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Influence of Redox Potential and Current Density on Polarization Curves with Polypropylene Polymer

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Experiments were carried out to measure the corrosion potential and current density variations in the polarization curves of polypropylene. In particular, the results were examined to identify those influences affecting the corrosion potential, such as temperature, pH, salt, and oxygen. The Tafel slope for the anodic dissolution was determined based on the polarization effect under various conditions. Furthermore, the optimum conditions for the most rapid transformation were establish based on a variety of conditions, 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_f/I_f). This I_f/I_f value was then used to measure the critical corrosion sensitivity of polypropylene. The potentiodynamic parameters of corrosion were obtained using a Tafel plot.

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

1. Introduction

In response to the increasing concern over environmental issues, The European Commission (EC), the administrative arm of the European Union(EU), will soon launch a consultation program examining the environmental issues related to polyvinylchloride. The EC has already adopted a green paper evaluating the environmental aspects of PVC with specific provisos that the consultation be based on science and include related human health aspects. The paper sets out details of the recent studies the EC has conducted in this area. It also invites discussion 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 the project is to give the EC the scientific basis to develop a comprehensive strategy on PVC by early 2001. Although it is encouraging to see that the EC emphasizes that PVC is an important product with numerous applications, representing 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, MacDiarmid, and Heeger made their seminal discovery in 1977, the idea that plastic could conduct electricity like metal seemed ludicrous as organic polymers were, and for the most part still are, known as insulators. However, these three researchers found that by dopping a known conjugated polymer(polyacetylene) they could make it 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 the electronic and optical properties of metals and inorganic semiconductors. Furthermore, these materials have, 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, even playing "a major role as a radar-absorbing screen coating in

stealth bombers", according to chemistry professor Andrew B. Holmes, who directs the Melville Laboratory for polymer synthesis at the University of Cambridge. Professor Holmes told Chemical and Engineering News(C & EN) that a light-emitting conducting polymer is now being included in mobile phone displays. Other applications of conducting polymers that could soon emerge include lightweight batteries for cars, electromagnetic shielding, ultra-thin computer monitors and TV sets, artificial nerves, and sensors, according to Daryle H. Busch, President of the American Chemical Society.[2)]

However, no previous reports exist on the corrosion of polymers. Accordingly, this paper is the first attempt to correlate corrosion tests performed using an electrochemical method. In addition, this study also investigates the detailed influence of varied conditions, such as temperature, pH, salt, and casting time with oxygen.

2. Materials and Methods

The polypropylene 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 tetrabutylammoniumperchlorate(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 ㎠ piece of silver(thickness 0.1 mm) 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 deoxygenated by purging with pre-purified nitrogen for at least 15min. All experiments were performed at a scan rate of 10 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 +1.5 V 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 polypropylene(Average Mw ca. 14,000) from Aldrich was used in preparing a nonaqueous solvent($C_6H_5Cl_3$:DMF = 4:1). All solutions were deaerated for 10 min' with nitrogen and the experiments were carried out at 25℃.

3. Results and Discussion

3.1. Electrochemical Characteristic

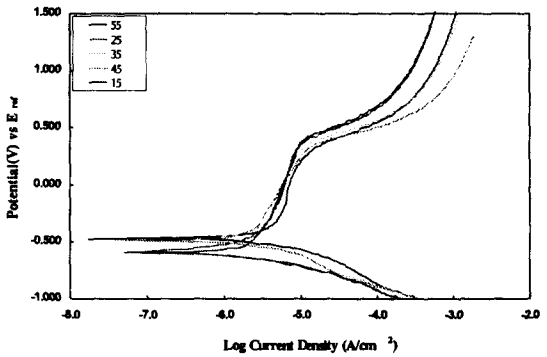


Fig. 1. Polarization curves of polypropylene in nonaqueous solvent(scan rate : 10mV/s).

Fig. 1 shows the polypropylene electrochemical polarization curves in a nonaqueous solvent(toluene and dimethylformamide(4 : 1)) at 25℃. The cathodic and anodic polarization curves for the step potentials and current densities were all measured in an organic solvent. The corrosion potentials of the two specimens were measured within a range of +1.0 V to -1.0 V, vs S.C.E. The polypropylene steady state corrosion potentials were obtained at -0.58 V and +0.32 V. The results are summarized in Table 1.

3.2. Effect of Temperature on Corrosion

Fig. 2 was drawn based on data from the external cathodic and anodic polarization curves, as presented in Fig. 1. As shown in Fig. 2, with polypropylene, the potential efficiency of the 1st wave was exhibited by the cathodic potential, whereas the 2nd wave was maintained by the anodic

Table 1. Parmeter of oxidation effect with various conditions

Parameter	Temperature(℃)					pH					0.1M $MgCl_2$(℃)					O_2(droplet/sec)				
	15	25	35	45	55	3.0	5.0	7.0	9.0	11.0	15	25	35	45	55	20	40	60	80	100min
1st-wave	-0.58	-0.58	-0.47	-0.47	-0.47	-0.31	-0.37	-0.37	-0.24	-0.37	-0.17	-0.20	-0.24	-0.26	-0.43	-0.42	-0.42	-0.32	-0.32	-0.32
2nd-wave	0.37	0.34	0.32	0.32	0.32	0.37	0.05	0.05	0.26	0.24	·	·	·	·	·	0.32	0.32	0.32	0.32	0.32
3rd-wave	·	·	·	·	·	·	0.40	0.50	·	·	·	·	·	·	·	·	·	·	·	·

The sign(·) was not polarization curves.

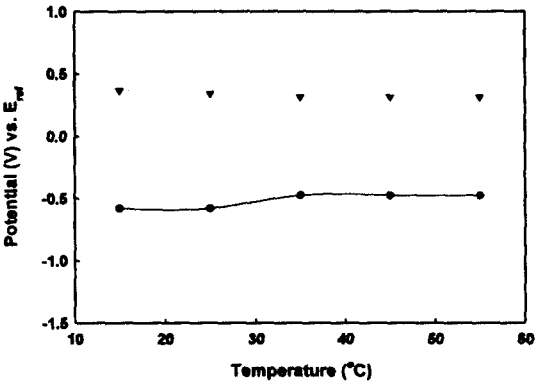


Fig. 2. Variation of temperature and corrosion potential(● : 1st wave, ▼ : 2nd wave).

potential at all temperatures. Oxidation occurred when the 2nd wave reached 15℃(E = 0.37 V), 25℃(E = 0.34 V), 35℃(E = 0.32 V), 45℃(E = 0.32 V), and 55℃(E = 0.32 V), respectively. The series of corrosion tests related to the 2nd wave indicated a lower potential than oxidation from 35 to 55℃. Accordingly, the most efficient corrosion temperature was between 35 to 55℃.

3.3. Effect of pH on corrosion

Fig. 3 presents the variation in the corrosion potential derived from the polyproplyene polarization curve in an electrolytic solution.[3,4] The effect of pH on the polypropylene corrosion potential shifted from a positive potential, with the second and third waves, 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 oxidation from the second and third waves exhibited a pH of 5.0(E=0.05 V), (E=0.40 V) and pH 7.0(E=0.05 V), (E=0.50 V), respectively. Therefore, corrosion can be expected at pH 5.0 and 7.0.

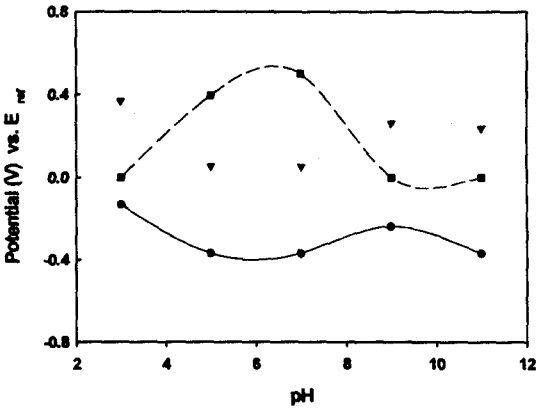


Fig. 3. Variation of pH and corrosion potential(● : 1st wave, ▼ : 2nd wave, ■ : 3rd wave).

3.4. Optimum Temperature for Corrosion Potential with Salt

As shown in Fig. 4, corrosion tests were carried out to qualitatively determine the effect of various temperatures on the corrosion of polypropylene in a 0.1M $MgCl_2$ solution. It was found that all the corrosion potentials were negative. However, the variation in the corrosion potential from the 1st wave exhibited an optimum temperature at 15℃ (-0.71 V). The efficiency of the corrosion was established based on a comparison of the 1st wave between the addition and absence of salt(0.1M $MgCl_2$). The corrosion potential(-0.58 V of 15℃) without salt was higher(0.01 V)than that in the presence(-0.17 V) of salt. Accordingly, it was established that the corrosion was more rapid with

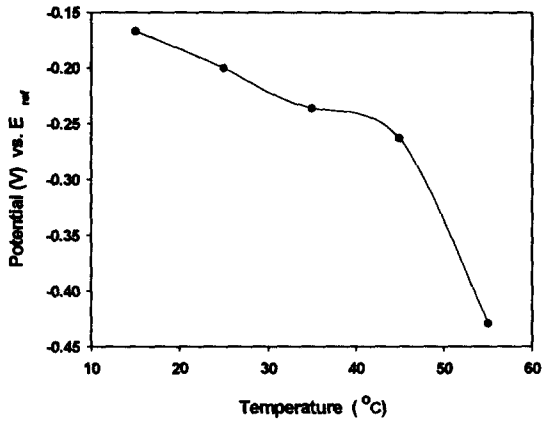


Fig. 4. Variation of corrosion potential at temperature with 0.1M $MgCl_2$ added.

the addition of salt. However, no oxidation potential was exhibited for the 2nd and 3rd waves, thereby indicating the corrosion effect of temperature in a salt solution.

3.5. Effect of dissolved oxygen

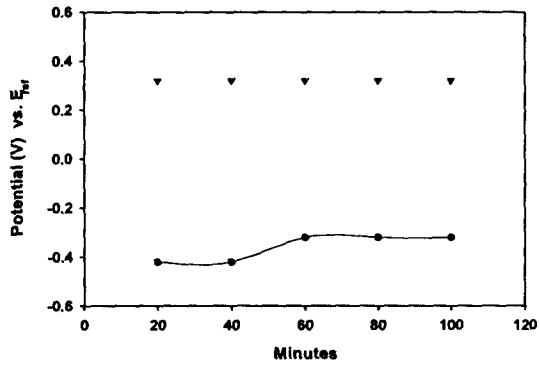


Fig. 5. Variation of corrosion potential according to the casting times with oxygen(● : 1st wave, ▼ : 2nd wave).

Fig. 5 shows the influence of the corrosion potential relative to the casting time with oxygen. Fig. 5 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 related to the reduction process. Accordingly, the corrosion potential was actually observed from the second wave. As shown in Fig. 5, the variation in the corrosion potential from the second wave exhibited the same corrosion potential (+0.32 V) within a range of 20, 40, 80, and 100 minutes. However, the optimum casting time was found to be longer than 60 minutes(-0.32 V) based on the 1st wave. The corrosion efficiency of the dissolved oxygen is listed in Table 1, together with data from previous literature for comparison. Based on this data, the optimum condition for a rapid corrosion rate was exhibited after 60 minutes.

3.6. 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.[5] Polarization resistance(R_P) and rate(mm/yr) can be presented by linear polarization curves.[6,7] The value of the corrosion resistance(R_P)[8] and rate(mm/yr)[9] were obtained using a Tafel plot, and the corrosion resistance was obtained from the following equation:

$$R_P = \frac{\Delta E}{\Delta i} = \frac{\beta_A \cdot \beta_C}{2.30\, I_{corr}(\beta_A + \beta_C)} \quad ; \text{ where}$$

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

$$\text{Corrosion rate} = \frac{0.13 I_{corr} \times E_q \times W}{d} \quad ;$$

where d = sample density(g/㎤) and $E_q \times W$ = equivalent weight(g).

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 anodic branch with slope (1- α)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 irreversible under all conditions.[10,11] The Tafel slope for the anodic dissolution was determined based on 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(15,

Table 2. Effect of various condition on the electrochemical characteristics

Parameters	Best condition	Resistance(R_P) ($k\Omega cm^2$)	Oxidation sensitivity (I_r/I_f)	Corrosion rate (mm/yr)	Reversibility (α)
Sample solution + temperature	35℃	66.67	0.65	0.07	0.60
Sample solution + pH	pH 5.0 and 7.0	14.93	0.75	0.64	0.87
Sample solution + 0.1M $MgCl_2$	15℃	68.01	0.00	0.19	1.00
Sample solution + Oxygen	60~100min	94.10	0.51	0.06	0.53

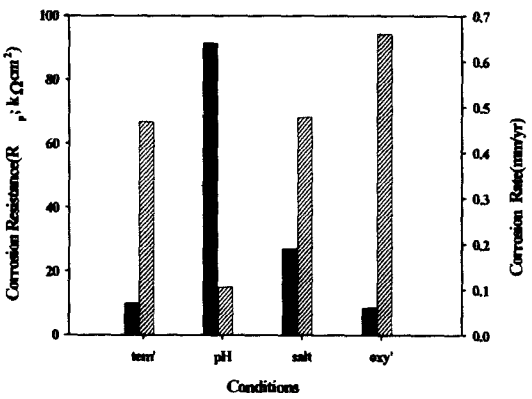


Fig. 6. Variation of resistance(R_p) and rate with various conditions(temperature, pH, salt($MgCl_2$), oxygen ; ▨ : Corrosion Resistace, ■ : Corrosion Rate).

25, 35, 45, and 55℃). These results are summarized in Table 2.

Fig. 6 presents the variations in the corrosion resistance and rate at the various temperatures in Tables 1 and 2. This was determined based on the optimum potential effects of pH, temperature, salt, and oxygen. As shown in Fig. 6, the oxidation rate was the most rapid with the lowest resistance, whereas the pH conditions exhibited the slowest oxidation rate with the highest resistance. In contrast, temperature and salt produced a reasonably balanced relationship between the resistance and the oxidation rate. Therefore, the optimum condition was found to be oxygen.[12]

3.7. Effect of Corrosion Sensitivity relative to Current Density

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, see Fig. 7. The susceptibility was examined using the maximum current density(forward and reverse scan). This was obtained using the polarization

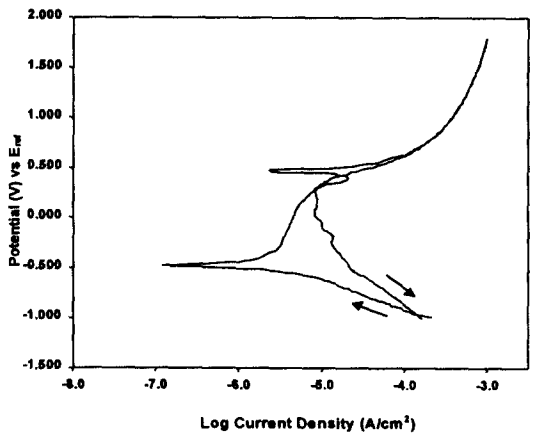


Fig. 7. Potential current density curve of polypropylene polypropylene obtained by potentiodynamic polarization(forward and reward scan rate:10mV/s).

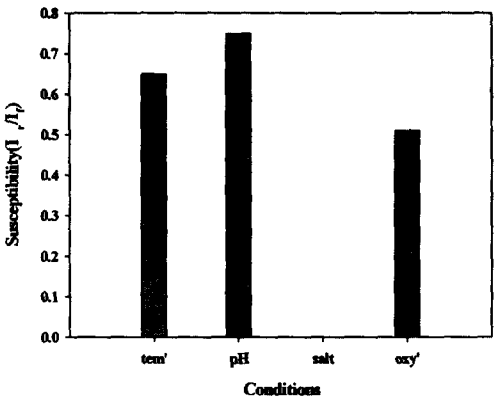
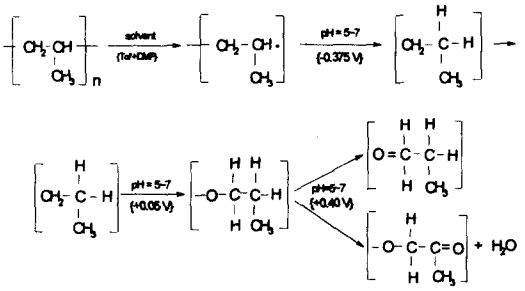


Fig. 8. Effect of susceptibility with potenitodynamic polarization curves(maximum current density) on the forward and reverse scan(conditions:temperature, pH, salt($MgCl_2$), oxygen).

curves when measuring with added factors(temperature, pH, salt, and oxygen). The corrosion susceptibility, as shown in Fig. 8, was obtained in the following order salt < oxygen < temperature < pH . Since these results can not be explained as an effect of the oxidation reaction, they would appear to result from an increase in the current density due to another factor. For this reason, it was clearly not due to the reactivity with oxygen. 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 polypropylene 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 35℃ to 55℃ and the corrosion pH was from pH 5.0 to pH 7.0. The optimum condition of temperature with salt was the most(-0.17 V) at 15℃ and the casting time with oxygen was the most after 60 minutes. It would appear that the resistance effect of temperature was minimized at 35℃, which is where the corrosion rate increased the most. 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 following order salt<oxygen<temperature<pH. The mass transfer coefficient(α) obtained was higher than 0.5. From this value, it is clear that the electrode reaction is an irreversible process.

Acknowledgement

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