

Affecting of Corrosion Potential and Current Density on Variation Polarization Curves with Polyvinylchloride [I]

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In this study, we carried out the experiments for measuring the variations of corrosion potential and current density for polarization curves with polyvinylchloride. The results exhibited especially the influence affecting the corrosion potential and various conditions (temperature, day, pH, bacteria, and added salt). The second anodic current density peak and the minimum passive current density are designated I_p/I_0 , respectively. The value of I_p/I_0 is used as a measurement for the extent of degradation of the polyvinylchloride. The potentiodynamics parameters of the corrosion were obtained using Tafel equation.

Key Words : corrosion, potential, anodic, Tafel' s equation.

1. Introduction

The development of polymer chemistry began in the 1920s. Chemists were making great progress in clarifying the chemical structure of various substances but they were generally puzzled by the behaviour of certain materials, including wood, gelatin, cotton, and rubber. These observations strongly suggested the presence of very high molar mass solutes, but chemists were not ready at that time to accept the idea that such giant molecules could exist. Instead, they postulated that materials such as rubber consist of aggregates of small molecular units, held together by inter-molecules force. Once the structures of these macromolecules were understood, the way was into the manufacturing polymers, which now pervade almost very aspect of our daily lives. About 90 percent of today's chemists including biochemists, work with polymers. Polymers are very large molecules containing hundreds or thousands of atoms,

people have been using polymers since prehistoric time, and chemists have been synthesizing them for the past century. Natural polymers are the basis of all life processes, and our technological society is largely depends on synthesis polymers (Chang, 1994; Brydson, 1995). The 1960s is known to some as the space decade. Undoubtely the 1970s will similarly be known as the environmental, ecological, or pollution decade, it is in this decade that environmental pollution has become a popular cause for concern. Much of the material spoken and written about environmental pollution has been presented with great emotion from a position firmly on oneside or the other of the issues (Stocker, 1972). In this article we attempt to provide an overview of the ways in which corrosion polarization techniques can be used to enhance our knowledge of the chemical behaviour of polymer systems. In particular, we would like to discuss the applications of electrochemical methods to the study of nonaqueous solutions and corrosion of polymeric systems.

2. Experimental

Polyvinylchloride was obtained from MD (Mun-Dung)corporation in Kwang Ju. The working electrode, cast in solution to expose an all side shaped face of 1cm^2 , are way end with platinum line. The reference electrode was calomel electrode (silver/silver chloride) and counter electrode was graphite carbon rod. The corrosion polarization measurements was carried out under a nitrogen atmosphere(on the sample solution).

All experiments were performed at a scan rate of 50 mV/sec by CMS 100(Garry Instruments, Inc) interfaced with a PC.

Tafel plots were obtained from $\pm 200\text{ mV}$ region at the steady state potential. While vinylchloride content was maintained at 10^{-3} mol , and the pH of the solution were controlled by sodium hydroxide or sulfuric acid. In order to observe the effects salt was added to magnesium chloride. The experiment of oxygen content in solution was cast to expose in air at room temperture. The temperatures were obtained from $20\text{ to }45^\circ\text{C}$ region and the effect of enzyme was tested with bacteria(fungi).

3. Results and Discussion

3.1. Electrochemical Polarization Characteristics

Fig. 1 shows the electrochemical polarization curve of polyvinylchloride containing THF + DMF(80:20) dissolved oxygen in air at room temperature. Cathodic and anodic polarization curves were measured for all three steps potentials and current density in organic solvent. The corrosion potentials of two specimens were measured within the range $+3.0\text{ V}$ to -2.0 V , vs. S.C.E. The steady state corrosion potentials of the

polyvinylchloride were obtained for -0.6 V , $+0.11\text{ V}$, and $+0.37\text{ V}$.

3.2. Effect of Dissolved Oxygen in THF + DMF(80:20) Solution

Fig. 1 shows the variation of polarization curve with platinum electrode of dissolved oxygen in THF + DMF(80:20) solution.

As shown in Fig. 1, the polyvinylchloride exhibits a total of three redox waves and one of the potential curves was reduction peak and two curves were oxidation peak(corrosion).

Reduction(cathodic) peak potential was $E_{pc1} = -0.50\text{ V}$ and oxidation(anodic) peak potentials were $E_{pa1} = +0.08\text{ V}$ and $E_{pa2} = +0.58\text{ V}$ observed, respectively. From the corrosion current-potential, it is speculated that the cathodic currents are decreased due to the gradual decrease in oxygen reduction reaction and corrosion potentials from $+0.08\text{ V}$ to $+0.58\text{ V}$ were increased. The results indicated that the first cathodic current peak was not corrosion indicating but the second and third anodic current peaks were obvious on the corrosion plarization curves(Do, 1992).

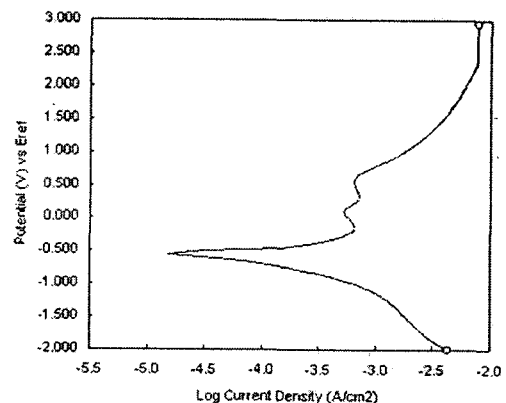


Fig. 1. Polarization Curve of Polyvinylchloride in Solution Containing Dissolved Oxygen.

3.3. Effect of pH

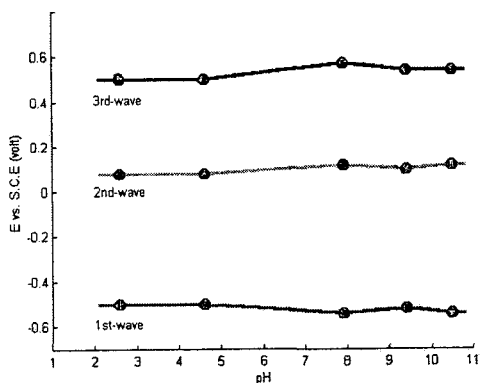
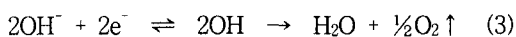
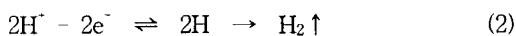
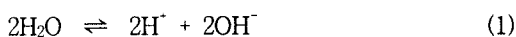


Fig. 2. Variation of pH and E_{corr}(Corrosion Potential).

Fig. 2 organized the variation of corrosion potential derived from polarization curve of polyvinylchloride in electrolytic solution with pH adjusted by sulfuric acid or sodium hydroxide, respectively. The first wave of three potential curves resulted from sufficient supply of hydrogen ion leading to hydrogen reduction reaction(Katch, 1994).



Accordingly, this electrode reaction is reduction. However, when the second and third waves were observed, the anodic current density continued oxidation reaction. The variation of corrosion potential from 2nd and 3rd waves exhibited to pH 2.6(+0.08 V and +0.50 V), pH 4.6(+0.08 V and +0.50 V), pH 7.9(+0.12 V and +0.57 V), pH 9.4(+0.12 V and +0.10 V) pH 10.5(+0.12 V and +0.54 V), respectively.

In the range of pH 2.6 to 4.6, the corrosion rate was confirmed to be nearly stabilized. But in case of pH higher than 10, the corrosion rate decreased

even further formation(oxidation)(Kim, 1997).

3.4. Effect of Fix a Days

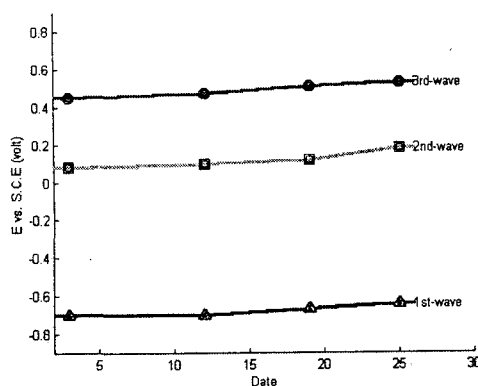


Fig. 3. Variation of Potential Versus Date.

Fig. 3 was obtained at room temperature using an identical stepwise technique for potentiostatic cathodic and anodic polarization measurement. Potentiostatic polarization curves were determined for all 3, 12, 19, and 25 days. The corrosion current density potential was recorded on a three step polarization curve.

After establishing a steady state corrosion potential, the potential of the cathodic reduction wave was moved stepwise to a value anodic oxidation potentials. These potentials value were obtained 3 day(1st wave(-0.70 V), 2nd wave(+0.08 V) and 3rd wave(+0.45 V)); 12 day(-0.70 V), (+0.10 V), and (+0.47 V); 19 day(-0.67 V), (+0.12 V), and (+0.15 V); and 25 day(-0.64 V), (+0.18 V), and (+0.55 V), respectively.

3.5. Influence of Degradation with Current Density

The polarization curve with a second anodic current peak is shown in Fig. 4. The second anodic current density peak and the minimum

passive current density are designated as I_p/I_0 , respectively (I_p : maximum peak current; I_0 : minimum peak current). A normalized second anodic current density value of I_p/I_0 is used as a measurement for the extent of degradation of the polyvinylchloride. It is known that the polyvinylchloride impoverished grain boundaries of polyvinylchloride have higher corrosion rate.

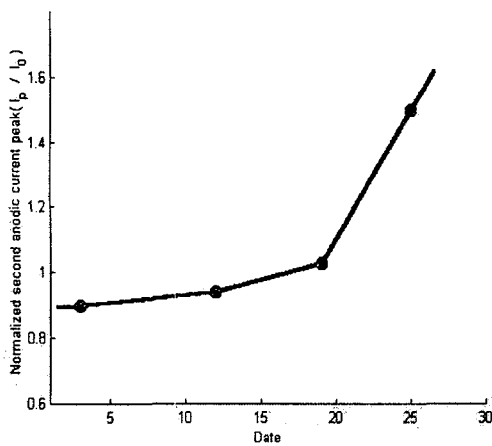


Fig. 4. Relation of Normalized Second Anodic Current Density Peak I_p/I_0 Service Times (I_p : max. peak currents; I_0 : min. peak current).

The polyvinylchloride used at room temperature for nearly 25 days are tested by electrochemical polarization. The second anodic current peak increased with service time. This is caused by increase of oxidation reaction. A normalized second current peak value I_p/I_0 read from electrochemical polarization curves is used to estimate the aging degradation. A close relation between the normalized anodic current density value and the service time is observed (Mao, 1993).

3.6. Effect of Temperatures

Fig. 5 shows the influence of dissolved oxygen on polarization curves from 20°C to 45°C. Fig. 5

can be drawn with the data from those external cathodic and anodic polarization curves. The negative potential value from the first wave increased reduction actively proceeds and positive potential value observed to be increased oxidation proceeds from second and third waves.

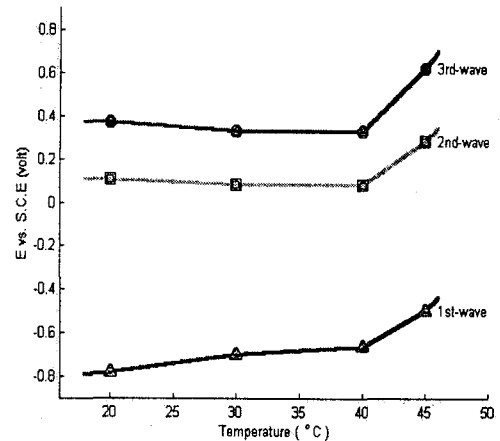


Fig. 5. Variation of Potential (E_{corr}) and Temperature.

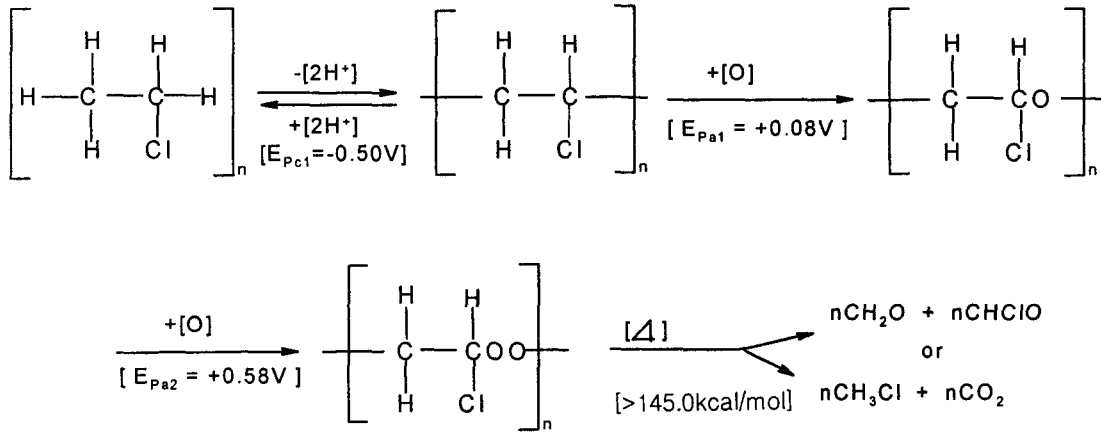
Therefore, negative potential value obtained from the first wave was likely to be negligible value because these potential values was reduction potential values.

We found that the corrosion potentials could be evaluated positive potentials. However, reduction wave with first step as decreased while oxygen content is increased continuously.

And so, the corrosion rate was observed to be increased with second and third waves. We were known that the corrosion potentials were obtained the second peak (+0.11 V to 20°C), (+0.08 V to 30°C), (+0.08 V to 40°C) and (+0.28 V to 45°C) to third peak (+0.37 V to 20°C), (+0.33 V to 30°C), (+0.33 V to 40°C) and (+0.62 V to 45°C), respectively.

The best potentials of corrosion rate was observed to be +0.08 V on ranges between from 30 to 40°C.

Corrosion mechanism of polyvinylchloride (Jayaseharan, 1998).



3.7. Effect of Bacteria(Fungi)

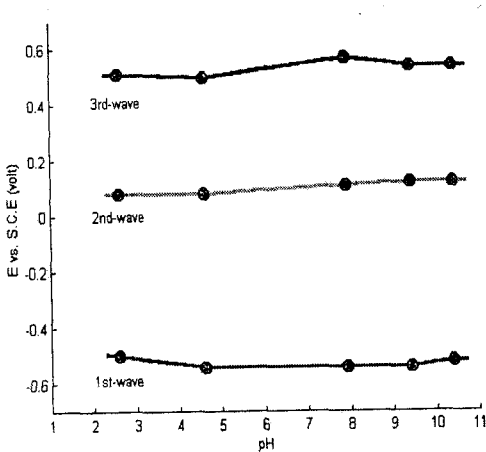


Fig. 6. Variation of pH and E_{corr} According to Bacteria(Fungi).

Fig. 6 shows the experiment for measuring the variations of corrosion potentials from polarization curves with variation of pH with added bacteria.

Fig. 6 can be drawn with the data from those polarization curves which are measured in controlled 1 mol sulfuric acid and sodium

hydroxide solutions. It was found that the corrosion potentials were getting from the first wave (pH 2.6, $E_p = -0.50$ V), (pH 4.6, $E_p = -0.54$ V), (pH 7.9, $E_p = -0.54$ V), (pH 9.4, $E_p = -0.54$ V), (pH 10.4, $E_p = -0.54$ V); second wave (pH 2.6, $E_p = +0.08$ V), (pH 4.6, $E_p = +0.08$ V), (pH 7.9, $E_p = +0.11$ V) (pH 9.4, $E_p = +0.12$ V) (pH 10.6, $E_p = +0.12$ V); third wave (pH 2.6, $E_p = +0.58$ V), (pH 4.6, $E_p = +0.51$ V), (pH 7.9, $E_p = +0.57$ V), (pH 9.4, $E_p = +0.54$ V), (pH 10.4, $E_p = +0.54$ V), respectively.

The negative potential value obtained from the first wave was likely to reduce the corrosion rate to a stable or negligible value. The effect of pH on the polyvinylchloride corrosion potential shifted toward positive to negative potentials with first wave each condition on pH. The pH on the pitting corrosion were found to be in a region between from pH 2.6 till pH 4.6. Accordingly, it is considered that the second and third waves were known to be rapidly oxidation reactions from pH 2.6 ($E_{p2} = +0.08$ V, $E_{p3} = +0.51$ V) till pH 4.6 ($E_{p2} = +0.08$ V, $E_{p3} = +0.50$ V) in comparison with corrosion potential.

3.8. Effect of Added Salt

The influences of characteristics MgCl₂ solution in nonaqueous. Fig. 7 shows the potential current density potentiodynamics characteristics of Pt electrode. In order to observe the salt effect of polyvinylchloride, the potentiodynamic characteristics of polyvinylchloride in DMF was compared to corrosion potential of MgCl₂ an addition to temperature constantly maintained.

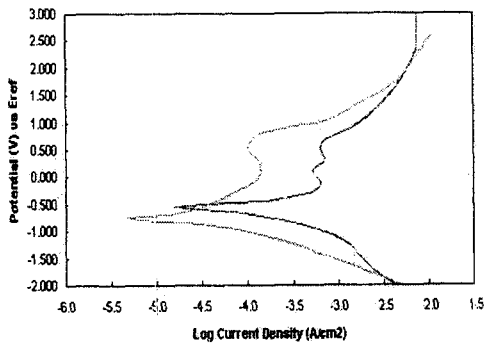


Fig. 7. Effect of Potential and Current Density with Magnesium Chloride Added.

- (a) Polyvinylchlorided + Solvent (THE + DMF)
- (b) Polyvinylchlorided + Solvent (THE + DMF) + MgCl₂

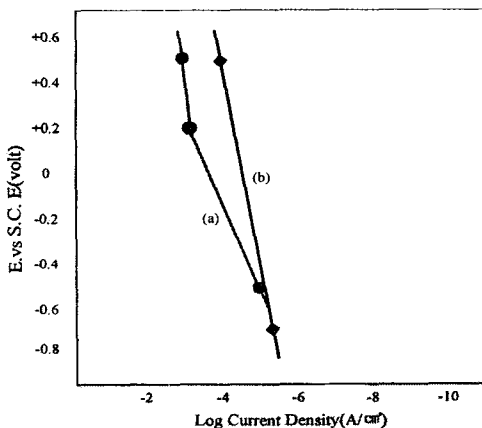


Fig. 8. Current-Potential Characteristics of Pt-Electrode to Added 1M MgCl₂ Solution in THE + DMF Solution.

- (a) Non-MgCl₂
- (b) MgCl₂ 첨가

Fig. 7 shows the polarization curves of current density potentials when adding MgCl₂ at room temperature. As shown to Fig. 7, it was found that polarization curves of current density-potentials obtained two waves curves. Fig. 8. organized the variation of corrosion potential from polarization curves with Fig. 7, Fig. 8 was drawn with the data from those external cathodic and anodic polarization curves. As the comparison of (a) with (b) was known to occur moving potential. It was found that redox potentials were to be decreased from three curves to two curves. Also, it was obvious that the corrosion rate in Fig. 8(b) (E_{pa2} = +0.51 V) exhibited with low potential. Accordingly, we found that the corrosion rate are better Fig.8 (a) than (b) when the compared with fig.8(a) (E_{pa2} = +0.20 V) and (b)(E_{pa2} = +0.51 V).

3.9. Effect of Temperatures with Added Bacteria(fungi)

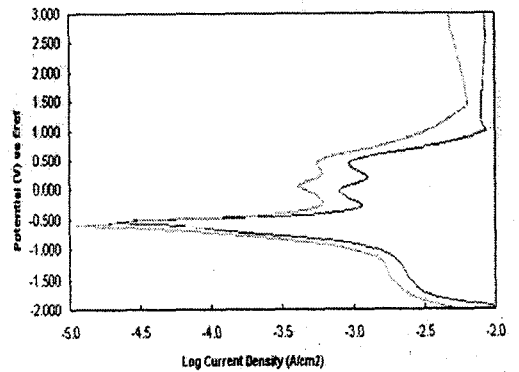


Fig. 9. Polarization Curves Current-Potential at Dissolved Oxygen on Corrosion.

- (a) Polyvinylchloride + dissolved
- (b) Polyvinylchloride + dissolved + bacteria(fungi)

Fig. 9 shows the influence of dissolved oxygen with two polarization curves. Fig. 10 can be drawn with the data from those external cathodic and anodic polarization curves. Here, negative potential value obtained from the first wave was

to be of negligible value because those potential values was reduction processes.

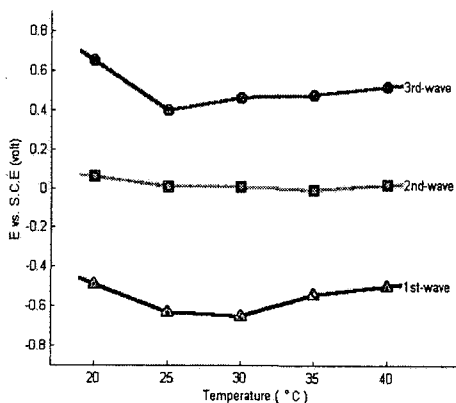


Fig. 10. Variation of Temperature Versus E_{corr} (PVC + Fungi).

And so, the corrosion rate was observed to be increased with second and third waves. In the mean time, the variation of corrosion potential from 2nd and 3rd waves exhibited to be observed the best temperature of corrosion rate on ranges between from 25°C ($E_{P2} = +0.02$ V and $E_{P3} = +0.04$ V) to 30°C ($E_{P2} = +0.01$ V and $E_{P3} = +0.46$ V), respectively.

3.10. Relation of Tafel's Coefficient and Reversibility

All conditions for measuring the Tafel's coefficient was determined using variations of the best conditions (temperature, day, pH and $MgCl_2$). The potentiodynamic parameters of the corrosion were obtained using Tafel equation. The results are summarized in Table 1.

Table 1. Tafel Coefficient for Mass Transfer.

parameter coefficient (α)	Temperature (30~40°C)	Dates (3~12)	pH (2.6~4.6)	Bacteria (fungi)	Salt ($MgCl_2$)
α	0.98	0.98	0.97	0.98	0.86

Tafel plots, A plot of $\log i$ vs η , known as a Tafel's plot is a useful device for evaluating kinetic parameters. In general, there is an anodic branch with slope $(1-\alpha)nF/2.3RT$ and cathodic branch with slope $-\alpha nF/2.3RT$. η (overpotential) = $E - E_{eq}$ (real electrode potential-equilibrium potential).

$$\eta = a + b \log(i)$$

As shown in Table 1, those value were obtained with more than 0.50 V. We can easily recognize that the electrode reaction is a reversible process (Bard, 1980; Nagasubramanian, 1994).

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

$$a = \frac{2.3RT}{\alpha nF} \log I \quad (25^\circ\text{C}),$$

$$b = \frac{-2.3RT}{\alpha nF} \quad (25^\circ\text{C})$$

The transfer coefficient α can be evaluated from slope $(1-\alpha)nF/2.3RT$.

4. Conclusions

The corrosion polarization curves of polyvinylchloride exhibits a total of three redox waves. The cathodic peak potential was $E_{pc1} = -0.50$ V and anodic peak potentials were $E_{pa1} = +0.08$ V and $E_{pa2} = +0.58$ V observed, respectively. The second anodic current peak increases with service time. (I_p/I_0). Because this is caused by the increase of oxidation reaction.

We found that the corrosion potentials could evaluate positive potentials. We was known that the best potential of corrosion rate observed to be

+0.08 V on ranges between from 30 to 40°C. The pH on the pitting corrosion were found to be region between from pH 2.6 till pH 4.6. The in the corrosion rate exhibited good when not adding MgCl₂.

The effect of mass transfer was obtained more than $\alpha = 0.5$. Accordingly, this approach has the advantage of being applicable to electrode reactions that are totally reversible.

Acknowledgement

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