Journal of the Korean Chemical Society
2001, *Vol. 45, No. 2*
Printed in the Republic of Korea

비수용액 내에서 중합체의 산화

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(2001. 1. 19 접수)

Oxidation of Polymers in Nonaqueous Solutions

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(Received January 19, 2001)

요 약. 이 연구에서 온도, pH, 효소, 그리고 염의 첨가에 따라 부식(산화)전위에 영향을 준 인자들을 알아보기위해 비수용액 poly(vinylchloride) (PVC)와 poly(carbonate) (PC)의 산화전위와 전류밀도을 측정하였다. Tafel 기울기는 분극곡선의 Tafel polt으로부터 결정되어졌다. 전달계수 α는 기울기$(1-\alpha)nF\ 2.3RT$에서 얻어질 수 있고 인식된 전극 반응은 모든 조건에서 비가역적으로 나타났다.

ABSTRACT. In this study we measured oxidation potentials and current densities for poly(vinylchloride) (PVC) and poly(carbonate) (PC) in nonaqueous solutions, in order to find out how corrosion (oxidation) potentials depend on temperature, pH, enzyme, or added salts. The Tafel's slopes were determined from the Tafel plots of polarization curves. The transfer coefficients (α) were evaluated from the slope $(1-\alpha)nF/2.3RT$, and the electrode reactions appeared irreversible under all conditions.

INTRODUCTION

Polymers are large molecules containing hundreds or thousands of atoms, people have used polymers since prehistoric time, and chemists have synthesized them for past centuries. Our technological society is largely depend on synthetic polymers.[1,2] In response to the increasing concern over environmental issues,[3] the European Commission (EC) 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 related human health aspects. The paper invites discussions on two major areas: (1) the use of additives such as lead, cadmium, and phthalates; (2) the waste management of PVC. Poly(carbonate) (PC) is partially soluble in aromatic solvents and readily soluble in chlorinated hydrocarbons.

Many synthetic organic polymers are oxidized when in contact with atmosphere. Studies of redox potential and current density for film corrosion can give the information about forms of oxidized films. In this paper, we tried to show that electrochemical methods can be utilized to demonstrate the electrochemical behaviour of the PVC and PC systems. In particular, we put an emphasis on the applications of these methods in nonaqueous solutions. To our best knowledge, this study is probably the first attempt to investigate the oxidations of these polymers by electrochemical methods. In addition, we have also determined the detailed influences of various factors such as temperature, pH, salts, and enzyme on oxidation of these polymers.[4]

EXPERIMENTAL SECTION

Materials and instrumentation. The poly(vinlychloride) (PVC) are commercial products of the Lucky, Ltd. LS-080, LS-100, and LS-130, with $\overline{M}_w=50{,}000$, 62,500 and 81,250, respectively. Poly(carbonate) (PC) was obtained from Aldrich Chemical Company.

The electrochemical and polarizing measurements were performed in tetrahydrofuran (THF) and dimethylformamide (DMF). The supporting electrolyte was either tetrabutylammonium perchlorate (TBAP) or lithium perchlorate (Aldrich), which was used as received. The supporting electrolyte concentration was typically 0.01 M. The electrochemical cell is a triple coaxial glass cell is and filled with 100 mL of solution.[5] The reference electrode is a saturated calomel electrode (SCE: Koslow Scientific Company, P/N 1004), and a graphite carbon rod is used as a counter electrode. The electrode tip of a working electrode system consists of a 1 cm^2 silver piece (thickness=0.1 mm), together with a silver and platinum wire. All solutions were typically of 1 mM in the redox-active species, and were deoxygenated by purging with nitrogen gas for at least 15 min. All experiments were performed at the scan rate of 7–10 mV/s by CMS 100 and 105 (Gamry Instruments, Inc.) with a computer.

Tafel plots were obtained at steady-state potentials (~200 mV). The potentiodynamic polarization curves were obtained from −1.0 to +1.5 V at steady-state potentials. The temperature range was from 15 °C to 55 °C. The pH of the solution was adjusted with sodium hydroxide (NaOH) and hydrochloric acid (HCl). An enzyme[6,7] (3.0 U/mg lipase; Fluka) was dissolved at a concentration of 0.2 mg/mL (unit).

RESULTS AND DISCUSSION

Electrochemical characteristics. The electrochemical (oxidation-reduction) potentials of polymers (PVC and PC) were measured in nonaqueous solvents within the range of +1.5 to −1.0 V versus SCE.

Steady-state potentials were observed at E_{pc1}−0.67 V, E_{pa1}−0.01 V, and E_{pa2}−0.20 V for the PVC solutions and at E_{pc1}−0.33 V, and E_{pa1}−0.38 V for the PC solutions. The three observed potentials for the PVC solutions suggest that the first wave (from the bottom) results from reduction and the second and third waves from oxidation. On the other hand, the two observed potentials of the PC solutions indicate one oxidation (the first wave) and one reduction (the second wave).[8] These results are summarized in *Table* 1, in which E_{pc} and E_{pa} denote reduction (cathodic) and oxidation (anodic) potential, respectively.

Influence of temperature. *Fig.* 1(a) shows the influence of temperature on oxidation potentials for PVC from 20 to 50 °C and is drawn with data from the external cathodic and anodic polarization curves. As shown in *Fig.* 1(a), the PVC exhibits a total of three redox waves. The first potential wave (from the bottom) corresponds to reduction and the second and third waves to oxidation. The second wave has a potential range of 0.08–0.28 V, and the third wave has a rather wide range of 0.33–0.62 V. Whereas the 1st wave develops with the reduction of proton to hydrogen, the 2nd and 3rd waves appear as oxygen is consumed. The lowest oxidation potentials of the 2nd and 3rd waves appear between 30 and 40 °C. Therefore, the most efficient temperature range for the oxidation of PVC seems to lie between 30 and 40 °C.

As shown in *Fig.* 1(b) for PC, the 1st wave (from the bottom) corresponds to reduction. The 2nd wave, which corresponds to oxidation, has a potential range of 0.38–0.43 V from 15 to 55 °C. A series of oxidation potentials on the 2nd wave indicate that the lowest oxidation potential is E−0.38 V at 45 °C. Therefore, the most efficient temperature for the oxidation of PC seems to be around 45 °C. When compared the efficient oxidation temperatures obtained for PVC and PC, PVC is oxidized at lower temperatures, compared with PC.

Influence of pH. *Fig.* 2(a) and 2(b) show the variation of potentials with pH, which is adjusted with HCl or

Table 1. Parameters of the poly(vinylchloride) oxidation effect under various conditions

Parameter	Concentration (1mM)								Salt (0.1M $MgCl_2$)						Enzyme (lipase)				
	(°C)				pH				(°C)						(°C)				
Redox steps	20	30	40	50	3.0	5.0	7.0	9.0	11	15	20	25	30	35	15	25	35	40	50
1st wave	−0.70	−0.70	−0.65	−0.65	−0.50	−0.50	−0.55	−0.50	−0.55	−0.63	−0.53	−0.57	−0.50	−0.50	−0.48	−0.53	−0.47	−0.47	−0.41
2nd wave	0.11	0.08	0.08	0.28	0.08	0.08	0.12	0.12	0.12	0.07	0.01	−0.07	−0.13	0.27	−0.03	0.00	−0.09	−0.09	−0.13
3rd wave	0.37	0.33	0.33	0.62	0.50	0.50	0.57	0.55	0.54	0.40	0.40	0.76	0.40	0.80	0.42	0.39	0.20	0.43	0.42

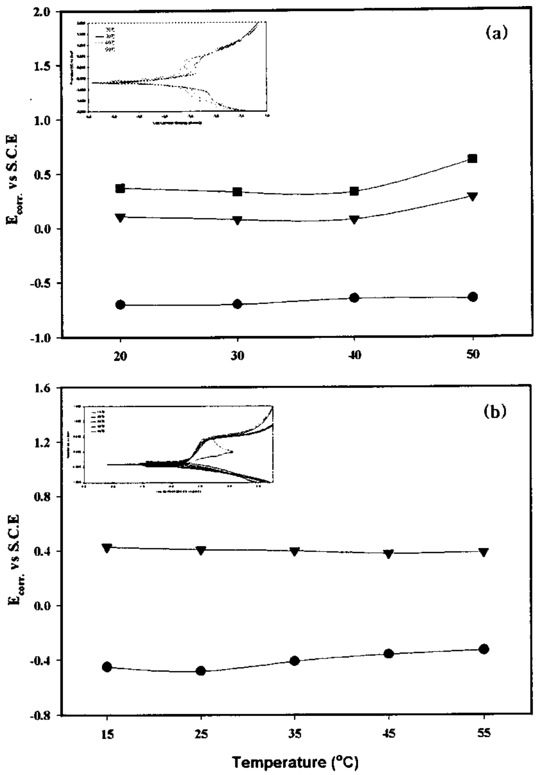

Fig. 1. Variation of oxidation potential as a function of temperature for (a) poly(vinylchloride) (b) poly(carbonate) (● : 1st wave; ▼ : 2 nd wave; ■ : 3rd wave).

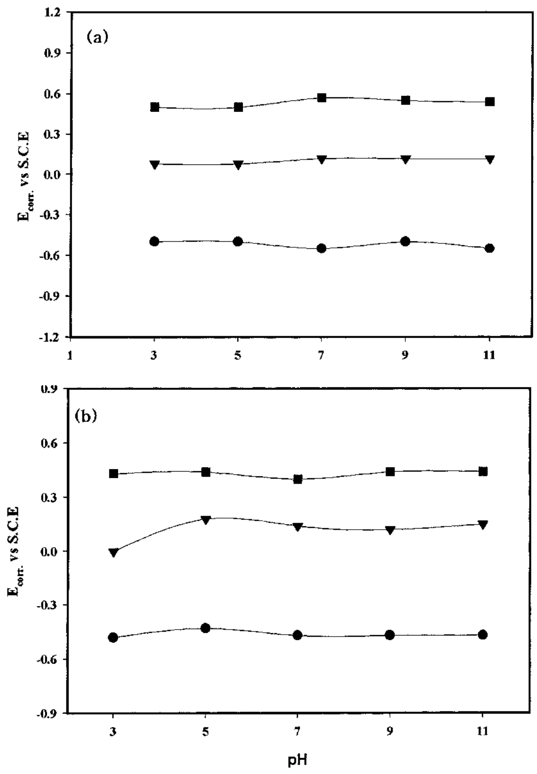

Fig. 2. Variation of oxidation potential as a function of pH for (a) poly(vinylchloride) (b) poly(carbonate) (● : 1st wave; ▼ : 2 nd wave; ■ : 3rd wave).

NaOH. From *Fig.* 2(a), the first wave (from the bottom) results from reduction of proton (eqs 1-3) at the electrode.[9,10] The second and third waves correspond to oxidation reactions.

$$2H_2O \rightleftharpoons 2H^+ + 2OH^- \quad (1)$$

$$2H^+ + 2e \rightleftarrows 2H\ H_2\uparrow \quad (2)$$

$$2OH\ 2e \rightleftarrows 2OH \rightarrow H_2O + 1/2O_2\uparrow \quad (3)$$

The variation of oxidation potentials on the 2nd and 3rd waves for PVC (*Table* 1) shows a pH dependence: 0.08-0.12 V for the 2nd wave and 0.50-0.57 V for the 3rd wave between pH=3.0 and pH=11. At pH=3.0 and pH=5.0, oxidations occur at lower potentials, compared with those at other pH values. The reason seems to the fast oxidation due to the increased amount of oxygen.[11,12] At pH>7.0, the oxidation becomes slower (or less efficient). Thus, the best pH range for oxidations appears to be pH 3.0-5.0.

Table 2 and *Fig.* 2(b) show the variation in the poten-

Table 2. Parameters of the poly(carbonate) oxidation effect under various conditions

Parameter	Concentration (1mM)										Salt (0.1M $MgCl_2$)					Enzyme (lipase)				
	(°C)					pH					(°C)					(°C)				
Redox steps	15	25	35	45	55	3.0	5.0	7.0	9.0	11	15	25	35	45	55	15	25	35	45	55
1st wave	−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	−0.49	−0.45	−0.48	−0.36	−0.32
2nd wave	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	−0.16	−0.18	−0.26	0.00	0.00
3rd wave	0.00	0.00	0.00	0.00	0.00	0.43	0.43	0.40	0.44	0.44	1.34	1.26	1.16	1.01	0.90	0.42	0.40	0.37	0.43	0.40

tials for PC. As is the case for PVC, the 1st wave results from the reduction of proton to hydrogen, and the 2nd and 3rd waves (oxidations) occur with the consumption of oxygen. The 2nd and 3rd waves exhibited oxidations at a pH=5.0 (E=0.11 V, 0.43 V) and pH=7.0 (E=0.12 V, E=0.40 V). These observations suggest that the effective oxidations occur at these pH values.

When compared the 2nd oxidation steps (the 3rd waves) in *Tables* 1 and 2, the PVC oxidation occurs fastest at 0.50 V (pH=3.0–5.0) and the PC oxidation at 0.40 V (pH=7.0). Therefore, the most efficient oxidation potential of PVC is higher than that for PC. On the bases of the above arguments, PC is more easily oxidized than PVC.

Effect of oxidation with MgCl$_2$. *Fig.* 3(a) and 3(b) show potential waves for PVC and PC in the presence of MgCl$_2$. The potentials of the 1st wave (from the bottom) show negative values at all temperatures, and so suggest reduction. The 2nd wave shows oxidation processes at 0.07 V (15 °C), 0.01 V (20 °C), and 0.27 V (35 °C). By contrast, it shows reduction processes at −0.07 V (25 °C) and −0.13 V (30 °C). On the other hand, the 3rd wave exhibits oxidation at all temperatures. Therefore, the most efficient temperature for PVC oxidation seems to be around 20 °C.

As shown in *Fig.* 3(b) and *Table* 2 for PC, the 3rd wave (from the bottom) suggests a facile oxidation at 55 °C (E=0.90 V) in the presence of 0.1 M MgCl$_2$. By comparison, the oxidation potential in the absence of MgCl$_2$ is 0.39 V (55 °C). The presence of the added salt (MgCl$_2$) has turned out to slow down the PC oxidation.

Effect of oxidation with an enzyme. *Fig.* 4(a) and *Fig.* 4(b) show potential waves in the presence of lipase (0.2 mg/mL) for PVC and for PC, respectively.[13] The 1st and 2nd waves in both figures have negative potentials, whereas the 3rd wave positive ones. In *Fig.* 4(a), oxidation is observed on the 3rd wave at 0.42 V (15 °C), 0.39 V (25 °C), 0.20 V (35 °C), 0.43 V (40 °C), and 0.42 V

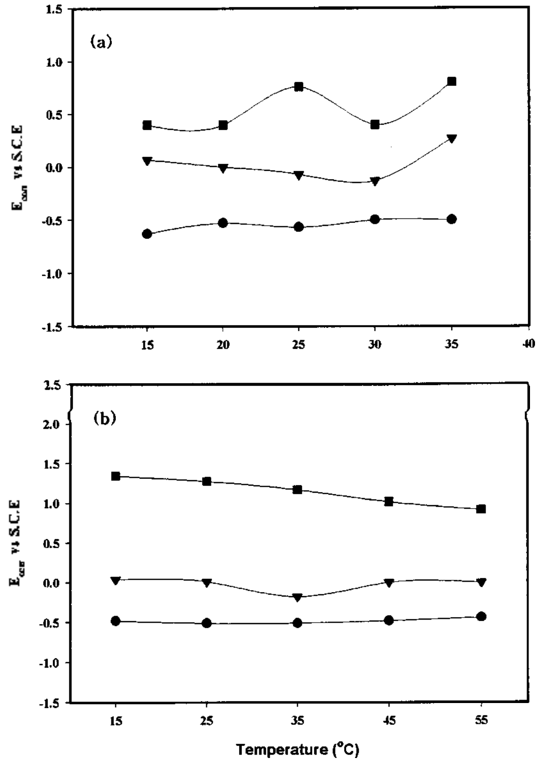

Fig. 3. Dependencies of oxidation potential on temperature (a) poly(vinylchloride) (b) poly(carbonate) in the presence of 0.1 M-MgCl$_2$ (● : 1st wave; ▼: 2nd wave; ■: 3rd wave).

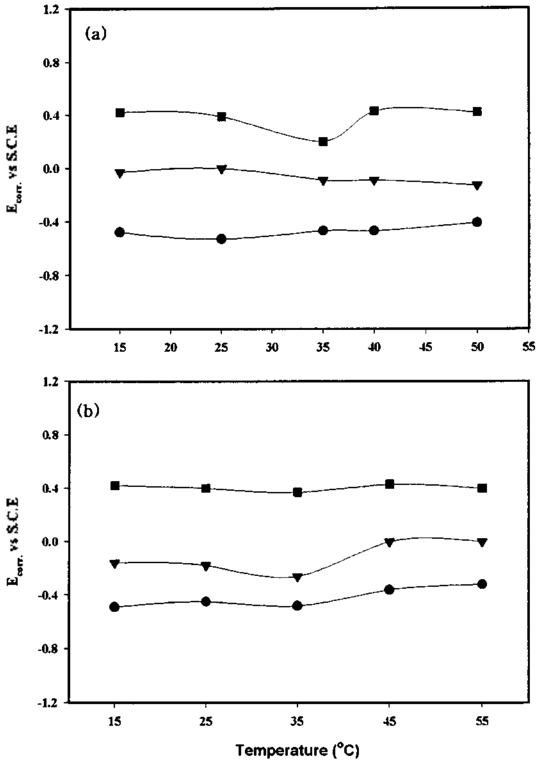

Fig. 4. Variation of oxidation potential with temperature on addition of enzyme (lipase): (a) poly(vinylchloride) (b) poly (carbonate) (● : 1st wave; ▼ : 2 nd wave; ■ : 3rd wave).

(50 °C). Therefore, the most efficient temperature for oxidation appears to be around 35 °C (E=0.20 V) in the presence of the enzyme and around 25 °C (E=0.20 V) in the absence of the enzyme. Therefore, the enzyme has a negative effect for the PVC oxidation.

Fig. 4(b) shows that oxidation also occurs at the 3rd step, which has the range of oxidation potentials of 0.37-0.43 V. The oxidation potential appears to largely change at around 35 °C. The oxidation of PC in the absence of the enzyme occurs at lower potentials at 35 °C. Consequently, the added enzyme (lipase) has negative effects on the PC oxidation.

Tafel's coefficient and reversibility. The Tafel's coefficients were determined by varying conditions (temperature, pH, $MgCl_2$, and lipase). The potentiodynamic parameters of oxidation were determined from the Tafel's equation. A plot of log i against η, known as Tafel's plot, is a useful device for evaluating kinetic parameters. There is an anodic branch with a slope of $(1-\alpha)nF/2.3RT$ and a cathodic branch with a slope of $-\alpha nF/2.3RT$. Overpotential and transfer coefficient(α) can be experimentally determined from a knowledge of the current/voltage characteristics for reversible and irreversible electrode reactions: (1) η (overpotential)=$E-E_{eq}$ (real electrode potential-equilibrium potential) and (2) $\eta=a+b\log i$. Because the values obtained in our experiments are greater than 0.50, we can easily recognize that the electrode reactions is irreversible.[14,15] Here, a and b are Tafel's constants (at 25 °C, $a=(2.3RT/\alpha nF)$ log i, $b=(-2.3RT/\alpha nF)$ log i), and i is current density. The transfer coefficient α can be evaluated from the slope $(1-\alpha)nF/2.3RT$.[16]

CONCLUSIONS

We have performed electrochemical experiments for poly(vinylchloride) poly(carbonate). From these experiments, we have found the following observations: (1) PVC readily oxidizes at E=0.08 V and PC at E=0.33 V. (2) The most appropriate pH range for PVC oxidation is pH=3-5 and that for PC is pH=5-7. (3) The most appropriate temperature for PVC oxidation is around 35 (30-40 °C) and that for PC is around 45 °C. (4) The inorganic salt ($MgCl_2$) and enzyme (lipase), which are added to the PVC and PC solutions, slow down oxidation processes. (5) The mass-transfer coefficients (α) obtained are greater than 0.5, which indicates that electrode reactions are irreversible.

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