V to 1.01V) to 55°C(0.01V to 0.90V), respectively. The efficiency of the corrosion was established by a comparison between the addition and absence of salt(0.1M MgCl₂). The corrosion potential without

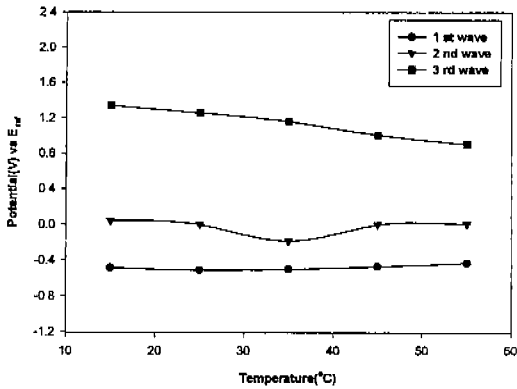


Fig. 6. Variation of corrosion potential relative to temperature adjusted with addition of salt. (0.1M MgCl₂)

salt was lower(0.01V)than that in the presence of salt. Accordingly, it was established that the corrosion was more rapid with the addition of salt.

3.5.2. Optimum pH for Corrosion Potential with Salt Effect.

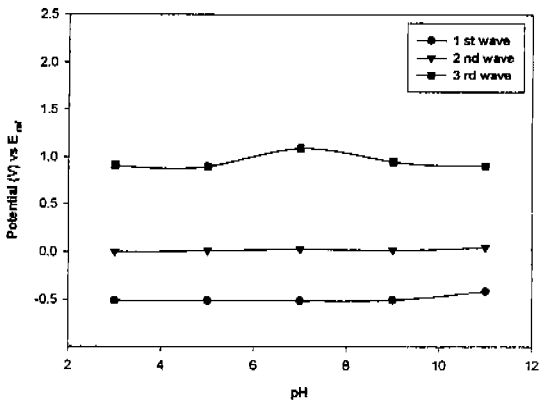


Fig. 7. Variation of corrosion potential relative to pH adjusted with addition of salt.(0.1M MgCl₂)

The specimen was exposed to air saturated in a 0.1M MgCl₂ solution for a few day(more than one day). Fig. 7 shows the corrosion effect of the pH in a 0.1M MgCl₂ solution. The polycarbonate polarization curves exhibited three redox waves. In Fig. 7, the negative potential of the first wave was not a corrosion potential. However, it is clear that the corrosion potentials of the second and third waves were oxidized values. However, 2nd step occurred before oxidation at 0.00V(pH3.0), 0.01

V(pH5.0), 0.03V(pH7.0), 0.02V(pH9.0), and 0.05V(pH11.0), respectively. Yet the variation in the corrosion potential from the 3rd step was exhibited at 0.91V(pH3.0), 0.90V(pH5.0), 1.09V (pH7.0), 0.95V(pH9.0) and 0.91V(pH11.0), respectively. Accordingly, the optimum pH for corrosion efficiency was 5.0. It was established that the corrosion potentials were obtained at 0.01V(pH5.0) for the 2nd step and at 0.90V(pH5.0) for the 3rd step. The oxidation potential without the addition of salt(0.1M MgCl₂ solution) was obtained at -0.33V for the 1st step and at 0.38V for the 2nd step. However, no oxidation potential was exhibited for the 3rd step. Therefore, when comparing the value of the 2nd step with and without the addition of salt, the oxidation potentials were higher in the presence of the 0.1M MgCl₂ solution. Accordingly, a rapid corrosion rate was exhibited with the addition of the 0.1M MgCl₂ solution.

3.6. Influence of Temperature and pH with Enzyme.

3.6.1. Corrosion Potential of Temperature for Enzyme(Citrate Lyase)

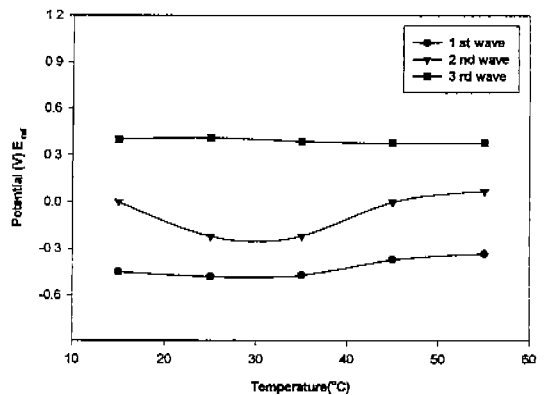


Fig. 8. Variation of corrosion potential relative to temperature adjusted with addition of Enzyme.(9 unit/ml Citrate)

To observe the effect of 9 unit/ml Citrate Lyase, the polarization method was used with a constantly maintained temperature. As shown in Fig. 8, the series of corrosion testes at varying temperatures indicated an oxidation potential from 15 to 55°C. Accordingly, it would appear that the 1st and 2nd

steps exhibited a reduction potential while, with the exception of 55 °C (0.07V), the oxidation potential at the 3rd step was available at all temperatures. Corrosion was observed at the 3rd step where these steps were attributed 15 °C (0.40V), 25 °C (0.41V), 35 °C (0.39V), 45 °C (0.38V), and 55 °C (0.38V), respectively. Therefore, it would appear that rapid corrosion began from 45 °C to 55 °C. It is also of interest to compare the difference in potential in terms of the possible effects on the enzyme catalyzed reaction. Therefore, when comparing the 2nd step with and without the addition of the enzyme, the oxidation potentials were higher in the presence of the enzyme. Accordingly, the a rapid corrosion rate was exhibited with the addition of the enzyme. The best temperature of corrosion was observed to be within the range of 45 to 55 °C.

3.6.2. Corrosion Potential of pH with Enzyme (Citrate Lyase)

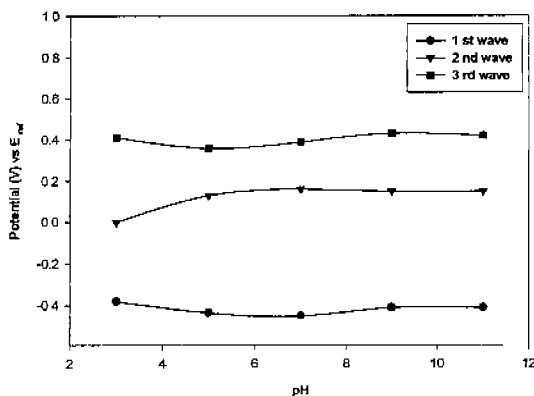


Fig. 9. Variation of corrosion potential relative to pH adjusted with addition of Enzyme. (9 unit/ml Citrate)

Fig. 9 shows the corrosion potential efficiency for the enzyme (Castro, 1989) relative to the pH. As shown in Fig. 8, polycarbonate with an added enzyme exhibited a reduction potential in the first step at all pH whereas the 2nd and 3rd steps exhibited oxidation potentials. Except for the 1st step, corrosion occurred at the 2nd and 3rd steps along with the consumption of oxygen and the 1st step of the reducing the reduced hydrogen ions to hydrogen in air. This phenomenon results from a sufficient supply of hydrogen ions leading to

a hydrogen reduction reaction as well as the presence of chloride ions which lead to pitting. In the case of the 2nd step, a pH of 3.0 (0.00V), 5.0 (0.13V), 7.0 (0.16V), 9.0 (0.15V) and 11.0 (0.15V), and for the 3rd step a pH of 3.0 (0.41V), 5.0 (0.36V), 7.0 (0.39V), 9.0 (0.43V), and 11.0 (0.42V), respectively. In the case of pH 5.0, oxidation occurred below the potentials. The reason for this may be that the corrosion potential is rapid due to the gradual increase in the oxygen oxidation reaction. This phenomenon is relative to the corrosion rate. It is also of interest to compare the difference in potential in terms of its possible effects on the enzyme-catalyzed reaction. In the case of pH 5.0, lower corrosion potentials were observed at the 2nd and 3rd steps. Accordingly, the optimum pH for corrosion was observed at pH 5.0. Therefore, when comparing the 2nd oxidation step from Table 1, the 2nd oxidation step potential was observed at 0.13V in the presence of the catalyzed whereas the 3rd oxidation step potential was observed at 0.38V in the absence of the catalyzed enzyme. However, there was also a significant difference in the oxidation potentials in the presence of the catalyzed enzyme. Based on the above arguments, the importance of this effect has been previously recognized as rapid oxidation by an added catalyzed enzyme. Based on these results, it can be concluded that the oxidation of polycarbonate in the presence of an enzyme occurred more rapidly at a pH of 5.0.

3.7. Effect of dissolved oxygen

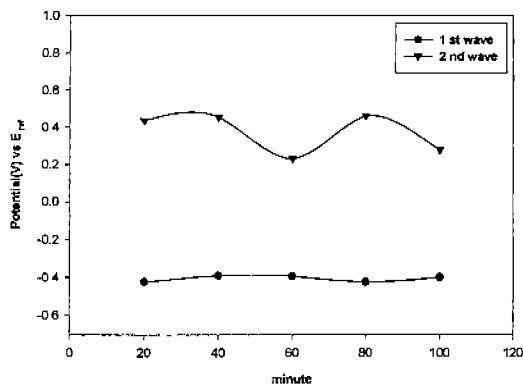


Fig. 10. Variation of corrosion potential relative to casting times with oxygen. (oxygen casting times)

Fig. 10 shows the influence of the corrosion potential relative to the casting time with oxygen. Fig. 10 was drawn based on data from the external cathodic and anodic polarization curves. In this case, the negative potential value obtained from the first wave was negligible because the potential values were reduction processes. Meanwhile, a variation in the corrosion potential was observed from the second wave. As shown in Fig. 11, the variation in the corrosion potential from second wave exhibited a slow corrosion rate within the ranges of 20(+0.44V), 40(+0.46V) and 80(+0.46V), 100 minutes(+0.28V), however, the optimum casting time was exhibited at 60 minutes(0.23V). The corrosion efficiency of the dissolved oxygen is listed in Table 1, together with data from previous literature for comparison. Based on the data, the optimum condition for a rapid corrosion rate was exhibited after 60 minutes.

3.8. Effect of Corrosion Sensitivity relative to Current Density

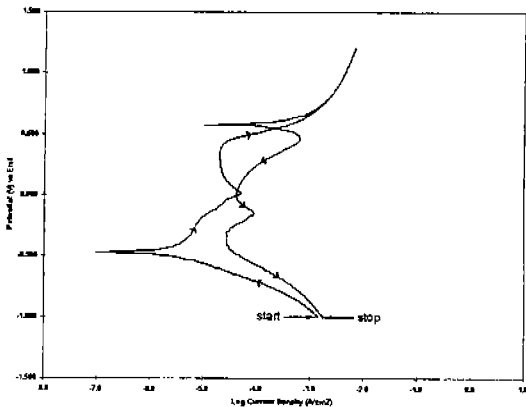


Fig. 11. Potential current density curve of polycarbonate(polymer) obtained by potentiodynamic polarization. (forward and reverse scan rate : 10mV/s)

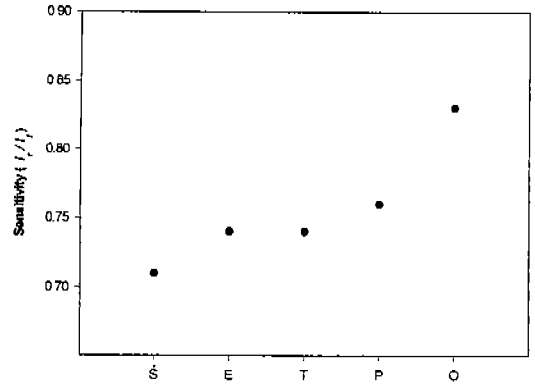
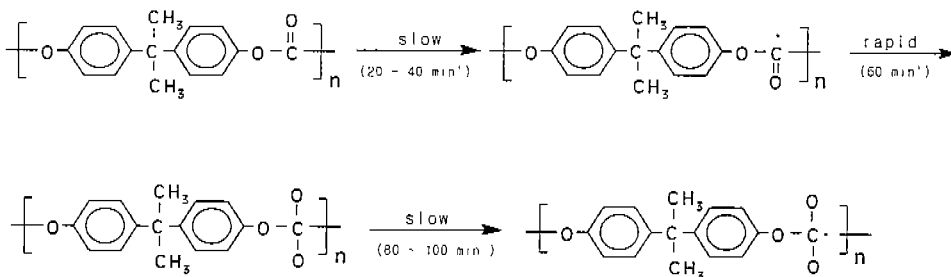


Fig. 12. Effect of sensitivity on potentiodynamic polarization curves(maximum current density) in forward and reverse scan.(S : salt ; E : Enzyme ; T : Temperature ; P : pH ; O : O₂)

Fig. 12 presents the variation in the current density ratios with a reverse current(I_r) versus a forward current(I_f) from the anodic polarization curve in Fig. 11. The susceptibility was examined using the maximum current density(forward and reverse scan). This was obtained using the polarization curves when measuring with added factor's(salts, enzyme, temperature, pH, and oxygen). The corrosion susceptibility, as shown in Fig. 12, was obtained in the following order : salt < enzyme < temperature < pH < oxygen. These results can be explained as an effect of the oxidation reaction. Accordingly, these results were due to the increase of current density with an increased oxidation. For this reason, it was obviously due to the reactivity with oxygen. The susceptibility of the forward and the reverse scan appears to be an effect of the oxidation reactions, as discussed previously. The potentiodynamic polarization measurements during the forward and reverse scan offered additional information regarding the

corrosion mechanism.

Because of these reactions, the corresponding can also be included in this study.

4. Conclusions

The corrosion polarization curves of polycarbonate in a nonaqueous solvent showed two redox waves. The potential efficiency of the 1st wave exhibited a cathodic reduction potential at all temperatures, whereas the 2nd wave was maintained for the anodic oxidation potential. The optimum corrosion temperatures were between 45°C to 55°C and the optimum corrosion pH was from pH 5.0(2nd wave : 0.11V) to pH 7.0(3rd wave : 0.40V). It would appear that the resistance effect of temperature was minimized at 35°C, which is where the corrosion rate increased the most. In contrast, a pH of 5.0 produced the least resistance along with an insignificant increase in the corrosion rate. The optimum pH and temperature conditions for corrosion resistance were found to be at pH 5.0 and 35°C. The corrosion efficiency was higher (0.01V) in the presence of salt. Accordingly, a more rapid corrosion was exhibited with the addition of salt. The optimum corrosion pH and temperature with the addition of a catalyzed enzyme(Citrate Lyase) was observed within a temperature range of 45°C to 55°C and at a pH of 5.0. Polycarbonate was rapidly oxidized by a catalyzed enzyme. The optimum condition for the corrosion rate with rapid oxidation was after 60 minutes. The corrosion sensitivity relative to the added factors was in the order of salt < enzyme < temperature < pH < oxygen. These results establish these factors as the effect of the oxidation reaction. The mass transfer coefficient(α) obtained

was higher than 0.5. From this value, it can be clearly recognized that the electrode reaction is a irreversible process.

Acknowledgement

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