Fundamental Behavior of PVC Materials Degradation in Aqueous Solutions at Elevated Temperatures

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PVC materials were treated at 150-250°C in 0-7M NaOH solutions for 0-12 h, in order to study the degradation behavior of commercial PVC materials. The degree of weight loss due to the decomposition reached 31% in 3M NaOH during the temperature rised to 225°C, which corresponded to lose all the plasticizer(DOP) contained in PVC film. Under the same conditions, DOP was hydrolyzed quantitatively to phthalic acid and isooctyl alcohol by alkali hydrolysis. The degree of dehydrochlorination of PVC materials were reached about 100% at 250°C over 3 h. A lot of pores about 1-3 μm in size were observed in the residue from PVC materials treated in 3M NaOH at 225°C for 12 h.

1. Introduction

The amount of waste plastics dumped from domestics increases every year. Currently, there is no specialized treatment but reclamation,or incineration by which most of waste plastics are treated. The reclamation treatment is easy and cheep, but has many problems, such as a reduction of life-time and an unsettle of reclaimed site, due to a little specific gravity of plastics. In the case of incineration treatment, the incinerator gets damaged by the high calorie of waste plastics, produces of HCl, and forms of toxic substances such as dioxins.

Like the papers for PVC, dehydrochlorination reaction of PVC was started around at 200°C suddenly, almost terminated at 350°C . Dehydrochlorinated polymer becomes almost carbon and hydrogen. Therefore, as it is decomposed at 450-500°C powerfully, take benzene, compound with aromatic compound and most of residues.

PVC materials consist of chlorine, carbon and hydrogen and other various chemical species are formed according to its bond. In the pyrolysis, dehydrochlorination occurs certainly and polyene is produced at the same time. In addition, branching and aromatic ring structure on polyene are formed to make char containing a small amount of chlorine. Until now, in the chemical recycle of the PVC and polyvinyl chloride materials, they are studied the method that plasticizer separates from PVC using reprecipitation and conversion to oxalic acid and benzenecarboxylic acids with oxygen oxidation in alkaline solution, supercritical water and emulsifying by alkali addition. Moreover, it has been done to do the dehydrochlorination treatment by pyrolysis and then the steam activation treatment to convert to active carbon and so on.

Agricultural PVC film is one of important plastic wastes, which is demanded recycling, and its material recycling has been progressed from 1970 in Japan. Agricultural PVC film waste of 105,915 ton was recycled 45.0% in 1993 as cut-off mat, roadmat, drainage system

packing, floor tail material, pellet and so on. However, the demand for recycling became increasingly high, and development of new recycling process for chemical recycling is expected. In this paper, we studied the dehydrochlorination and decomposition behavior of PVC materials in aqueous alkaline solutions at elevated temperatures and considered for the advanced use for the purpose of chemical recycling.

2. Experimental

2.1 Experimental procedure

0.2g of PVC material (PVC film(5mm×2mm), flexible PVC pellet or rigid PVC pellet(4mm×2mm)), and 20ml of 0-7M NaOH solutions were put in 25ml SUS-316 tubes. These were put in an Al block heated to the prescribed temperature and held at 150-250°C for 0-12 h. After the reaction, the tubes were set out, and cooled at room temperature. Reaction product was filtered with a 1G4 glass filter weighed previously. Residues were washed with water and dried in a silicagel desiccator.

2.2 Analysis

One portion of the reaction solution was passed through a H^+ cation exchange column in order to remove Na^+ ion, and phthalic acid and chloride ions were determined by ion chromatography. The surface of residues was observed by a scanning electron microscope(SEM). Carbon, hydrogen, and chlorine contents were measured by elementary analysis of CHN and Cl.

2.3 Definition

The degree of dehydrochlorination and weight loss are calculated as follows:

Dehydrochlorination	(%)	$\{(m_{Cl,0} - m_{Cl,t}) / m_{Cl,0} \} \times 100$	(1)
Weight loss	(%)	$\{(W_0 - W_t) / W_0 \} \times 100$	(2)
Phthalic acid	(%)	$(m_{ph} / m_{DOP}) \times 100$	(3)

Where, $m_{Cl,0}$ is numbers of moles of Cl in the reaction solution, $m_{Cl,t}$ is numbers of moles of Cl contained in PVC, W_0 and W_t are quantities of sample before and after the reaction, respectively. m_{DOP} is number of mole of DOP contained in PVC film, and m_{ph} is numbers of mole of phthalic acid in the reaction.

The degree of dehydrochlorination obtained by equation (1) was equal to the degree from elementary analysis of Cl in residues within an error of 1%.

3. Results and Discussions

3.1 Degradation of PVC film

3.1.1 Reaction process

Fig.1 shows the effect of reaction time on the observed weight loss and the calculated weight loss from degree of dehydrochlorination of PVC film. The degree of weight loss due to the decomposition reached 31% in 3M NaOH during the temperature rised to 225°C, which

corresponded to lose all the plasticizer (DOP) contained in PVC film. Zero hour mean the time when the reactor attains the prescribed temperature by heating. Under the same conditions, DOP was hydrolyzed quantitatively to phthalic acid and isooctyl alcohol by alkali hydrolysis. Therefore, the plasticizer contained 30% in PVC film may be leached in alkali solutions before the occurrence of dehydrochlorination.

3.1.2 The effect of reaction conditions on the hydrolysis-extraction of DOP

DOP contained in PVC films was hydrolyzed and extracted to phthalic acid and isooctylalcohol. It was difficult to collect isooctylalcol quantitatively because it evaporated while being filtered. Therefore, the effect of reaction conditions on the yield of phthalic acid was examined. Fig.2 shows the effect of NaOH concentration on the yield of phthalic acid at 225°C. The yields of phthalic acid increased greatly with increasing NaOH concentration and reached ca.100% over 3M NaOH.

Fig.3 shows the effect of temperature on the yield of phthalic acid at 3M NaOH. The yield of phthalic acid was 12% during the temperature rised to 150°C, however, increased with a steep slope and with increase in temperature. Thus, it reached 89% at 200°C and ca.100% over 225°C.

3.1.3 Morphology of residues

SEM photographs of PVC film residues formed at 225°C in 3M NaOH are shown in Fig.4.

The black parts show the pores formed by leaching of DOP and the matrix is residual PVC. The pores, 5-10 μm in size were produced on the PVC matrix by the leaching of DOP, besides the succeeding dehydrochlorination of PVC matrix produced smaller pores and brought about a shrinkage of the PVC matrix. Consequently, the pore size became smaller about 1-3μm for 12 h.

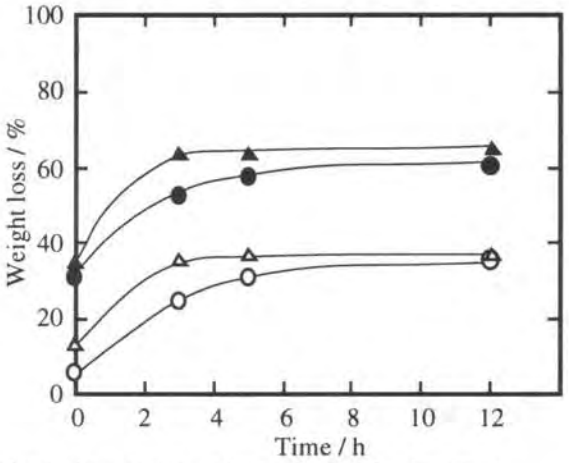


Fig.1 Comparison of observed and calculated weight losses of agricultural PVC film in 3M NaOH at 225 °C and 250 °C.
Observed weight loss: ● 225°C, ▲ 250°C.
Calculated value due to the dehydrochlorination : ○ 225 °C, △ 250°C.

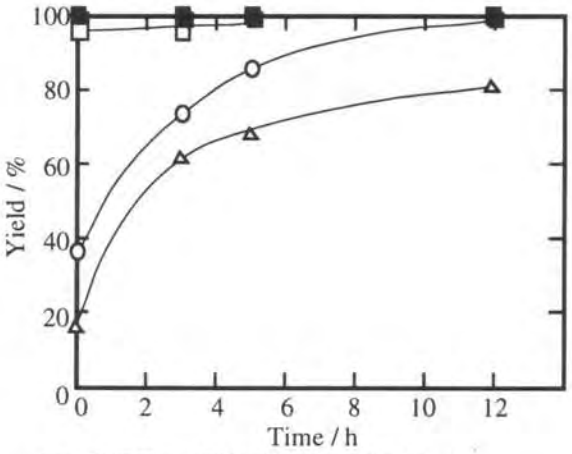


Fig. 2 Effect of NaOH concentration on the yield of phtalic acid at 225 °C.
NaOH conc./M: △ 0, ○ 1, □ 3, ● 5, ■ 7.

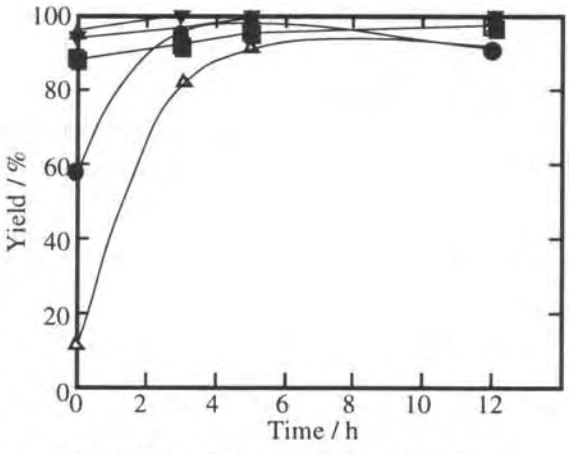
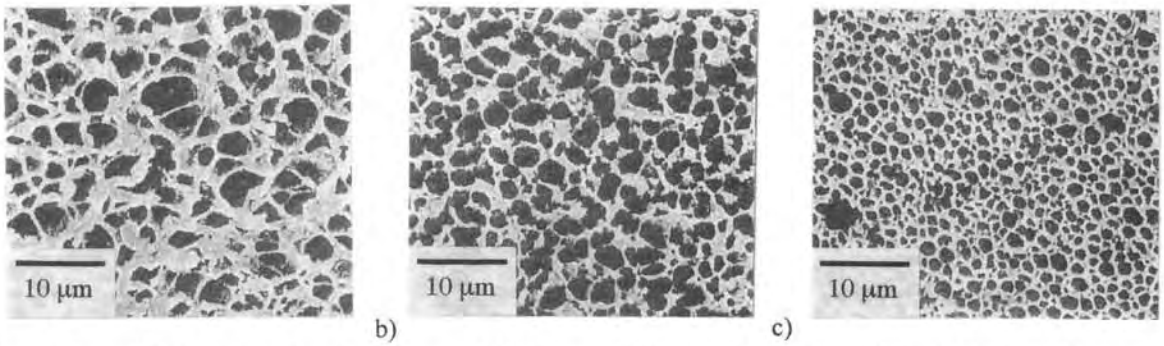


Fig. 3 Effect of temperature on the yield of phtalic acid at 225 °C.
Temp../°C : △ 150, ● 180, ■ 200, ▲ 225, ▼ 250.



a) b) c)

Fig.4 SEM photographs of residues of PVC film at 225°C in 3M NaOH. a) 0h, b) 3h, c) 12h

3.2 Kinetics and mechanism of the dehydrochlorination

The degree of dehydrochlorination of PVC materials (X) increased with increasing of reaction temperature, and reached about 100% at 250°C over 5 h. The dehydrochlorination proceeded by the first order reaction with X in the alkaline solution. The first order plot of X for the PVC materials showed a good linearity, though these lines did not pass through the origin at 0h due to the preheat time. Arrhenius plots of the apparent rate constant k, calculated from these slopes are represented in Fig.5. The Arrhenius plots were linear and the apparent activation energy was 30kcal/mol for PVC film. Similarly, dehydrochlorination of flexible PVC pellet and rigid PVC pellet proceeded in the first order with X, and the apparent activation energies were 27kcal/mol and 23kcal/mol, respectively.

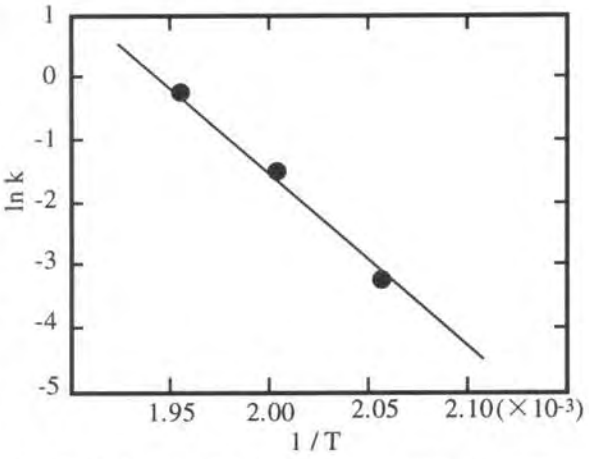


Fig. 5 Arrhenius plot of the apparent rate constant for agricultural PVC film in 3M NaOH.

4. Conclusions

1) DOP was hydrolyzed quantitatively to phthalic acid and isooctyl alcohol in the alkaline solution.
2) The degree of dehydrochlorination of PVC materials increased with increasing reaction temperature, and reached about 100% at 250°C over 3 h.
3) The dehydrochlorination of PVC in the PVC materials proceeded by a first order reaction with X in the alkaline solution.
4) A lot of pores about 1-3 μm in size were observed in the residue from agricultural PVC film at 225°C, in 3M NaOH for 12h.
5) The apparent activation energies were 30 kcal/mol and 23 kcal/mol, respectively in 3 M NaOH for P.F.. and rigid PVC pellet, and 27 kcal/mol in 5 M NaOH for flexible PVC pellet.