

Affect of Corrosion Potential and Current Density on Polarization Curves Variations of Polyvinylchloride[II]

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(Manuscript received on July 27, 1999)

This study performed experiments for measuring corrosion potential and current density variations in the polarization curves of polyvinylchloride. The results were examined to identify particular influences affecting the corrosion potential such as temperature, pH, enzyme, and salt. The lines representing 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 using the polarization effect with varying conditions. The slope of the polarization curves describing the active-to-passive transition region was noticeably shifted in the potential direction. In addition, using the variation in conditions, the best temperature and pH were determined for the corrosion rate, and resistance of corrosion. The second anodic current density peak and maximum passive current density were designated as degraded(IP/IO). The value of IP/IO was used in measuring the extent of the degradation of the polyvinylchloride. The potentiodynamic parameters of the corrosion were obtained using a Tafel plot.

Key words : corrosion, potential, anodic, current, Tafel, polarization, degradation.

1. Introduction

Natural polymers are the basis of all life processes plus today's technological society is largely depend on synthetic polymers(Chang, 1994 ; Brydson, 1995). Certainly, the 1970s can be designated as the environmental, ecological, or pollution decade, since this decade marked the beginning of public concern for environmental pollution. Much of the material that has been presented about environmental pollution has taken a firm position on one or other side of an issue(Stocker, 1972). However, the corrosion of polymers has not been previously reported. Accordingly, this paper is a first attempt to correlate corrosion tests performed using an electrochemical method. This study also attempted to determine the detailed influence of variation factors such as temperature and pH, along with the corrosion effect of the enzyme(Castro, 1989) and salt.

2. Experimental

Polyvinylchloride was obtained from the Mu-

Dung corporation in Kwang Ju. The electrochemical and polarizing measurements were performed in tetrahydrofuran or dimethylformamide. The supporting electrolytes were tetrabutylammonium-perchlorate(TBAP) (G.F.S.Chemicals), or lithium perchlorate(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 1 cm² silver piece in the area(thickness 0.1 mm) of the conducting material, which, together with a silver wire for electrical conductance was sealed perpendicular to the rod(wire) axis. A reference electrode was used for the 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. The solutions for the electrochemistry were typically 1mM in a redox-active species and deoxygenated by purging with pre-purified nitrogen for at least 8 min. All experiments were performed at a scan rate of 10 mV/s using a CMS100 and 105(Gamry Instruments, Inc) with

a computer. The pH was measured with a pH meter (ORION model 960) and conductance was measured using a ORION model 142. Tafel plots were obtained from -2.0 to +3.0V at a steady state potential. The pH of the solution was controlled by either sodium hydroxide or hydrochloric acid, which was added to the sodium chloride in order to observation the effects of salt. The enzyme (Lipase : Aldrich, grade reagent) was nonaqueously dissolved at a concentration of mg/ml (unit).

3. Results and Discussion

3.1. Electrochemical Polarization Characteristic of pH from Added Salt

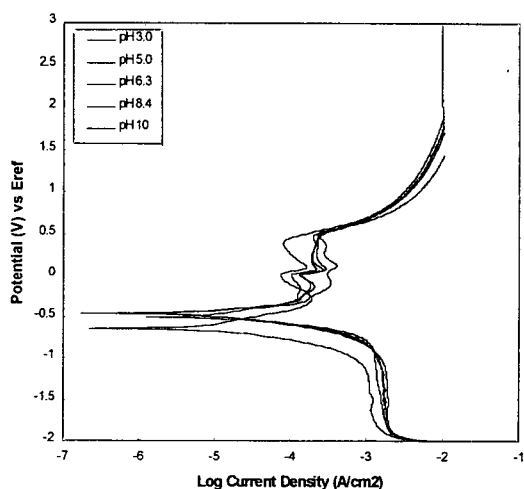


Fig. 1. Polarization curves of polyvinylchloride relative to pH in 1.0M NaCl. (scan rate : 10mV/s)

Fig. 1 shows the electrochemical polarization curves of polyvinylchloride in a nonaqueous solvent (tetrahydrofuran and dimethylformamide (80 : 20)). Corrosion tests were carried out to qualitatively determine the effects of several variables on the corrosion of polyvinylchloride in 0.1M sodium chloride solution. Fig. 1 shows the effect of pH on the cathodic and anodic polarization of polyvinylchloride in 0.1M NaCl. The solution was air saturated and one atmosphere of air filled the free space of the autoclave at room temperature (Do, 1992).

3.2. Effect of pH on Corrosion

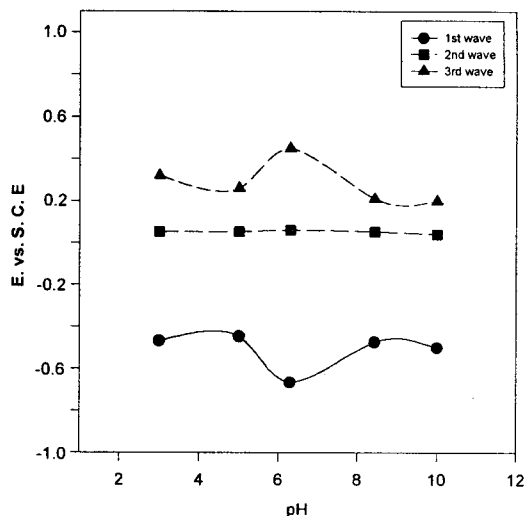


Fig. 2. Variation of corrosion potential on pH in 0.1M NaCl solution.

The specimen was exposed to air saturated 0.1M NaCl at room temperature (20~25 °C) for a few days (Kato, 1994 ; Kim, 1997). The solution was saturated with air and one atmosphere of air filled the free space of the autoclave at room temperature. Fig. 2 indicates that the first cathodic current peak did not exhibit any corrosion, however, it is clear from the corrosion polarization curves that the second and third anodic current peaks were oxidized. From the current-potential, it was speculated that the cathodic potential of the first wave was a reduction peak and the anodic potentials of the second and third waves were oxidation peaks. Accordingly, there was a stepwise movement from the potential of the cathodic reduction towards the anodic oxidation potential. These pH potential values were recorded on a three step polarization curve. As a result, the rapidity of the oxidation from the second and third waves was 0.04 V and 0.20 V with a pH of 11.0.

3.3. Effect of Temperature on Corrosion

As shown in Fig. 3 with polyvinylchloride, and the potential efficiency of the 1st wave was exhibited as a cathodic potential when the 2nd and 3rd waves were maintained as anodic potentials at all temperatures. The curves of the 2nd and

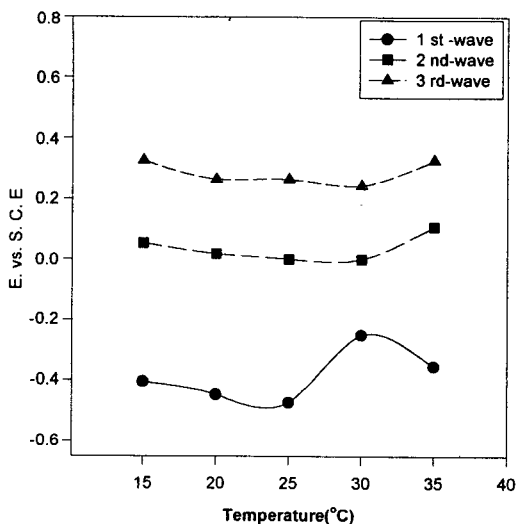


Fig. 3. Variation of corrosion potential on temperature efficiency in 1.0M-NaCl solution.

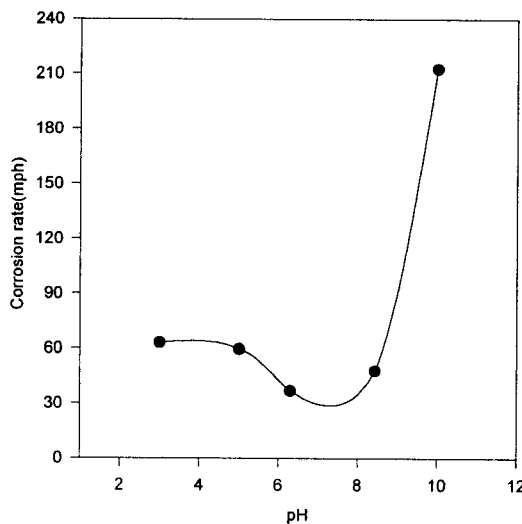


Fig. 4. Variation of corrosion rate on pH in 1.0M-NaCl solution.

3rd waves occurred while the oxygen was consumed, and the 1st wave of the cathodic reaction consisted of the reduction of hydrogen ions to hydrogen in air. The corrosion efficiency was delayed at 35 °C, however, corrosion became more steady with an increase in temperature. A series of corrosion tests from the 2nd wave with varying temperatures indicated a higher potential than oxidation at 15, 20 and 35 °C yet the corrosion was lower than the potential(0.01V) when the temperature was between 25 and 30 °C. The 3rd wave indicated that the corrosion was lower than the potential(0.24V) at 30 °C. Accordingly, the best corrosion temperature efficiency was between 25 to 30 °C.

3.4. Effect of pH on Corrosion Rate

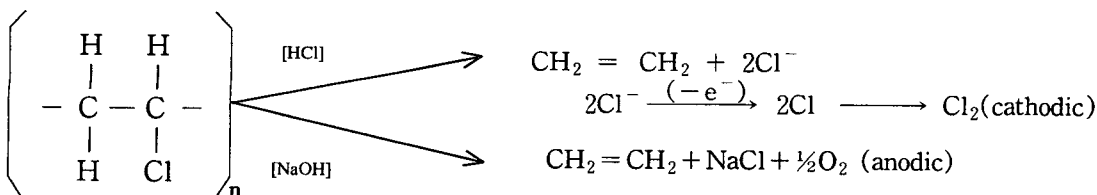
Fig. 4 organizes the variations in the corrosion rate derived from the polarization curves of polyvinylchloride in an electrolytic solution with the pH adjusted by hydrochloric acid or sodium hydroxide. The corrosion rate increased to a pH

of 3.0 and 5.0. However, the maximum was found at an alkalinity of pH 10.0. This corrosion phenomenon resulted with a sufficient supply of hydrogen ions produced a hydrogen reduction reaction as well as the presence of chloride ions which resulted in pitting(Do, 1992 ; John, 1968).

In the case of a pH higher than 8.7, an increasing corrosion rate was observed. A pH of 10.0 represented the rate-limiting step of the corrosion rate determined by the oxygen diffusion rate. It can be speculated that the increase in the corrosion rate is due to the gradual increase in the oxidation reaction in oxygen.

3.5. Effect of Temperature on Corrosion Rate

Fig. 5 shows the variations in the corrosion rate at various temperatures, and these results are summarized in Table 1. From the results in Fig. 5, it can be seen that the corrosion rate gradually increases with higher temperatures from 15 to 25 °C, with a maximum at 30 °C, and then decreases at



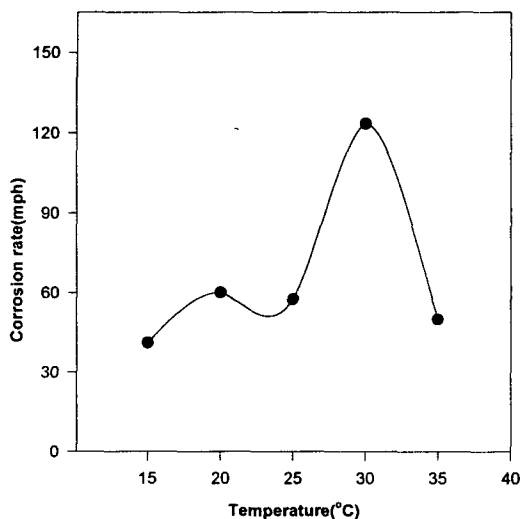


Fig. 5. Variation of corrosion rate at temperature in 1.0M-NaCl solution.

$$\text{corrosion rate} = \frac{0.13 (I_{corr}) \times (E_q \cdot W)}{d} ; d = \text{sample density (g/cm}^3\text{), } E_q \cdot W = \text{equivalent weight (g)}$$

3.6. Influence of Added Enzyme

3.6.1. Corrosion Potential of Temperature with Enzyme

Fig. 6 shows the electrochemical polarization curve of the potential efficiency for the enzyme (Castro, 1989) at various temperatures.

As shown in Fig. 7, the series of corrosion tests at varying temperatures indicated an oxidation potential from 15 to 50 °C. From these results, a higher potential for corrosion than for oxidation was exhibited at 15, 25, 40, and 50 °C, yet this was still lower than the potential (E = 0.20 V) up to 35 °C. Therefore, the best corrosion temperature efficiency was at 35 °C.

It was previously established that the corrosion

Table 1. Parameter of corrosion effect for polyvinylchlorde with salt.

Parameter	Corrosion Polarizing (V)	Cyclic voltammetry (V)	Conductivity (Λ)	Electron Charge (e)	0.1M NaCl (E(V))									
					(°C)					pH				
					15	20	25	30	35	3.0	5.0	6.3	8.4	10.0
2nd	0.01	0.05	13.36	0.01	0.05	0.02	0.01	0.01	0.11	0.05	0.05	0.06	0.05	0.04
3rd	0.20	0.35			0.27	0.26	0.26	0.24	0.34	0.32	0.26	0.45	0.21	0.20

Parameter	R _P (ohm cm ²)										Corr' rate (mph)									
	(°C)					pH					(°C)					pH				
	15	20	25	30	35	3.0	5.0	6.3	8.7	10.0	15	20	25	30	35	3.0	5.0	6.3	8.7	10.0
0.1M NaCl	×10 ³ 5.08	3.00	3.8	2.3	4.23	3.7	3.95	6.3	4.5	1.9	41.20	60.18	57.52	123.43	50.06	63.08	59.40	36.89	47.76	212.83

35 °C. Accordingly, the best corrosion rate efficiency was determined at 30 °C. In addition, the maximum corrosion rate of polyvinylchlorde was identified at 30 °C because at this temperature it is exposed to an aggressive electrolytic due to the oxidation reaction to form a passive one. However, we know lowered to below that corrosion rate did not rise to be degradation due to non-passive at high temperature(35 °C).

The corrosion rate can be obtained from the following equation(Korb, 1987).

potential is obtained at +0.33V from the third peak at 35 °C while in the absence of an enzyme(Choi, 1988).

When comparing +0.20V from the present study with the above value(0.33V), the oxidation potentials are lower when in the presence of an enzyme. Accordingly, this implies more rapid corrosion.

3.6.2. Corrosion Potential of pH with Enzyme

Fig. 8 shows the corrosion potential effect of

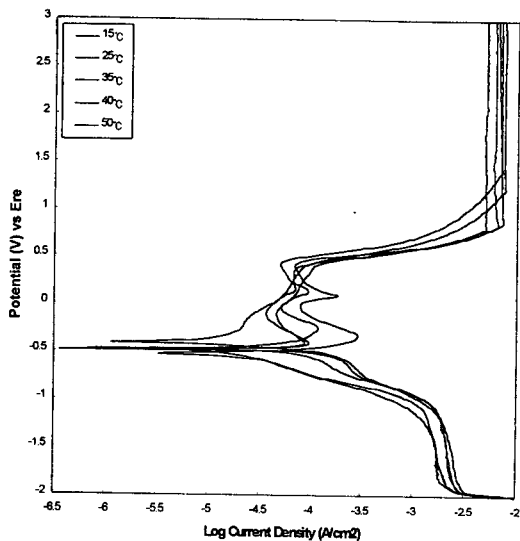


Fig. 6. Polarization curves of polyvinylchloride at temperature with enzyme(Lipase) added.

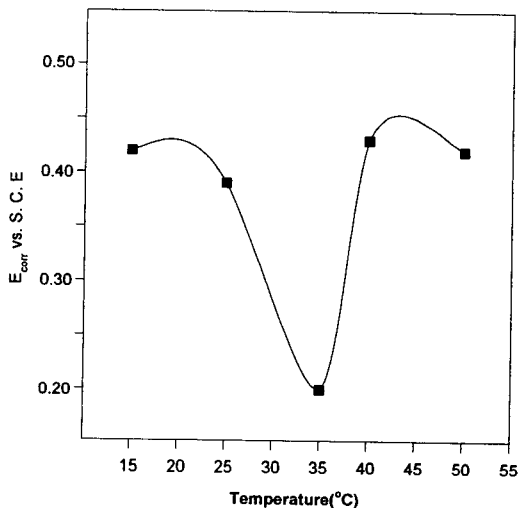


Fig. 7. Variation of corrosion potential at temperature adjusted with enzyme(Lipase) added.

pH on polarization(Temmali, 1972 ; Antonian, 1988). As shown in Fig. 8, polyvinylchloride with an added enzyme exhibited a cathodic reduction potential in the 1st and 2nd waves at all pHs when the 3rd and 4th waves were kept for the anodic oxidation. Except for the curve of the 1st and 2nd waves, the 3rd and 4th waves where the corrosion occurred consumed oxygen and the 1st and 2nd

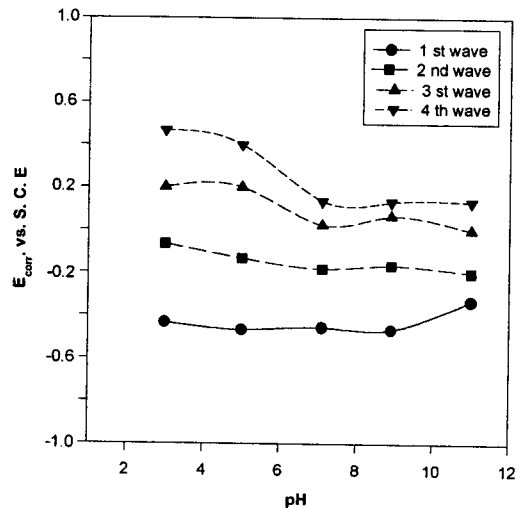


Fig. 8. Variation of corrosion potential on pH with enzyme(Lipase) added.

waves of the cathodic reaction reduced hydrogen ions to hydrogen in air.

In the case of pH acidity is observed higher than corrosion potential. This phenomena 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 pH 7.0 and 11.0, anodic oxidation occurred lower than potentials. The speculated reason for this is that the corrosion potential is rapid due to the gradual increase in the oxygen oxidation reaction. These phenomena are the same as those for the corrosion rate. It is also of interest to compare the difference in potential in terms of the possible effects on the enzyme catalyzed reaction.

Accordingly, when comparing the 3rd oxidation step between Table. 1 and Table. 2, a shifted potential can be observed. as the 3rd oxidation step potential was at +0.20V without the presence of a catalyzed enzyme. However, there was also a significant difference in the oxidation potentials among the 3rd oxidation steps as they were observed with +0.20V(pH 3.0~5.0), +0.13V(pH 8.9), and +0.30V(pH 11.0), respectively while in the presence of a catalyzed enzyme. These assignments are based on the fact that the same potential difference(+0.20V) and a different potential difference(0.13V and 0.03V) were observed in the ab-

Table 2. Parameter of corrosion effect with enzyme.

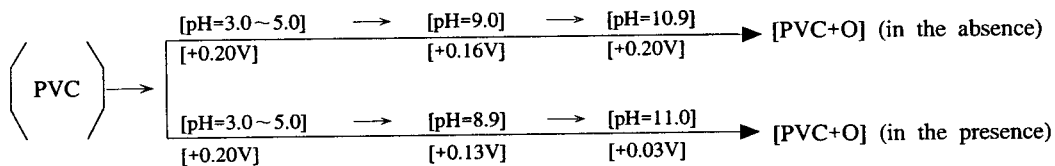
Parameter	E (V)					R _p (ohm cm ²)					Corr' rate (mph)				
	pH	pH				pH					pH				
		3.0	5.0	8.9	11	3.0	5.0	7.0	8.9	11	3.0	5.0	7.0	8.9	11
En- zyme	waves														
Lipase	anodic(3)	0.20	0.20	0.13	0.03	6.2	9.9	3.1	2.2	2.0	40.66	24.57	292.58	28.54	105.94
	(4)	0.46	0.40	0.15	0.15	×10 ³	×10 ³	×10 ³	×10 ³	×10 ³					

Parameter	Degradation (I _a /I _o)				E(V)				Transfer Coefficient(α)		
	°C	pH			°C				pH		
		35	3.0	11.0	15	25	35	40	50	5.0	7.0
Lipase	1.00	0.99	1.00	0.42	0.39	0.43	0.43	0.42	0.91	0.92	0.93

sence and presence of a catalyzed enzyme, respectively.

Based on the above arguments, the importance of this effect has been previously recognized as the rapid oxidation by an added catalyzed enzyme.

pH on the impedance behavior of an electrode by the electrolyte. The impedance responses were related to the dissociation with the charge transfer processes and can be given by the product of the interfacial charge transfer resistance(Cook, 1994 ;



These results are summarized in Table 2.

3.6.3. Corrosion Rate Effect of pH

The Fig. 9 organizes the variations of corrosion rate with an adjusted pH. The corrosion rate as shown in Fig. 9 was determined by the previously stated equation(in section 3.5). These results reveal that the corrosion rates were increased with a pH of 3.0(40.66 mph) and pH of 11.0(105.94 mph). Accordingly, it can be concluded that the oxidation of polyvinylchloride in the presence of an enzyme occurred more rapidly at a pH of 3.0 and 11.0. The increased corrosion rate in alkalinity rather than in acidity was expected owing to the gradual increase in oxygen due to the resolution and dissociation of sodium hydroxide.

3.6.4. Resistance Effect of pH

Fig. 10 shows the effect of a variation in the

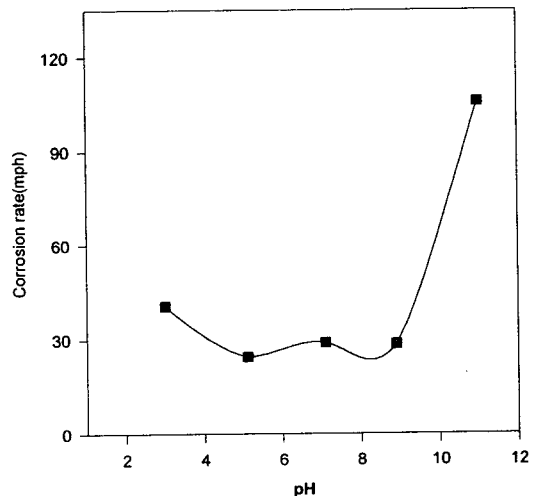


Fig. 9. Variation of corrosion rate on pH adjusted with enzyme(Lipase) added.

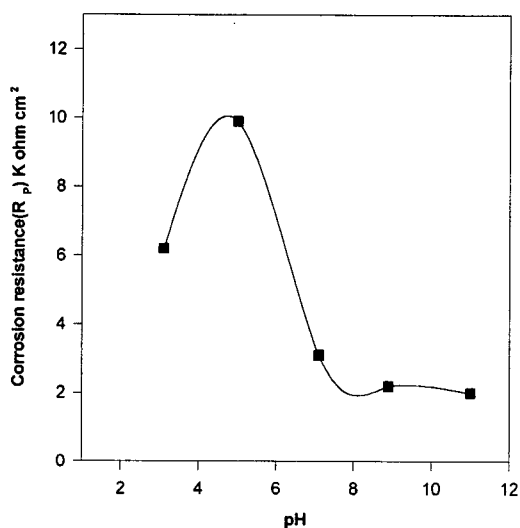


Fig. 10. Variation of resistance on pH adjusted with enzyme(Lipase) added.

Cascagrande, 1992) from following equation.

R_p =polarization resistance,
 ΔE =corrosion potential difference,
 Δi =corrosion current difference,
 β_A =anodic Tafel constant,
 β_C =cathodic Tafel constant.

The Fig. 10 shows plots of corrosion resistance with polarization curves. The results are summarized in Table 2. The resistance(R_p) values from Fig.11 and Table.2 show only a slight difference in the anodic values. However, this difference is smaller than the values of the electrolyte resistance(R_p) to pH 8.9 and pH 11.0 . Accordingly, smaller values were obtained in neutrality and alkalinity.

3.6.5. Degradation Effect of pH and Temperature

Fig. 11 was obtained from the second anodic maximum current density peak(I_p) and minimum current density peak(I_o) with various temperatures.

The result of the corrosion susceptibility, as shown in Fig. 11, increased when the pH values were pH 3.0 and 11. This is due to the increase in oxidation with an increased current density(John, 1968). Accordingly, the current density efficiency for the anodic oxidation of the enzyme(Lipase) was smaller with acidity and more significant with alkalinity.

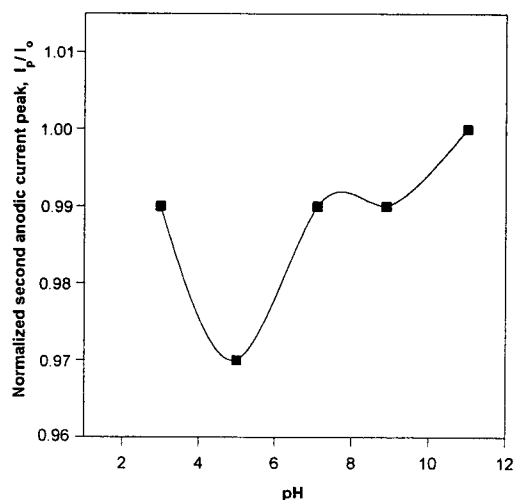


Fig. 11. Degradation of normalized second anodic current density peak I_p/I_o vs pH enzyme (Lipase) added.

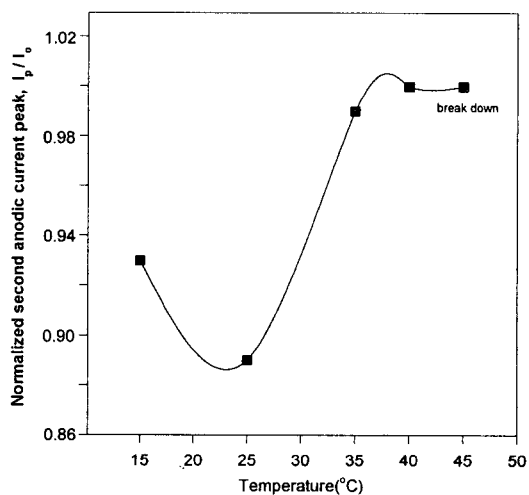


Fig. 12. Degradation of normalized second anodic current density peak I_p/I_o vs Temperature with enzyme(Lipase) added.

Fig. 12 compares the data from the anodic current density of a polarization curve and degradation at various temperatures. These degradation results appear to increase from 15 °C until 35 °C, however, the peaks suffer a break down higher than 35 °C. This phenomenon can occur in the absence of corrosion and can be explained by a reduction reaction or break down. Accordingly, in this case it can be explained as an effect of oxidation from

15 °C to 35 °C (Wheeler, 1979).

3.6.6. Relation of Mass Transfer Coefficient(α)

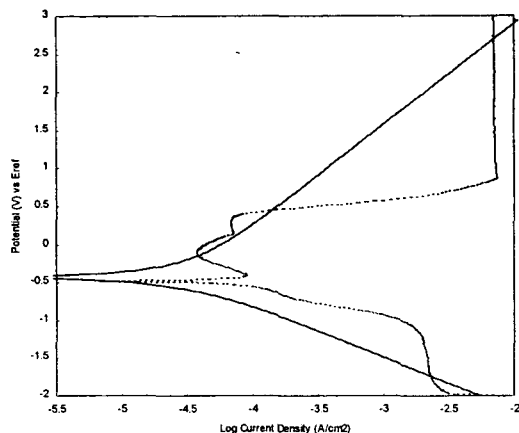


Fig. 13. Tafel plot of polarization curve for polyvinylchloride with Lipase(35 °C)(scan rate : 10mV/s)

Fig. 13 shows a Tafel plot of the polarization curves for polyvinylchloride in the presence of Lipase. The measurement of the Tafel coefficient was determined according to variations in the best pH and temperature conditions. The potentiodynamic parameters of the corrosion were obtained using a Tafel equation. The plot of $\log i$ vs η is a useful device, Tafel's plot, for evaluating kinetic parameters. In general, there is an anodic branch with a slope $(1-a)nF/2.3RT$. The mass transfer coefficients(α) were obtained from the slope $(1-\alpha)nF/2.3RT$. The results are summarized in Table 2.

η (overpotential) = $E - E_{eq}$ (real potential - equilibrium potential). ($\eta = a + b \log i$)

As shown in Table 2, the values (α) obtained were more than 0.50. It can be easily recognized that the electrode reaction is irreversible (Nagabramanian, 1994 ; Bard, 1980) in all conditions.

a and b = Tafel's constant; i = current density

$$a = \frac{2.3RT}{\alpha nF} \log i; \quad b = \frac{-2.3RT}{\alpha nF}$$

4. Conclusions

The corrosion polarization curves of polyvinylchloride in 0.1M NaCl exhibits a total of three redox waves. The potential efficiency of the 1st

wave exhibited a cathodic reduction potential at all temperatures when the 2nd and 3rd waves were maintained for the anodic oxidation potential. The best corrosion temperature efficiency was at 25 °C to 30 °C and the corrosion pH efficiency was near pH 10.0.

The best pH and temperature conditions for the corrosion rate were found to be pH 5.0 in acidity, and pH 10.0 in alkalinity at 30 °C. It is speculated that the resistance effect of temperature and pH decreased the gradual minimum at 30 °C and this was the least near an acid pH of 3.0~5.0 and alkaline pH of 8.7~10.0. The best corrosion temperature with the additional enzyme(Lipase) was at 35 °C, and at a pH of 7.0 or 11.0. The corrosion of polyvinylchloride was rapidly oxidized by a catalyzed enzyme. The degradation effect of pH and temperature increased when the pH was changed from 8.9 to 11.0 at 35 °C.

The effect of mass transfer was obtained more than $\alpha = 0.5$.

Accordingly, these reactions imply that the electrode reaction is totally irreversible.

Acknowledgement

This study was supported by research funds from Chosun University, 1998.

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