

Thermal Degradation of Polyvinyl Chloride

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Polyvinylchloride (PVC) powder was dehydro-chlorinated under N_2 flow at 200 - 400 °C for 10 min - 5 hours. The dehydrochlorination initially progressed on an apparent zero order reaction with respect to the degree at each temperature. The apparent activation energy was 28 kcal/mol and agreed approximately with previous works between 80 and 280 °C, but that from 300 to 400 °C was obtained 5 kcal/mol. On the other hand, the rate of dehydrochlorination in higher degree was decreased and arranged by a first order reaction. The apparent activation energy from 200 to 280 °C was 13 kcal/mol. This result indicated that the dehydrochlorination rate is controlled by the chemical reaction from 200 to 280 °C, but that from 300 to 400 °C was 3.4 kcal/mol. These results indicate that the rate of the dehydrochlorination is controlled by the chemical reaction at low temperature, but that from 300 to 400 °C is controlled by heat transfer rate. The mechanism is discussed with chemical structure of residues and evolved degradation products.

Introduction

Plastics waste has increased, the amount of them reached 9 million tons (1998) in Japan, and most was treated by incineration and landfills. As "*The law for promotion of sorted collection and recycling of containers and packaging*" and "*The law for promotion of sorted collection and recycling of electric appliances for household use*" were taken institution and enforcement in 1996, collecting and recycling of plastics have increased gradually. The object will be all plastics used as containers and packaging are recycled until the year 2000. Therefore effective recycling process must be established as early as possible.

Conversion into oil from waste plastics has expected as one of the most effective recycling process, and several pilot plants are running in Japan. However, polyvinylchloride (PVC) contained ca. 10% of plastic in municipal solid waste evolves mainly hydrogen chloride and a few harmful organochlorine compounds, such as dioxin, during incineration and thermal decomposition. The technologies of dehydrochlorination have been studied since the 1970, but no process has been operated on a industrial scale as a results of technical and economical problems.

Recently, degradative extrusion processes for dehydrochlorinating thermoplastics with a counter-rotating twin-screw extruder are studied in Germany and Japan as a pretreatment for liquefaction of waste plastics. Saito et.al [1] and Menges et al [2] reported that chlorine content inbasic plastics waste reduces less than 0.1% at 300 - 400°C. But the quality of produced oil is not satisfactory as chlorine and some chlorine compounds are contained.

Many works have reported the dehydrochlorination behavior of PVC since the 1930's later [3,4], then some mechanism, and many kinetic equations have been proposed [5-11]. The

objects of these works were almost stabilization of PVC, and experimental condition was investigated in the range of low temperature up to 260 °C and low degree of dehydrochlorination up to about 60%. Therefore it is important to understand and discuss the dehydrochlorination behavior of PVC in wide degree and the condition of higher temperature, such as 300 - 400 °C

In this study, PVC powder was held and degraded at each 200 to 400 °C with heating rate of 100 °C/min under nitrogen flow, and then kinetics until high degree of dehydrochlorination were discussed relating to the degraded products and chemical structure of a residue.

Experimental

Materials and apparatus

PVC sample was used a commercial powder ($\overline{M}_w = 62500$, particle size 0.1 mm) and others used guaranteed reagents. Imaging furnace used infrared red reflection type furnace. Sample on a quartz boat was placed in a quartz reaction tube (27 mm i.d., 610 mm long), which was placed in a furnace. Reaction temperature was measured by a thermocouple outside the reaction tube as confirmed to be nearly with in ± 2 °C equal to the temperature inside the tube, and was controlled by PID controller. Glass wool was filled into the reaction tube until 2/3 of the length to preheat N₂ flow gas effectively.

Procedure

PVC sample of 30 mg was held and degraded at the required temperature for 5 h with heating rate of 100 °C/min. under N₂ flow at 250 cm³/min. Evolved HCl was collected in 100 cm³ distilled water in HCl trap. The HCl solution was sampled 2 cm³ every 5 and/or 10 min and the amount of Cl⁻ was determined by ion chromatography to calculate the degree of dehydrochlorination.

The chemical structure of residue was analyzed by FT-IR spectroscopy, and the degraded products, which were collected in CH₃OH, were measured by GC/MS.

Results and discussion

Kinetics of dehydrochlorination

Effect of temperature on the dehydrochlorination is shown in Figure 1. The rate was constant in the range of low degree of dehydrochlorination at each temperature, but decreased gradually as the degree of dehydrochlorination was higher. Because the dehydrochlorination proceed zero order reaction initially, an apparent initial rate constant k can be defined as Eq.(1).

$$\frac{dX}{dt} = k \quad (1)$$

where X is the degree of dehydrochlorination. The dehydrochlorination

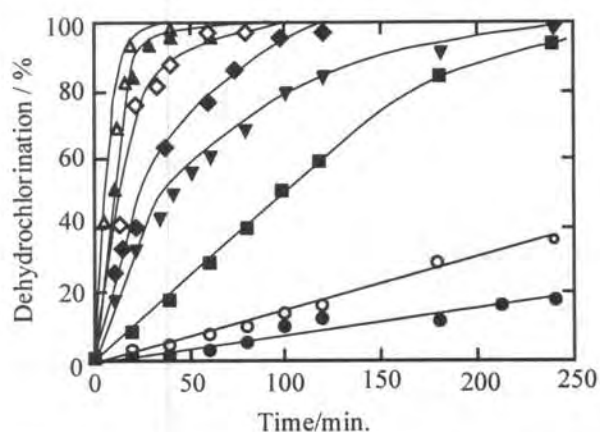


Figure 1 The degree of dehydrochlorination of PVC powder in N₂ atmosphere. Temperature/°C : ●200, ○220, ■240, ▼260, ◆280, ◇300, ▲350, △400

could be arranged by the zero order reaction in the range of low degree at all temperatures. Arrhenius plot of the apparent rate constants are shown in Figure 2 including the results of previous thermal dehydrochlorination in inert gases. The plot is clear straight line independent on experimental conditions at between 80 and 280 °C. The activation energies of these temperature range was 27.8 kcal/mol. This result indicates that the dehydrochlorination is controlled by chemical reaction.

But the slope of the straight line decreased rapidly higher temperature than 300°C and obtained the activation energy was 4.1 kcal/mol. According to the value, it is considered that the dehydrochlorination is controlled by the heat conduction rate.

On the other hand, the dehydrochlorination rate was arranged the range (high degree of dehydrochlorination) over the degree arranged apparent zero order reaction by apparent first order reaction (Eq.(2)).

$$\frac{d(1-X')}{dt} = kt \quad (2)$$

where X' is defined the degree of dehydrochlorination over the plot which can be arranged by the zero order reaction, t is the reaction time. The first order plot was approximately straight, and then the activation energy is 14.1 kcal/mol between 200 - 300 °C (Figure 3). On the other hand, the activation energy between 300 - 400 °C was 3.6 kcal/mol.

These results indicate that the dehydrochlorination is controlled by the heat conduction rate at 300 °C or higher temperature in the same manner as the range of the lower degree of dehydrochlorination.

3.2 Chemical structure of the residues

The most important peculiarity in the thermal degradation of PVC is that both of the chemical structure and chemical composition change with proceeding dehydrochlorination. The FT-IR spectra of residues are shown in Figure 6. An intensity of signal assigned C-Cl stretching (690 cm^{-1}) was decreased and that assigned C-H bendings for aromatics ring ($750 - 900\text{ cm}^{-1}$) was increased with increasing the degree of dehydrochlorination. Also, C-H stretchings ($2900 - 3030\text{ cm}^{-1}$) was expanded and its intensities was increased. On the other hand, C=C-H stretching ($3000 - 3030\text{ cm}^{-1}$), C=C stretching (1600 cm^{-1}), C-H bending ($750 - 900\text{ cm}^{-1}$) of aromatic rings, such as aromatic and the other's structure, were observed, as C-H

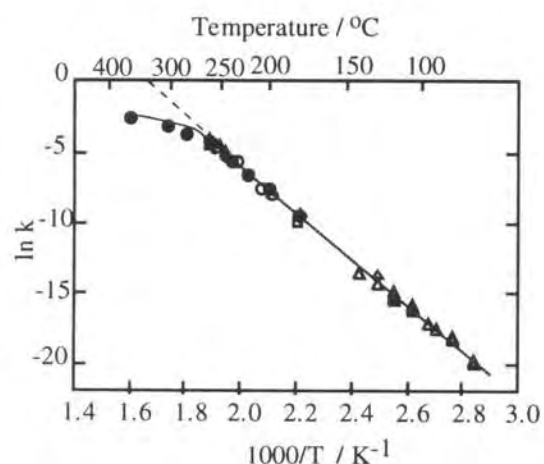


Figure 2 Arrhenius plot of the apparent zero order rate constants of dehydrochlorination of PVC. Comparison this work with previous data.

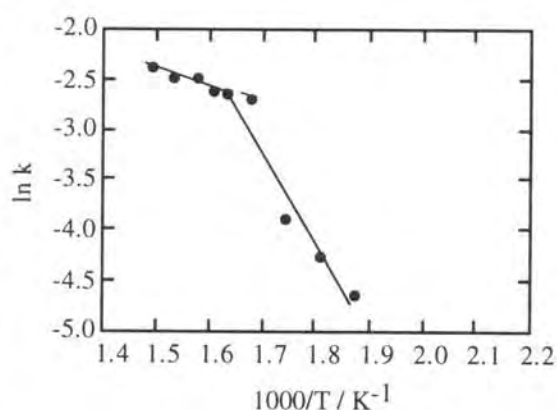


Figure 3 Arrhenius plot of apparent rate constants for the high degree of dehydrochlorination of PVC.

bending ($1200 - 1450 \text{ cm}^{-1}$) of aliphatic structure decreased with increasing the degree of dehydrochlorination. These results indicate that many types of C-H bonding are formed by the dehydrochlorination, since many types of structure are formed gradually by crosslinking and cyclization of polyenes.

Therefore, the hang of apparent rate from zero order to first order reaction with increasing the degree of dehydrochlorination seems to be caused by the change in the chemical structure of residue. It is well known that dehydrochlorination proceeds by zipper mechanism. The zipper mechanism is able to account for the zero order reaction of dehydrochlorination. On the other hand, the amount of Cl removed by the zipper mechanism is decreased with proceeding the dehydrochlorination, since the amount of isolated Cl in the structure of residue increases due to the crosslinking and cyclization is increased relatively. Thus, it is thought that the dehydrochlorination proceeds by first order reaction at high degree.

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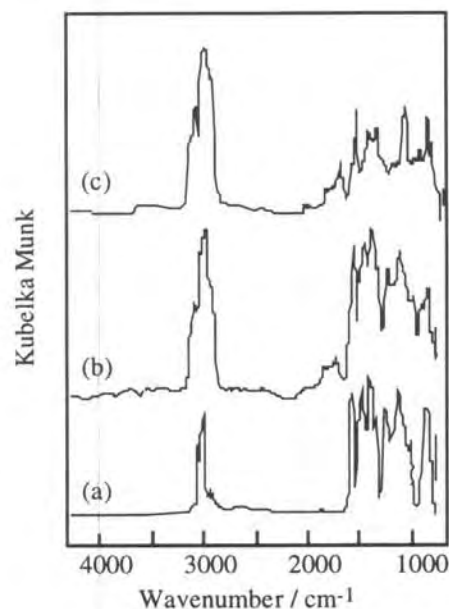


Figure 4 IR spectra of PVC residue at 260 °C.

(a) 0%(pure PVC powder), (b) : 21.8%, (c) 67.6%