Effect of Metal Compounds and Experimental Conditions on Distribution of Products from PVC Pyrolysis

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Effects of heating rate, gas flow rate, and type of metal compounds on the amount of hydrogen chloride, liquid, gas, and solid pyrolyzate obtained from the pyrolysis of poly(vinyl chloride) (PVC) were investigated. The pyrolysis experiments were carried out in both a thermogravimetric analysis (TGA) instrument and a fixed-bed reactor. Products from the fixed-bed reactor were collected and analyzed by using Fourier transform infrared spectroscopy (FTIR), gas chromatography-mass spectroscopy (GC-MS), titration technique, and gravimetry. It was found that heating rate in the TGA experiments did not affect the amount of released hydrogen chloride. However, the TGA profiles significantly changed with the rate. The onset of dehydrochlorination increased with the rate. In addition, as the heating rate was increased from 10 to 20°C/min, there was no solid residue left. The amount of liquid pyrolyzate obtained from the fixed-bed reactor can be either increased or decreased with the heating rate, depending on the gas flow rate and the actual residence time in the reactor. FTIR and GC-MS analysis indicated that the liquid pyrolyzates were mainly benzene, toluene, and styrene. By comparing the efficiency of various metal compounds in trapping the HCl, it was found that Ca(OH)2 was more efficient than Mg(OH)2, and that CaO was more efficient than MgO. These results are discussed in light of the reaction mechanism between HCl and the metal compounds.

KEY WORDS: Poly(vinyl chloride); pyrolysis; TGA; dehydrochlorination.

INTRODUCTION

Pyrolysis has been considered to be an alternative method of plastic recycling. In the pyrolysis process, organic material is decomposed at an elevated temperature in either an oxygen-free or low-oxygen atmosphere. When plastic such as poly(vinyl chloride) (PVC) is pyrolyzed, more than 50% of the initial weight is released as a form of HCl, which is considered to be corrosive and harmful. The dehydrochlorination is initiated by the scission of the Cl-C bond, resulting in a chlorine radical. Subsequently, the chlorine radical attacks the hydrogen atom in the polymer chains, leading to the formation of hydrogen chloride gas. It was believed that the degradation is related to the presence of some weak points along the PVC chains, such as the head-to-head configuration [1], allylic chlorine [2], and branching (tertiary chlorine) [3, 4]. The chlorine atoms on these positions are considered to be sites for the initiation of dehydrochlorination. This was confirmed by replacing labile chlorine with some stable ligands [5].

HCl may be, theoretically, condensed and reused. In practice, however, there exists today a great over-
abundance of HCl waste from many processes, such as TiO₂ plants, and thus there is no market for waste HCl. The HCl is usually transformed into NaCl or Cl₂ and subsequently utilized in relevant chemical processes. In Germany, HCl emitted from the incinerator is neutralized by caustic soda, and the resultant NaCl is used in the electrochemical process for generating chlorine and caustic soda [6]. Gupta et al. [7] studied the role of metal oxides in the pyrolysis of PVC through the use of thermogravimetric analysis (TGA). It was found that some metal oxides such as SnO₂, CuO, and Cu₂O promoted the PVC degradation. Kehat and co-workers [8] proposed a one-step process in which PVC is incinerated in the presence of CuO, producing CuCl, which can further be oxidized to chlorine and CuO. The chlorine can be reused in a PVC plant to reproduce new PVC, and CuO was recycled to the initial stage. In addition, there was a report [9] claiming that CuO increases the rate of formation of dioxins when PVC is incinerated at a temperature lower than 950°C. This, then, might be a drawback of the process.

Besides the HCl, some useful chemicals are generated from the pyrolysis of PVC. Scott [10] showed that fast pyrolysis of PVC produces approximately 56 wt% of HCl, 9.1 wt% of char, 6.3 wt% of liquid, and 28.6 wt% of hydrocarbon gases (including losses). Products such as liquids and gases are mainly aromatic hydrocarbon and its derivatives, which may be used as fuel or petrochemical feedstock. From a practical point of view, it would be desirable if we could control the released HCl and maximize the liquid pyrolyzate. In this study, we try to investigate the effect of PVC pyrolysis conditions such as heating rate and gas flow rate on the product distribution using both a TGA instrument and a fixed-bed reactor. In addition, the efficiency of various chemicals, including Mg(OH)₂, MgO, Ca(OH)₂, and CaO, in trapping the HCl was examined and compared.

EXPERIMENTAL

The PVC compound (B-0303CLA, K value = 54) was obtained from Thai Plastic and Chemicals Public Company Ltd. Thermal gravimetric analysis was performed by using a Perkin-Elmer (series 7) machine operating over the temperature range of 35 to 1500°C. Approximately 30 mg of sample was used. The experiments were conducted under nitrogen atmosphere and under various heating rates (5, 10, 20 and 100°C/min). All of the TGA experiments were repeated twice to ensure accurate results. For pyrolysis experiments carried out in a fixed-bed reactor, various metal compounds such as Ca(OH)₂, Mg(OH)₂, CaO, and MgO (general grade) were mixed with the PVC under three different conditions:

Condition 1: 0.4 mole of the metal compound (equivalent to the molar of HCl that could be obtained from 12 g of PVC) was mixed with PVC by using a two-roll mill operated at 135°C.
Condition 2: 0.4 mole of the metal compound was mixed with PVC by a simple dry blending.
Condition 3: an excess amount of the metal compound (1.0 mole) was mixed with PVC by a simple dry blending.

The pyrolysis experiment in a fixed-bed reactor was performed by heating the reactor containing approximately 12 g of PVC sample inside a furnace in a steam of nitrogen (see Fig. 1). The reactor was heated up to 700°C under two different heating rates (5 and 20°C/min) and two different gas flow rates (5 and 20 mL/min) and then the experiment was terminated. Volatile pyrolyzate was partly collected by passing through a series of condensers kept at 3°C. Uncondensed gases then passed through flasks containing NaOH aqueous solution to trap some HCl.

The pyrolysis products may be classified into three groups: solid residue, liquid condensate, and gaseous product. Chemical functionality of the liquid was analyzed by Fourier transform infrared spectroscopy (FTIR) using a Bio-Rad, FTS 1750 machine. The liquid was cast onto a ZnSe cell and then dried. In addition, gas chromatography-mass spectroscopy (GC-MS) (Varian, Saturn 2000 machine) was used to confirm the chemical structure of the liquid. A 30 m × 0.25 m CP-sil 8 CB column (Chrompack) was used. Helium was used as a carrier gas, and the sample was heated up to 450°C.

The efficiency of each metal compound in trapping the HCl was determined by dissolving the solid residue in distilled water to remove metal chloride. After that, the solution was filtrated and then dried at 100°C before weighing. The amount of metal chloride was calculated and related back to an equivalent mole of HCl. The efficiency was defined as follows:

\[ \text{Efficiency} \% = \left( \frac{\text{Mole of trapped HCl}}{\text{Mole of released HCl}} \right) \times 100 \]

RESULTS AND DISCUSSION

Figure 2 shows a typical TGA thermogram of PVC obtained from the pyrolysis under nitrogen atmosphere at a heating rate of 10°C/min. The weight-loss curve reveals two transitions. The first one involves a dehy-