

## Redox Reaction of Poly(ethyleneterephthalate) Polymer in Aprotic Solvent

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We carried out to measure the variations of potential with current density (polarization curves) for poly(ethyleneterephthalate). The results were particularly examined to identify the influences on corrosion potential and corrosion rate of various factors including temperature, pH, exposure time, salt, and enzyme. 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 passive current density were designated as the relative corrosion sensitivity ( $I_p/I_r$ ). The mass transfer coefficient value ( $\alpha$ ) was determined with the Tafel slope for anodic dissolution based on the polarization effect with optimum conditions.

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

### 1. Introduction

In response to the increasing concern over environmental issues,<sup>1)</sup> the European Commission (EC), the administrative arm of the European Union (EU), will soon launch a consultation program examining the environmental issues related to poly(vinylchloride) (PVC). The EC has already adopted a green paper evaluating environmental aspects of PVC with the specific provisos that the consultation be based on science and include aspects related to human health. The paper is set 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 in order to develop a comprehensive strategy on PVC in early 2001. The EC emphasizes that PVC is to be product for practical applications 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 could conduct electricity like metal seemed ludicrous as organic polymers that known as insulators. However, these three researchers found that by dropping a known conjugated polymer (polyacetylene) make which 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 light-emitting

conducting polymer is now being included in mobile phone displays. Other application of conducting polymer 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.<sup>2)</sup>

However, no previous reports exists on the corrosion 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 various conditions, such as temperature, pH, salt and enzyme.

## 2. Materials and Methods

The poly(ethyleneterephthalate) was obtained from the Aldrich Chemical Company Inc(G.P.C Chemicals). The electrochemical 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 was used as received. The supporting electrolyte concentration was typically 0.10 M. The electrode tip of the working electrode system consisted of a 1 cm<sup>2</sup> 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), a graphite carbon rod was used as the counter electrode, and the electrolysis cells were of the conventional design.

All experimental solutions for the electro

chemistry 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 +1.0V 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 poly(ethyleneterephthalate) from Aldrich was used in preparing the nonaqueous solvent (dimethylsulfoxide). All solutions were deaired for 10 min with nitrogen gas and all experiments were carried out at 20°C.

## 3. Results and Discussion

### 3.1 Electrochemical Characteristic

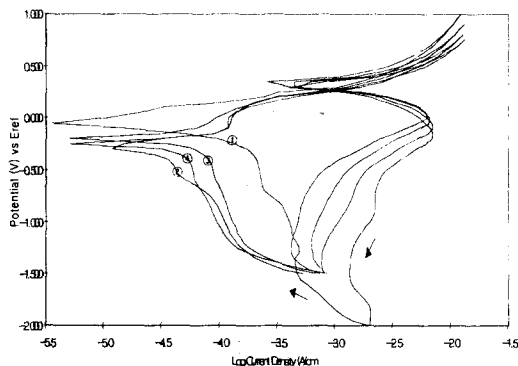


Fig. 1. polarization curves of 1mM poly(ethyleneterephthalate) at various temperature(① 20°C, ② 30 °C ③ 40°C, ④ 50°C).

Fig. 1 shows the poly(ethyleneterephthalate)

Table 1. Parameter of Redox on the various conditions

Parameter Redox steps(E(V))	Concentration (1mM)												Enzyme				MgCl <sub>2</sub>	
	(°C)				pH				Days				(°C)					
	20	30	40	50	3.20	4.10	9.20	10.30	1	4	8	12	20	20	30	40	50	20
1st wave	-0.70	-0.29	-0.24	-0.24	-0.21	-0.14	-0.36	-0.39	-0.50	-0.30	-0.24	-0.47	-0.16	-0.75	-0.75	-0.69	-0.60	-0.60
2nd wave	-0.50	-0.09	-0.20	-0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.45	-0.40	-0.25	-0.25	-0.50
3rd wave	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.05	0.10	0.10	0.14

electrochemical polarization curves in a non-aqueous solvent(dimethylsulfoxide) at 20°C. The cathodic and anodic polarization curves of poly(ethyleneterephthalate) obtained with three step potentials and current density. The corrosion potentials of the specimen were measured with in the range +1.0 V to -2.0 V, vs S.C.E. The poly(ethyleneterephthalate) steady state corrosion potential was obtained at -0.70 V, -0.50 V, and 0.07 V. The results are summarized in Table 1.

### 3.2. Effect of Temperature on Corrosion

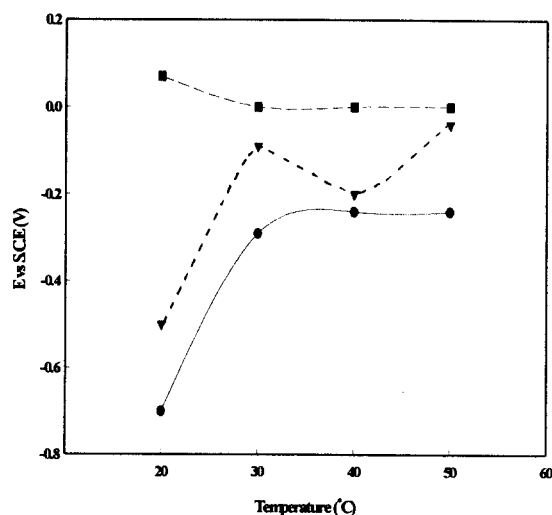


Fig. 2. Variation of potential according to variation of temperature (°C) (● : 1st wave; ▼ : 2nd wave; ■ : 3rd wave).

Fig. 2 was based on data from the external cathodic and anodic polarization curves, as presented in Fig. 1. As shown in Fig. 2, with poly(ethyleneterephthalate), the potential efficiency of the 1st and 2nd waves was exhibited by the cathodic potential, whereas the 3rd wave was maintained by the anodic potential at 20°C. Oxidation occurred when the 3rd wave reached 20°C ( $E = 0.07$  V). The series of redox tests related to the 1st and 2nd waves indicated a lower potential between 30 and 50°C. Accordingly, the most efficient corrosion temperature occurred rapidly at 20°C.

### 3.3. Effect of pH on Corrosion

Fig. 3 presents the variation in the corrosion

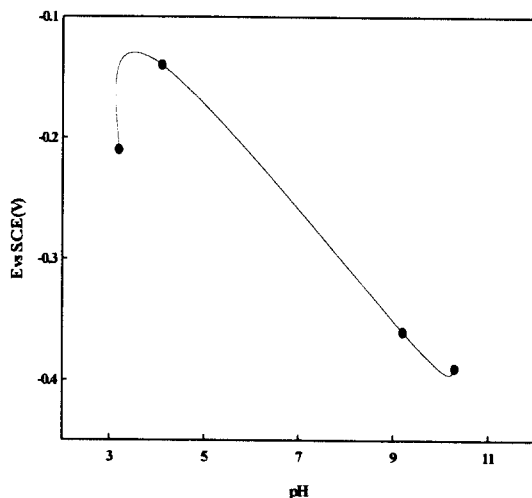


Fig. 3. Variation of potential according to pH.

potential derived from the poly(ethyleneterephthalate) polarization curve in an electrolytic solution.<sup>3,4</sup> The effect of pH on the poly(ethyleneterephthalate) redox potential shifted to a negative potential with the 1st wave of each pH condition. The curves of the 2nd and 3rd waves were not occurred the redox reaction and the 1st wave of the cathodic reaction consisted of the reduction of hydrogen ions to hydrogen. Accordingly, the negative potential from the 1st wave exhibited at pH of 3.20 ( $E = -0.21$  V), 4.10 ( $E = -0.14$  V), 9.20 ( $E = -0.36$  V), and 10.30 ( $E = -0.39$  V), respectively. Therefore, corrosion potential occurred rapidly at pH 4.10.

### 3.4. Effect of Exposure Time in Air

Fig. 4 was obtained from the cathodic and anodic polarization measurement at 20°C. As shown in Fig. 4 and Table 1, redox tests were carried out for 1, 4, 8, 12, and 20 days. Therefore, the 1st wave exhibited negative potentials when the 2nd and 3rd waves were not observed for all the time. These potential values were obtained from the oxygenation time for 1 day ( $E = -0.50$  V), 4 day ( $E = -0.30$  V), 8 day ( $E = -0.24$  V), 12 day ( $E = -0.47$  V), and 20 day ( $E = -0.16$  V), respectively.

Accordingly, redox reaction was reduction processes, but the variation of redox potential exhibited increase to oxidation potential according to the increase of exposure time in air.

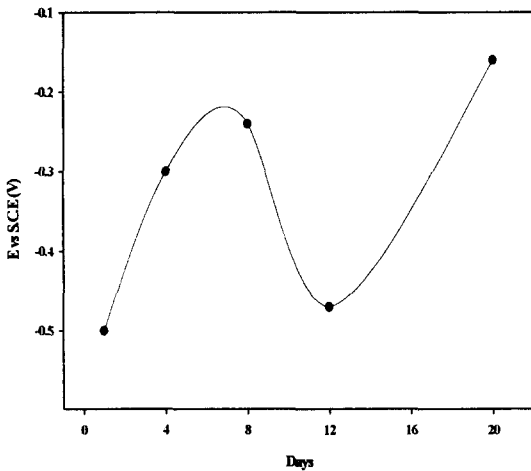


Fig. 4. Variation of potential according to exposure time(days).

### 3.5. Influence of Redox Potential with Salt

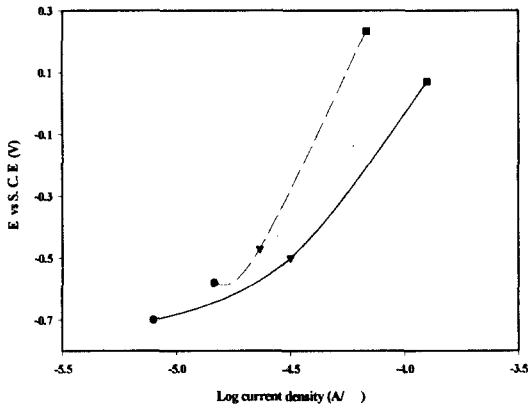


Fig. 5. Comparison of corrosion potential with salt (0.1 M MgCl<sub>2</sub>) (---: in the presence; —: in the absence).

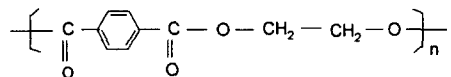
As shown in Fig. 5 redox tests were carried out to quantitatively measure the effect of various temperatures on the redox of poly(ethyleneterephthalate) in a 0.1 M MgCl<sub>2</sub> solution. The efficiency of the redox was established by a comparison of the two waves between the presence and absence of salt(0.1 M MgCl<sub>2</sub>).

It was found that the redox potential of the 1st and 2nd waves were negative and positive potential of the 3rd wave. The redox potential in the absence of salt were E = -0.70 V(1st wave), E = -0.50 V(2nd wave), and E = +0.07 V(3rd wave) at 20 °C.

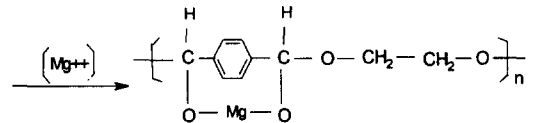
However, in the presence of salt, it was exhibited E = -0.60 V(1st wave), E = -0.50 V(2nd wave), and E = +0.14 V(3rd wave), respectively. Here, negative potential value obtained from the 1st and 2nd waves were to be negligible value because those potential values were reduction processes.

In the meantime, the variation of the corrosion potential from the 3rd wave was established by comparison of the results in the presence and absence of salt (0.1 M MgCl<sub>2</sub>). A series of corrosion tests from the 3rd wave indicated an oxidation potential(E = 0.14 V) and (E = 0.07 V) in the absence of salt. The corrosion potential in the presence of salt was higher than that in the absence of salt. From these results, corrosion efficiency of salt was exhibited slowly oxidation rate in the presence of salt.

From these reasons, we were known because of complex formation with magnesium ion in salt.



[Poly(ethyleneterephthalate)]



[Poly(ethyleneterephthalate) magnesium]

### 3.6. Effect of Temperature from Added Enzyme

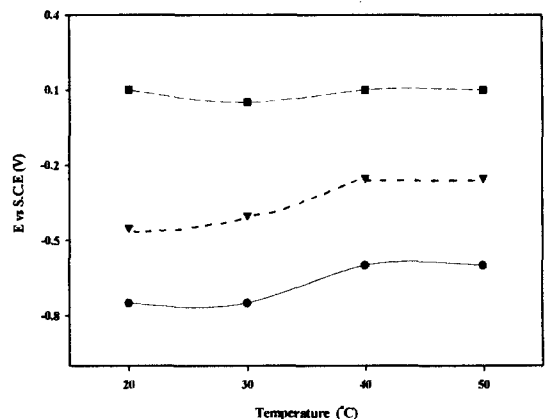


Fig. 6. Variation of potential according to variation of temperatures with enzyme(fungi) added (● : 1st wave ; ▼ : 2nd wave ; ■ : 3rd wave).

Fig. 6 was based on data from the external cathodic and anodic polarization curves. It is the variation in the oxidation potential derived from the polarization curves relative to temperature. The potential efficiency of the 1st and 2nd waves was a cathodic potential when the 3rd wave was maintained as an anodic potential at various temperatures. In this case, the negative potential value obtained from the 1st and 2nd waves was to be negligible because the potential values were related to the reduction process. Oxidations occurred with the three step wave were as follows: 20°C ( $E_1 = -0.75$  V,  $E_2 = -0.45$  V,  $E_3 = +0.10$  V); 30°C ( $E_1 = -0.75$  V,  $E_2 = -0.40$  V,  $E_3 = +0.05$  V); 40°C ( $E_1 = -0.69$  V,  $E_2 = -0.25$  V,  $E_3 = +0.10$  V); and 50°C ( $E_1 = -0.60$  V,  $E_2 = -0.25$  V,  $E_3 = +0.10$  V), respectively.

A series of oxidation at 30°C ( $E_3 = +0.05$  V) from the three step wave with varying temperatures was lower than potential values at 20°C ( $E_3 = 0.10$  V), 40°C ( $E_3 = 0.10$  V) and 50°C ( $E_3 = 0.10$  V), respectively. Accordingly, temperature efficiency of oxidation was rapid at 30°C. Therefore, as previously mentioned, enzymatic reactions of the temperatures would be appear lower potential than in the absence of enzyme. Also, it would seem that enzymes are not active in an organic solvent.

### 3.7. 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. Electrochemical techniques such as linear polarization, can be used for the rapid measurement of polarization resistance.<sup>5)</sup> Polarization resistance ( $R_p$ ) and rate (mm/yr) can be presented by linear polarization curves.<sup>6,7)</sup> The value

of corrosion resistance ( $R_p$ )<sup>8)</sup> and rate (mm/yr)<sup>9)</sup> were obtained using a Tafel plot and the corrosion resistance was obtained from the following equation:  $R_p = \frac{\Delta E}{\Delta i} = \frac{\beta_A \times \beta_C}{2.30 I_{\text{corr}} (\beta_A + \beta_C)}$

where  $R_p$  = polarization resistance,  $\Delta E$  = corrosion potential difference,  $\Delta i$  = corrosion current difference,  $\beta_A$  = anodic Tafel constant, and  $\beta_C$  = cathodic Tafel constant.

Corrosion rate =  $\frac{0.131 I_{\text{corr}} \times E_q \times W}{d}$ ; where  $d$  = sample density (g/cm<sup>3</sup>), and  $E_q \times W$  = equivalent weight (g).

These values are the slope at  $E_{\text{corr}}$  of a plot of  $I$  versus  $E$  in the region of  $E_{\text{corr}}$ . 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 ( $\alpha$ ). The values ( $\alpha$ ) obtained, as summarized in Table 2, were higher than 0.50. Accordingly, it is clear that the electrode reaction was irreversible under all conditions.<sup>10,11)</sup> The Tafel slope for the anodic dissolution was determined by the polarization effects of the pH and temperature. 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 with different temperatures (20, 30, 40, and 50°C). These results are summarized in Table 2.

Table 2 presents the variations in the redox resistance and rate under the various conditions. This was determined by the optimum potential effects of pH, temperature, salt, and enzyme. As shown in Table 2, the oxidation rate was the most rapid with the lowest resistance (for 20 days), whereas the various conditions exhibited the slowest oxidation rate with the highest resistance.

Table 2. Electrochemical characteristics under various condition

Conditions	Parameter	Best Condition	Corrosion Potential V (S.C.E) (1st)	Corrosion rate (mm/yr)	Resistance ( $R_p$ ) $K \Omega \text{cm}^2$	Susceptibility ( $I_f/I_r$ )	Reversibility ( $\alpha$ )
PET soln	°C	20 (°C)	-0.70	1.38	3.05	0.41	0.98
PET soln	pH	4.10	-0.14	2.56	1.80	0.47	0.97
PET soln	Salt	0.1 (M)	-0.60	1.96	5.51	0.39	0.86
PET soln	Enzyme	50 (°C)	-0.60	1.20	5.21	0.37	0.90

In contrast, temperature and salt produced a reasonably balanced relationship between resistance and oxidation rate. The optimum condition of resistance and rate were found on the time of exposure.<sup>12)</sup>

### 3.8. Effect of Corrosion Sensitivity Relative to Current Density

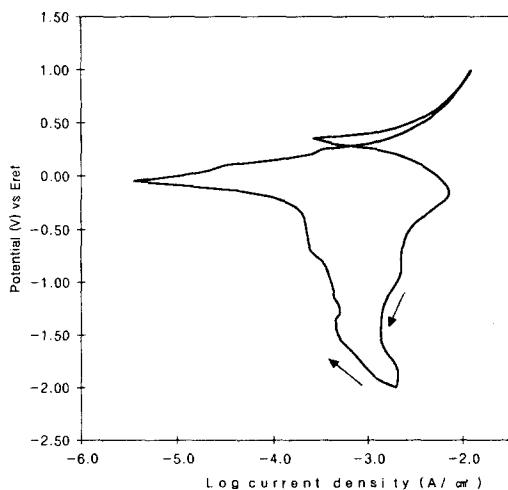


Fig. 7. Current density curve of poly(ethyleneterephthalate) obtained by potentiodynamic polarization (forward and reverse scan rate: 7 mV/s).

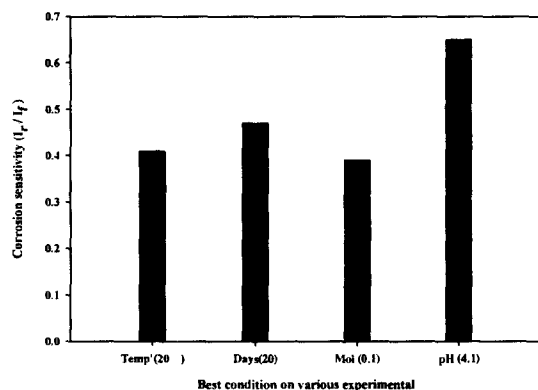


Fig. 8. Effects of sensitivity with maximum current density on various conditions (forward and reverse scan).

Fig. 8 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 Fig. 7. This was obtained by the polarization curves

when measuring with added factors (temperature, pH, salt, and enzyme). 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. 8, the redox susceptibility was found to be in the following order to enzyme < salt < temperature < pH. Since these results can not 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 the reactivity with oxygen.

## 4. Conclusions

The corrosion polarization curves of poly(ethyleneterephthalate) in a nonaqueous solvent showed two or three redox waves. The potential efficiency of the 1st (or 2nd) wave exhibited a cathodic reduction potential at all temperatures, whereas the 3rd wave was maintained for the anodic oxidation potential. The optimum corrosion temperature was at 20°C and the corrosion pH was at pH 4.1. The efficiency of oxidation potential in air was increased oxidation according to increasing the time of exposure, enzymatic reactions of the temperatures would be appear a lower potential than in the absence of enzyme (at 20°C). However, enzymatic reactions of the temperature in presence of enzyme exhibited rapidly oxidation at 30°C. The oxidation rate was the most rapid with the lowest resistance, and it found on the long time of exposure in air.

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