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# Degradation Behavior of PVC Sheet

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**Absrtact:** The heat treatment of PVC film containing PVC 65%, DOP(Dioctyl Phthalate) 32% as plasticizer, Ca-Zn stearates and surface agent was performed under several conditions to study the degradation behavior of PVC sheet. In the case of $H_2SO_4$, the dehydrochlorination was ca.100% at 250℃ for 3h. The char involving the smaller pores was produced with hydrothermal treatment. The pore size became small with increasing the treatment time and temperature. In the case of treatment with $Ca(OH)_2$, the sizes of pores produced in char were about sever ~ 10㎛ at 225℃ for 12h. In the case of $H_2SO_4$, the size of pores were about 1㎛ in 5M $H_2SO_4$ for 12h.

**Keywords: PVC, DOP, Dehydrochlorination, Char, Hydrothermal**

## 1. Introduction

In a present society affected by the effect of high economic growth, the mass production, mass consumption were occupied as a basic form of the life of the people. This result, the amount of waste of plastics have been increased year by year. However, the incineration cost for intermediate treatment is more expensive than the cost for the final treatment of reclamation. In the case of incineration treatment, PVC reaching 10% of the total waste plastics causes evolution of HCl, damages an incinerator and yields toxics substances such as dioxins.

In this paper, effect of $Ca(OH)_2$, $H_2SO_4$ concentration and temperature on the behavior of degradation of PVC film has been studied to develope new feed stock recycle of PVC in aqueous solution at elevated temperatures.

## 2. Experiment

### 2.1. Sample and reagent

The composition of the PVC film used is shown in Table 1. All chemicals were

reagent grade.

Table 1. Composition of PVC film.(wt%)

| | |
|---|---|
| PVC | 64.5 |
| DOP | 32.2 |
| Epoxy plasticizer | 1.29 |
| Surface active agent | 1.29 |
| Ca-Zn stabilizer | 0.64 |
| UV absorption agent | 0.06 |

DOP: $C_6H_4(COOC_8H_{17})_2$

## 2.2. Reaction system

The experimental apparatus was a rotating electric furnace.[1][2]

## 2.3. Experimental procedure

PVC film (0.2g) and 20ml of $Ca(OH)_2$ solutions, $H_2SO_4$ solutions, and NaOH solutions were put in 25ml SUS-316 tubes. After the reaction by using laboratory grinder, the tubes were cooled at room temperature. The reaction product was filtered with a 1G4 glass filter, previously weighted. The filtrate was diluted to 100ml. Residues were washed with water and dried.

## 2.4 Defination

The degree of dehydrochlorination and weight loss were defined as follows:

$$\text{Dehydrochlorination } (\%) = [(m_{cl,o} - m_{cl,t}) / m_{cl,o}] \times 100 \quad \cdots\cdots\cdots (1)$$

$$\text{Weight loss } (\%) = [(W_o - W_t) / W_o] \times 100 \quad \cdots\cdots\cdots\cdots\cdots (2)$$

where, $m_{cl,o}$ is number of moles of Cl in the reaction solution, $m_{cl,t}$ is numbers of moles of Cl contained in PVC, $W_o$ and $W_t$ are quantities of sample and of residues after reactions, respectively.

# 3. Result and Discussion

## 3.1. Weight loss of PVC film

The weight loss of PVC film is decreased by hydrolysis of plasticizer and extraction together,(we call hydrolysis·extraction from now on) more decreased by proceeding of dehydrochlorination continuously in aqueous solution at elevated temperatures. Therefore, first of all, we observe the behavior of total weight loss, and then we can know the behavior of hydrolysis and extraction of plasticizer, eliminating the weight loss by dehydrochlorination

### 3.1.1. Behavior of decomposition in Water

Observed and Calculated weight loss curves of the PVC film examined at 250℃ in water is shown in Fig.1.

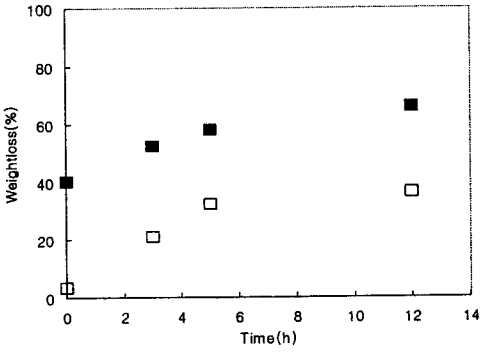



Fig. 1 Weightloss curves of PVC film in water at 250℃
Temp./℃: observed weight loss(obsd.): ■ 250℃
Calculated value due to the dehydrochlorinatio (calcd.): □ 250℃

The weight loss was increased with increasing reaction temperature and reaction time. The degree of weight loss by the decomposition reached ca.40% at 250℃ for 0 hour. Besides, It was larger than calculated value, and the difference between the observed and calculated values was almost

constant for all reaction time. This corresponded to loss of all the hydrolysis of plasticizer contained in PVC film before the occurrence of dehydrochlorination.

### 3.1.2. Behavior of decomposition in $H_2SO_4$

Observed and calculated weight loss curves of the PVC film examined at 225℃ in $H_2SO_4$ is shown in Fig.2.

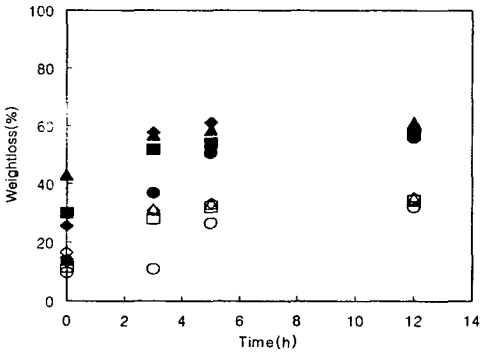



Fig. 2 Weightloss curves of PVC film in $H_2SO_4$ at 225℃.
$H_2SO_4$/M: obsd.: ● 1, ■ 3, ◆ 5, ▲ 7
calcd.: ○ 1, □ 3, ◇ 5, △ 7

The weight loss was larger than calculated value, and reached ca.30~43% for 0 hour. It was almost constant ca. 60% at 225℃, after 0 hour.

## 3.2 Dehydrochlorination of PVC film

### 3.2.1 Behavior of dehydrochlorination in water

The dehydrochlorination curves of PVC film in Water at 200~250℃ is shown in Fig.3. The dehydrochlorination was not almost proceeded, according to increasing of the reaction time. Which reached ca. 7% for 12 hour. The dehydrochlorination reached 5% at 225℃, 0 hour, and 2, 32, and 57% at 3, 5, and 12 hour, respectively. After that, degree of dehydrochlorination was increasing rapidly 62, 89 and 91% at 3, 5 and 12hour, respectively. Thus, as shown the Fig.3 this dehydrochlorination process can be expressed by the zero order reaction time. Equation(3) represents the zero order kinetics for the dehydrochlorination of PVC film in water.

$$X = kt \cdot \cdot \cdot \cdot \cdot \cdot \cdot (3)$$

X: the degree of dehydrochlorination,
k: apparent rate constant
t: reaction time.

An Arrhenius plot of the apparent rate constant k from the slope of Fig.3 is represented in Fig.4. The Arrhenius plot is linear and the apparent activation energy is 32 kcal/mol.

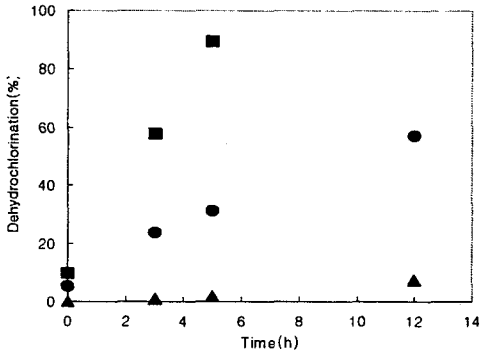



Fig..3 Dehydrochlorination curves of PVC film in water
Temp./℃: ▲ 200, ● 225, ■ 250

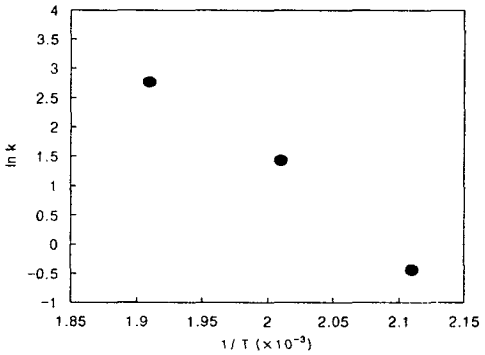



Fig.4 Arrhenius plot of the apparent rate constant for PVC film in water.

### 3.2.2 Behavior of dehydrochlorination in $H_2SO_4$.

The dehydrochlorination curves of PVC film in 1~7M $H_2SO_4$ at 225℃, 250℃ are shown in Fig.5 and Fig.6.

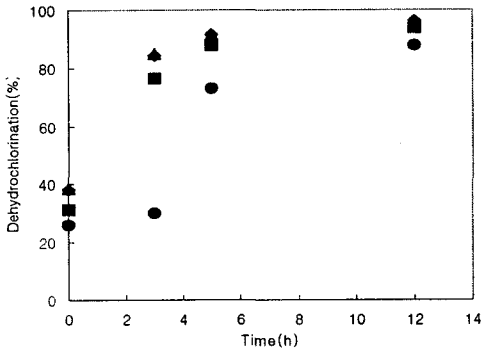



Fig.5 Dehydrochlorination behavior of PVC film in 1~7M $H_2SO_4$ at 225℃.
$H_2SO_4$/M : ● 1, ■ 3, ◆ 5, ▲ 7

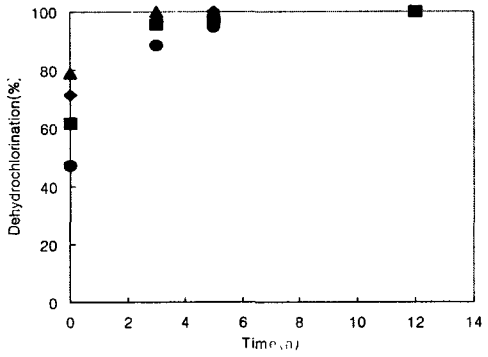
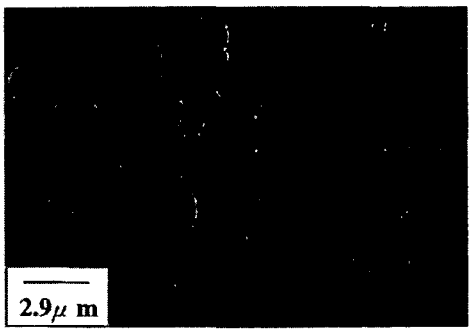



Fig.6 Dehydrochlorination behavior of PVC film in 1~7M $H_2SO_4$ at 250℃.
$H_2SO_4$/M : ● 1, ■ 3, ◆ 5, ▲ 7

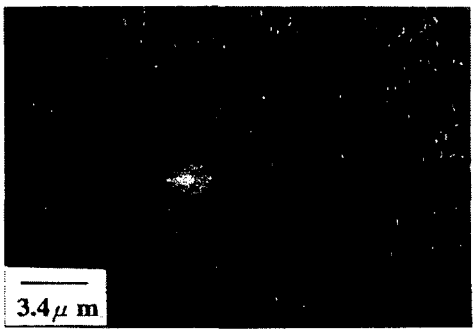
The dehydrochlorination was proceeded already in rising temperature, but its rate increased rapidly with increasing reaction temperature and reaction time.

## 3.3 Shape and Component of Residues

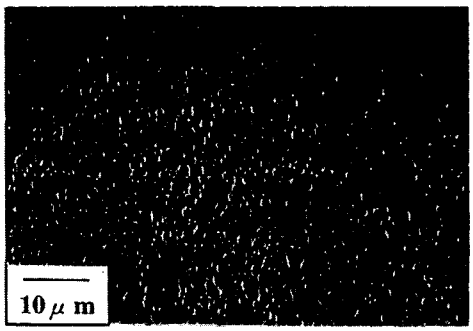
SEM photographs of PVC film residues formed at 225℃ in 5M $H_2SO_4$ are shown Fig.7. The black parts show the pores formed by leaching of DOP and the matrix is residual PVC. The pores, 3~5$\mu$m in size were produced by the leaching of DOP, besides the succeeding dehydrochlorination of PVC matrix produced smaller pores and brought about the shrinkage of the PVC matrix. Consequently, the pore size became smaller about 1$\mu$m for 12 hour.




(a)




(b)




(c)

Fig. 7 SEM photographs of residuals at 225℃ in 5M $H_2SO_4$. (a) : 0h, (b) : 3h, (c) : 12h

Table 2. Ultimate analysis, atomic ratio and the degree of dehydrochlorination of residues in 5M $H_2SO_4$ at 225℃.

| t/h | Elemental Analysis (wt%) | | | | Atomic ratio | | | D.H. |
|---|---|---|---|---|---|---|---|---|
| | C | H | Cl | O* | H/C | Cl/C | O/C | (%) |
| 0 | 49.76 | 6.16 | 30.36 | 13.72 | 1.42 | 0.21 | 0.21 | 31.3 |
| 3 | 63.45 | 6.76 | 11.40 | 18.39 | 1.28 | 0.06 | 0.22 | 84.9 |
| 5 | 77.92 | 7.85 | 6.71 | 7.52 | 1.21 | 0.03 | 0.07 | 91.5 |
| 12 | 73.75 | 7.04 | 3.79 | 15.42 | 1.15 | 0.02 | 0.16 | 95.5 |

a: difference D.H.: Dehydrochlorination

The Ultimate analysis and the degree of dehydrochlorination of residues in 5M $H_2SO_4$ at 225℃ are shown in Table 2. The dehydrochlorination was already proceeded at 0 hour, reached at 31.3%. When the degree of dehydrochlorination was high, the degree of carbonization was high. The H/C value decreased from 1.49 to 1.15 and then it approached to the value of polyene well produce by the dehydrochlorination. The value of Cl/C decreased from 0.21 to 0.02 shows the fact that the dehydrochlorination advanced enormously.

## 4. Conclusion

The following conclusions may be derived from the present study.

(1) The degree of weight loss of PVC film was increasing according to increasing of reaction time and temperature in $H_2SO_4$ and Water.

2) The rate of dehydrochlorination was proceeding slowly in aqueous solutions at elevated temperature, on the other hands, it was proceeding fast in $H_2SO_4$ and reached ca.100% at 250℃, 3hour.

3) Through hydrothermal treatment of PVC film, the micro pores produced,

## Reference

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