

# Chemical Recycling of Flexible PVC by Oxygen Oxidation in NaOH Solutions at Elevated Temperatures

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**ABSTRACT:** Oxidative degradation of a flexible PVC pellet (F-PVC) with oxygen was carried out in 1–25-mol/kg(m)-H<sub>2</sub>O NaOH solutions, at 150–260°C and  $P_{O_2}$  1–10 MPa. Dehydrochlorination of F-PVC occurred first, followed by oxidation. The major products were oxalic acid, a mixture of benzenecarboxylic acids, and CO<sub>2</sub>. We obtained 320 g of oxalic acid and 130 g of benzenecarboxylic acids (as phthalic acid) from 1 kg of F-PVC under conditions of a 15-m NaOH solution at 250°C and a  $P_{O_2}$  of 5 MPa for 5 h. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 129–135, 1998

**Key words:** chemical recycling; flexible PVC; oxalic acid; benzenecarboxylic acids; base-catalyzed oxygen oxidation; dehydrochlorination; NaOH solutions

## INTRODUCTION

Poly(vinyl chloride) (PVC) is never fabricated as a neat polymer, but provides an excellent base from which to create thousands of diverse products. A variety of additives are required to enhance the performance of products made from PVC, including heat stabilizers, which prevent dehydrochlorination, subsequent color formation, and loss of physical properties. Other additives, such as processing aids, impact modifiers, and lubricants, are used in rigid PVC. Plasticizers are materials which impart flexibility to PVC and are used mostly in the flexible product, although low levels of certain plasticizers increase the stability and processibility of PVC.

Recently, material- and energy-recycling techniques of commodity plastics, such as polyethyl-

ene, polypropylene, polystyrene, and poly(ethylene terephthalate), have received special attention and are being developed as an important method of solving environmental and energy problems. In particular, when PVCs are fired in an incinerator, hydrochloric acid (HCl) corrodes the boiler tubes of the incinerator and harmful gases are released. Therefore, the current incineration technique needs to be improved. In addition to direct firing and liquefaction,<sup>1,2</sup> a new chemical technique for recycling waste plastics needs to be developed because valuable chemicals can be produced.

Although many studies have been conducted concerning the thermal decomposition and stabilization of PVC,<sup>3–9</sup> with the exception of liquefaction, studies concerning the decomposition of PVC from the standpoint of chemical recycling are few. We found that products such as oxalic acid, benzenecarboxylic acids, and naphthalene carboxylic acids are formed by oxygen oxidation of pure PVC powder<sup>10</sup> and vinylidene chloride–vinyl chloride (VDC–VC) copolymer powder<sup>11</sup> in 1–25 mol/kg(m)-H<sub>2</sub>O NaOH solutions at 150–265°C and a  $P_{O_2}$  of 1–10 MPa. Sorensen and Bjerre described a

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**Table I** Composition of F-PVC Pellets

PVC	36.8 wt %
CaCO <sub>3</sub>	28.3 wt %
DINP	23.9 wt %
Chlorinated paraffin	6.99 wt %
Alkylbenzene	1.84 wt %
Pb stabilizer	1.10 wt %
Calcium stearate	0.74 wt %
Wax	0.37 wt %

DINP: C<sub>6</sub>H<sub>4</sub>(COOC<sub>9</sub>H<sub>19</sub>)<sub>2</sub>; chlorinated paraffin: C<sub>25</sub>H<sub>45</sub>Cl<sub>17</sub>.

combined wet oxidation alkaline degradation of PVC powder that yielding water-soluble acids, biodegradable products, and CO<sub>2</sub> under 0.33 mol/dm<sup>-3</sup> NaOH, 180–260°C, and a P<sub>O<sub>2</sub></sub> of 2 MPa.<sup>12</sup> The feedstock for recycling and treatment studies has consisted mainly of pure PVC, with the exception of the conversion of PVC egg cartons into fuel oil by thermal decomposition. However, commercially available PVCs are complex materials that contain various additives, such as antioxidants, plasticizer, pigment, and degradation inhibitors. Furthermore, numerous commercially available PVCs are applied to various manufacturing processes such as rigid PVCs in bottles, calendered sheet, pipe, siding, and window profiles and flexible PVCs in wire and cable jacketing, packing film, and agricultural film. This study examined the production of oxalic acid and benzenecarboxylic acids from commercially available flexible-PVC (F-PVC) pellets by oxygen oxidation in NaOH solutions at high temperatures in order to establish the fundamental conditions necessary for a new chemical recycling process for treating waste PVC.

## EXPERIMENTAL

### Materials

Commercially available F-PVC pellets 5 × 2 mm in size for extrusion blow molding that contained some additives were examined. The formulation and elemental analysis of the F-PVC pellets are shown in Tables I and II, respectively. All other chemicals used in this study were of reagent grade.

### Oxygen Oxidation

A mixture of 3 g of F-PVC pellets, 30 g of water, and 2.4–30 g of NaOH was placed in a PTFE

beaker (thickness 3 mm, o.d. 40 mm, and depth 150 mm). The PTFE beaker was placed into an SUS 316 stainless-steel autoclave of 300 cm<sup>3</sup> fitted with a magnet-driven stirrer under N<sub>2</sub> and heated to 150–260°C at 3°C/min in an electric furnace. After reaching the predetermined temperature, oxygen was added to the autoclave at pressures of 1–10 MPa. The reaction product in the beaker was washed out with water and diluted to 500 cm<sup>3</sup> to prepare a product solution.

### Analyses

After removal of sodium ions from the product solution using a cation-exchange column, the oxalate and chloride ion content was determined by ion chromatography (DIONEX Quick, Column: AS4, AG4) and the CO<sub>2</sub> content was determined by gas chromatography (Hitachi-164, TCD, SUS-silica). The yield of water-soluble acids was determined as the difference between the oxalic acid content and total organic carbon (TOC). Benzenecarboxylic acids in water-soluble acids extracted from the product solution using methyl ethyl ketone (MEK) were analyzed by gas chromatography [capillary column TC-5 0.2 mm × 25 m, column temperature: 100°C (5 min hold) → 240°C (10°C/min) → 300°C (5°C/min), sample injection temperature: 250°C] after esterification<sup>9</sup> and the amount of each benzenecarboxylic acid was determined by subtracting the amount of CO<sub>2</sub> and oxalic acid from TOC present in the reaction solution. Lead ion concentration in the product solution was determined by an ICP-AES (SEIKO 2400A).

### Definition

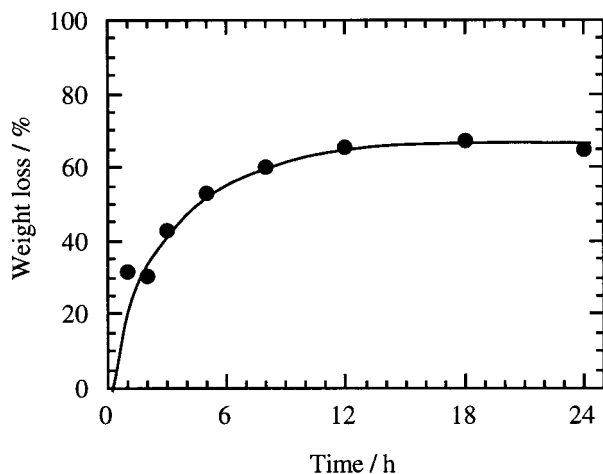
Degrees of weight loss and dehydrochlorination, yields of oxalic acid, CO<sub>2</sub>, water-soluble acids, and the Pb dissolution are defined as follows:

$$\text{Degree of weight loss} = \{(W_0 - W_t)/W_0\} \times 100 \quad (1)$$

**Table II** Ultimate Analysis of F-PVC Pellets

Wt %					
C	H	N	Cl	O <sup>a</sup>	Pb
41.28	4.86	0.00	18.86	34.83	0.17

<sup>a</sup> Difference.



**Figure 1** Weight loss curve of F-PVC pellets in 15 m NaOH at 250°C and  $P_{O_2} = 5$  MPa.

$$\text{Yield of oxalic acid} = (2m_{\text{ox}}/m_p) \times 100 \quad (2)$$

$$\text{Yield of CO}_2 = (m_{\text{CO}_2}/m_p) \times 100 \quad (3)$$

Yield of water-soluble acids

$$= (m_{\text{TOC}}/m_p) \times 100 - \text{yield of oxalic acid} \quad (4)$$

$$\text{Pb dissolution} = m_{t,\text{Pb}}/m_{0,\text{Pb}} \times 100 \quad (5)$$

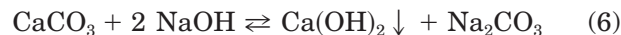
where  $W_0$  is the initial weight of F-PVC;  $W_t$ , the weight of the residue;  $m_p$ , the initial number of moles of carbon in F-PVC; and  $m_{\text{TOC}}$ ,  $m_{\text{ox}}$ , and  $m_{\text{CO}_2}$ , moles of carbon in the total organic carbon, oxalic acid, and  $\text{CO}_2$  in the reaction solution, respectively. In addition,  $m_{0,\text{Pb}}$  is the initial number of moles of lead in F-PVC and  $m_{t,\text{Pb}}$  is the number of moles of lead ion in the reaction solution. The degree of dehydrochlorination could not be analyzed in this study, because the chloride ions in the reaction solution originated from both PVC and chlorinated paraffin.

## RESULTS AND DISCUSSION

### Weight-loss Behavior of F-PVC Pellets in the Oxidative Degradation

The weight-loss curve of the F-PVC pellet is shown in Figure 1. Weight loss reached 67% at 16 h and was constant thereafter. The 33% residue consists of  $\text{Ca}(\text{OH})_2$ , because it was produced

by alkaline decomposition of  $\text{CaCO}_3$  in F-PVC in concentrated NaOH as shown in eq. (6):



Decomposition of the F-PVC pellets appeared to be completed by 12 h. This result corresponds to the results obtained for PVC powder and rigid PVC. For rigid PVC pellets that do not contain  $\text{CaCO}_3$ ,<sup>13</sup> the weight loss was 7.5% at 1 h, whereas that of the F-PVC pellets reached 31.5%. Dioctyl phthalate (DOP) in an agricultural film<sup>14</sup> has been reported to quickly hydrolyze to phthalic acid and octyl alcohol. The high degree of weight loss for F-PVC is due to both dehydrochlorination and quick hydrolysis of diisononylphthalate (DINP), used as a plastisizer, present at a level of 23.9%. This weight loss is accompanied by a decrease in molecular weight due to the production of  $\text{Ca}(\text{OH})_2$  from  $\text{CaCO}_3$ . Therefore, the decomposition of F-PVC pellets appears to consist of the dehydrochlorination of PVC, followed by the oxidation of the dehydrochlorinated PVC, the hydrolysis of DINP, and the decomposition of  $\text{CaCO}_3$ .

Lead dissolution in the F-PVC pellets is shown in Table III. These results indicate that the Pb stabilizer is decomposed according to the weight loss, after which lead in the stabilizer appears to be dissolved as  $\text{HPbO}_2^-$  or  $\text{PbO}_3^{2-}$  due to a change in the structure of PVC and an increase in specific surface area of the pellet by oxidative degradation.

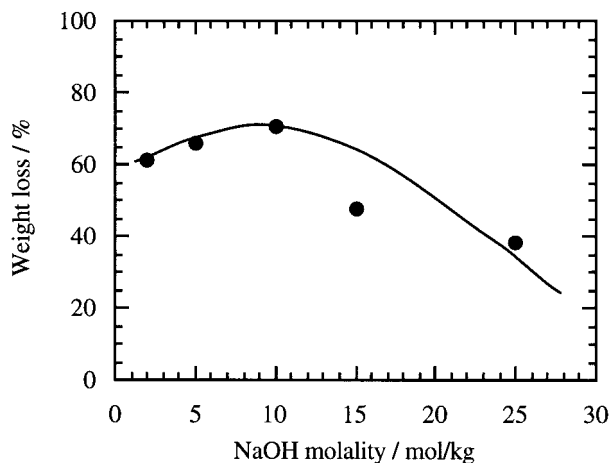
### Effect of Reaction Conditions on the Weight Loss

The effect of NaOH concentration on the weight loss of the F-PVC pellets is shown in Figure 2. The weight loss is maximized at 10 m NaOH and decreases greatly with increasing NaOH at concentrations over 10 m. Dehydrochlorination report-

**Table III** Weight Loss of F-PVC Pellets and Rate of Extraction of Pb

Time (h)	Weight Loss (%)	Rate of Pb Extraction (%)
2	31.4	51.3
5	52.8	65.4
12	65.3	101.6
24	64.9	100.0

15 m NaOH; 250°C;  $P_{O_2} = 5$  MPa.



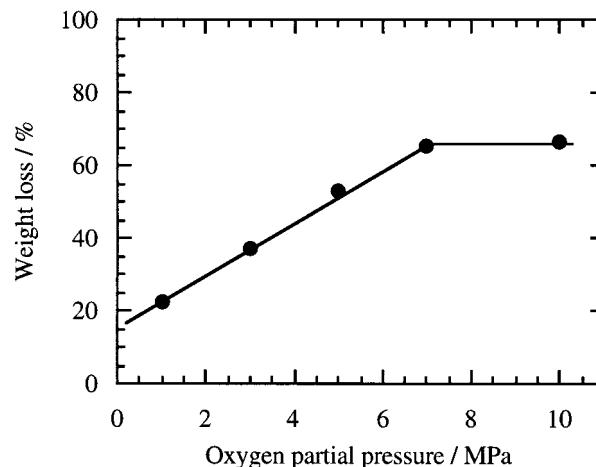
**Figure 2** Effect of NaOH concentration on the weight loss of F-PVC pellets at 250°C,  $P_{O_2} = 5$  MPa for 5 h.

edly occurs first in the oxidative degradation of PVC, oxidation follows, and the rate of dehydrochlorination reflects the rate of the weight loss. Pure PVC powder,<sup>10</sup> agricultural PVC film,<sup>14</sup> rigid PVC pellets, and PVC using quarternary ammonium salt as a phase-transfer catalyst<sup>15</sup> are examples that indicate the maximum rate for NaOH concentration. The decrease in weight loss over 10 m may be attributed to the lowering of the rate of dehydrochlorination which is promoted by oxygen due to the decrease in the solubility of oxygen in the concentrated NaOH solution.

In contrast, the weight loss appeared to increase linearly with increase of the  $P_{O_2}$  (Fig. 3); however, it did not cross the origin as observed in the case of PVC powder.<sup>10</sup> This is due primarily to the initial hydrolysis of DINP. The effect of temperature on the degree of weight loss for 5 h is shown in Figure 4. The temperature did not affect the rate of weight loss below 240°C; however, the rate accelerated for temperatures over 250°C. This indicates that DINP and  $CaCO_3$  were hydrolyzed at lower temperatures. The rapid increase at 250°C is due to the oxidative degradation of PVC in the F-PVC pellets.

#### Effect of Reaction Conditions on the Product Yield and Distribution

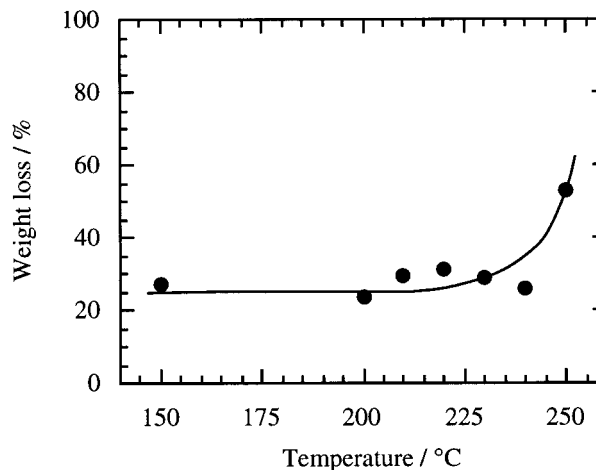
The major products in the oxidation of carbonaceous materials in F-PVC were oxalic acid,  $CO_2$ , and water-soluble acids composed of carboxylic acids. The product types are the same as those present in pure PVC powder,<sup>10</sup> VDC-VC copoly-



**Figure 3** Effect of oxygen partial pressure on the weight loss in the oxidation of F-PVC pellets in 15 m NaOH at 250°C for 5 h.

mer powder,<sup>11</sup> and rigid PVC on oxygen oxidation in alkaline solutions. There are many types of aromatic carboxylic acids present in water-soluble acids. These include phthalic acid, trimellitic acid, pyromellitic acid, mellitic acid, and benzenepentacarboxylic acid, as shown in Table IV. The formation of such aromatic carboxylic acids is caused by the oxidation aromatic rings in dehydrochlorinated PVC as it forms, due to bimolecular addition reaction<sup>16</sup> and/or coiling.<sup>17</sup> However, phthalic acid was produced mainly by the hydrolysis of DINP.

The effect of reaction time on the yield of products is shown in Figure 5. Water-soluble acids



**Figure 4** Effect of reaction temperature on the weight loss of flexible PVC pellets in 15 m NaOH at  $P_{O_2} = 5$  MPa for 5 h.

**Table IV** Yield of Benzenecarboxylic Acids (C %)

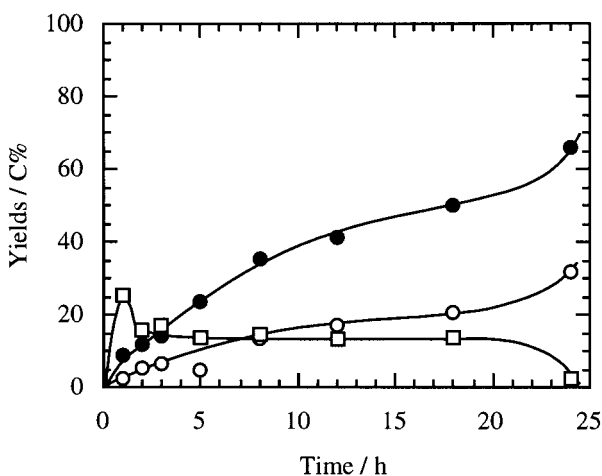
Benzoic acid	(Monobenzenecarboxylic acid)	1.29
Phthalic acid	(1,2-Benzenedicarboxylic acid)	8.73
Isophthalic acid	(1,3-Benzenedicarboxylic acid)	0.25
Terephthalic acid	(1,4-Benzenedicarboxylic acid)	0.45
Hemimellitic acid	(1,2,3-Benzenetricarboxylic acid)	0.29
Trimellitic acid	(1,2,4-Benzenetricarboxylic acid)	0.99
Trimesic acid	(1,3,5-Benzenetricarboxylic acid)	0.18
Prehnitic acid	(1,2,3,4-Benzenetetracarboxylic acid)	0.42
Pyromellitic acid	(1,2,3,4-Benzenetetracarboxylic acid)	0.35
Mellophanic acid	(1,2,3,5-Benzenetetracarboxylic acid)	0.54
Benzenepentacarboxylic acid	(1,2,3,4,5-Benzenepentacarboxylic acid)	0.35
Total		13.84

15 m NaOH; 250°C; 7 h; 5 MPa  $P_{O_2}$ .

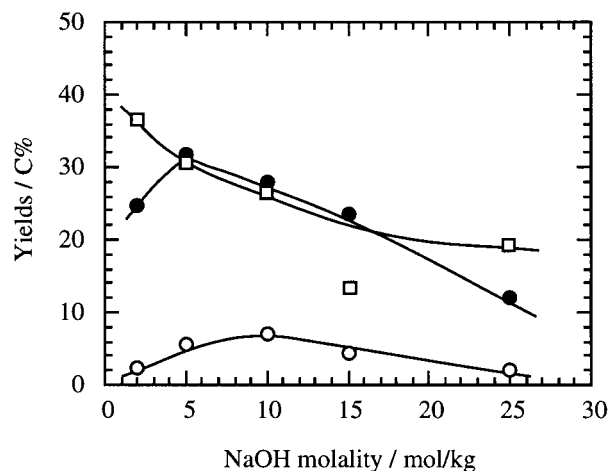
decrease with the simultaneous formation of oxalic acid and  $CO_2$ . In contrast, residue is slowly and completely oxidized to finally yield oxalic acid, water-soluble acids, and  $CO_2$ . Consequently, oxalic acid and  $CO_2$  yields continued to increase up to 18 h. However, the yield of water-soluble acids exclusively was decreased in two steps: The first step is the oxidation of phthalic acid from DINP, and the second step is the further oxidation of water-soluble acids to oxalic acid and  $CO_2$  proceeding under concentrated NaOH, according to the base-catalyzed mechanism.<sup>18</sup> A large amount of  $CO_2$  is formed from these substances, as in the case of coal tar pitch.<sup>19</sup> The yield of water-soluble acids was constant. It is thought

that the rate of oxidation of phthalic acid is almost equal to that of water-soluble acids caused by the oxidation of PVC between the first and the second steps.

The effect of NaOH concentration on the yield of products is shown in Figure 6. The yield of oxalic acid increased up to 10 m, whereas the yield of water-soluble acid decreased. This indicates that water-soluble acids are oxidized by the base-catalyzed oxygen oxidation with increasing NaOH molality. Carbon dioxide was produced by the decomposition of  $CaCO_3$  as a stabilizer and oxidation of carbonaceous materials in the NaOH solution. Carbon dioxide yields increased up to 5 m and then decreased. However, for this case,



**Figure 5** Effect of reaction time on the yields of oxalic acid,  $CO_2$ , and water-soluble acids in the oxidation of F-PVC pellet in 15 m NaOH at 250°C and  $P_{O_2} = 5$  MPa: (○) oxalic acid; (●)  $CO_2$ ; (□) water-soluble acids.



**Figure 6** Effect of NaOH concentration on the yields of oxalic acid,  $CO_2$ , and water-soluble acids in the oxidation of F-PVC pellet at 250°C and  $P_{O_2} = 5$  MPa for 5 h: (○) oxalic acid; (●)  $CO_2$ ; (□) water-soluble acids.



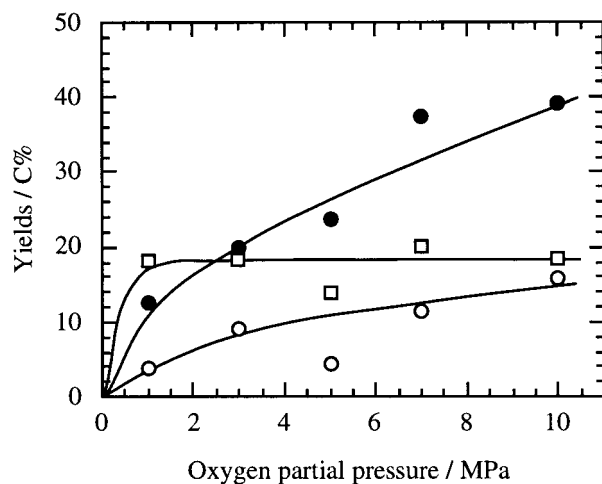
the CO<sub>2</sub> yield decreased according to the decrease in the weight loss shown in Figure 2. The decrease in the yields of oxalic acid and water-soluble acids with increasing NaOH concentration appears to be caused not only by a decrease in the oxidation of these materials but also by a lowering of the solubility of the reactants, for example, oxygen and water-soluble acids in highly concentrated NaOH solution due to the decrease in the weight loss of F-PVC.

The effect of the  $P_{O_2}$  is shown in Figure 7. The yields of oxalic acid and CO<sub>2</sub> increased with the  $P_{O_2}$ . Notably, the increase of the yield of oxalic acid indicates that the oxidative degradation of F-PVC is promoted by the base-catalyzed oxygen oxidation. In contrast, the yield of water-soluble acids was not affected by the  $P_{O_2}$ . This indicates that the oxidation of water-soluble acids to oxalic acid and CO<sub>2</sub> occurred easily and progressed easily.

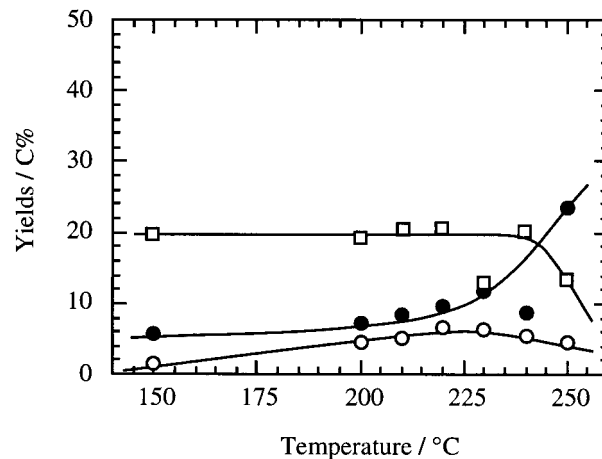
The effect of the reaction temperature in 15 m NaOH at  $P_{O_2}$  5 MPa is shown in Figure 8. Production of water-soluble acids of 20 C% (phthalic acid yield 12 C%) at 150°C indicates that DINP is easily hydrolyzed. In contrast, both the decrease of oxalic acid and water-soluble acids and the drastic increase of CO<sub>2</sub> at high temperatures indicates that PVC in F-PVC is oxidized completely.

## CONCLUSIONS

The present results revealed the following: The oxidation of F-PVC took place in 1–25-m NaOH



**Figure 7** Effect of oxygen partial pressure on the yields of oxalic acid, CO<sub>2</sub>, and water-soluble acids in the oxidation of F-PVC pellets in 15 m NaOH at 250°C for 5 h: (○) oxalic acid; (●) CO<sub>2</sub>; (□) water-soluble acids.



**Figure 8** Effect of reaction temperature on the yields of oxalic acid, CO<sub>2</sub>, and water-soluble acids in the oxidation of F-PVC pellets in 15 m NaOH at  $P_{O_2}$  = 5 MPa for 5 h: (○) oxalic acid; (●) CO<sub>2</sub>; (□) water-soluble acids.

solutions at 250°C under oxygen at pressure up to a  $P_{O_2}$  of 10 MPa. The products are oxalic acid and water-soluble acids. Under conditions of 15 m NaOH at 250°C and a  $P_{O_2}$  of 5 MPa for 5 h, 320 g of oxalic acid and 130 g of benzenecarboxylic acids (in the form of phthalic acid) can be obtained from 1 kg of F-PVC. The lead in F-PVC was extracted completely.

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