Analysis of Two Stages Dehydrochlorination of Poly(vinyl chloride) Using TG-MS

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Degradation behavior of poly(vinyl chloride) (PVC) was analyzed by means of simultaneous thermogravimetry-mass spectrometry (TG-MS). Weight loss and the production behavior of hydrogen chloride and organic materials with PVC degradation was clearly divided into three stages at lower heating rate. Dehydrochlorination was occurred mainly in the first and second stages. Benzene was formed mainly in the first stage with dehydrochlorination.

Degradation behavior of PVC is worth studying in order to improve the dehydrochlorination process in the feedstock recycling of waste plastics. Knümann et al. identified the products formed in the degradation of PVC by means of TG-MS, and found the formation of benzene, besides hydrogen chloride, in the dehydrochlorination stage and various aromatic hydrocarbons at the polyene decomposition stage.[1] Moreover McNeill et al. monitored the PVC degradation by MS and confirmed the two stages of degradation from the formation of the main product.[2,3] In the past, the degradation of PVC has regarded as these two stages degradation, which consists of dehydrochlorination and decomposition of carbonaceous materials after the dehydrochlorination. Wu et al. and R. Miranda et al., however, regarded the first stage as comprising two reactions based on the weight loss in the degradation of PVC at low heating rate using TG.[4,5] Although various studies have reported, two dehydrochlorination stages have never been confirmed from the point of the formation behavior of the products in detail. In the present study, the degradation of PVC was discussed from both the weight loss and the formation behavior of the products measured by means of simultaneous TG-MS.

The PVC powder free from any additive (polymerization degree 1000 ± 40, particle diameter 0.1 mm) was used. Degradation behavior of PVC was analyzed by means of simultaneous TG-MS connected directly TG (Seiko Instruments TG/DTA 6200) and MS(Hewlett Packard 5973). The experimental apparatus is shown in Figure 1. PVC powder of 10 mg, spread as a thin layer at bottom of a platinum pan was put on a balance in TG at 100 ml/min of helium flow. After helium purged out a residual air, the degradation of PVC powder was conducted up to 650 °C at eight heating rates of 0.5, 1.0, 2.0, 4.0, 5.0, 10.0, 20.0 and 40.0 °C/min. The degradation products were introduced to the ion source of MS through the inactivated stainless capillary tube heated at 250°C to prevent condensation of the evolved products.

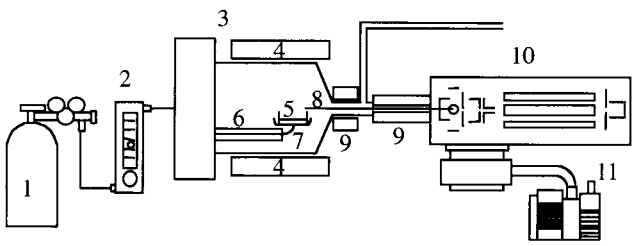

Figure 1. Experimental set up of the simultaneous thermogravimetry - mass spectrometry (TG-MS). [1:helium cylinder, 2:flowmeter, 3:TG, 4:furnace, 5:sample, 6:balance, 7:thermocouple, 8:inactivated capillary, 9:heater, 10:MS, 11:vacuum pump.]

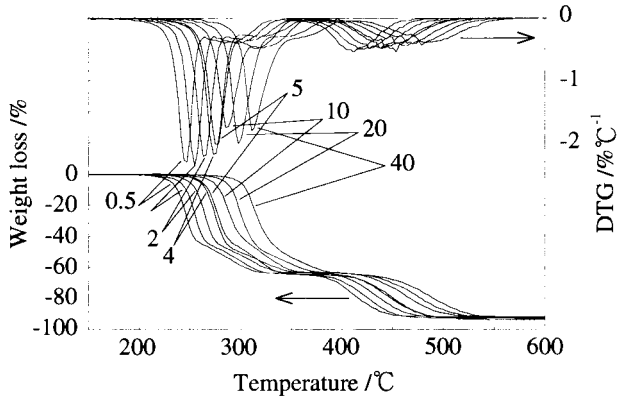

Figure 2. TG and DTG curves of PVC at heating rates of 0.5- 40 ℃/min.

Figure 2 shows the TG and DTG curves of PVC under helium as purge gas at different heating rates. The TG and DTG curves with lower heating rate are lower than or leftward to that with a higher heating rate. It is of interest to note that the degradation of PVC up to 400 °C is not just a simple. This can be seen from the inflectional point of TG curves at the fraction of about 41 – 45% under the lower heating rates under 4 °C/mim. This indicates that the degradation of PVC is divided into three stages, mainly first stage (weight loss ≦ 45%), second stage (weight loss ≦ 65%) and third stage (weight loss > 65%).

Signals of *m/z* = 36, 78, 92, 104, 106, 116, 118, 120, and 142 were observed in the PVC degradation up to 650 °C under helium. These signals correspond to the molecular ion peaks of hydrogen chloride (36), benzene (78), toluene (92), styrene (104), xylene or ethylbenzene (106), indene (116), indane (118), propylbenzene or ethylmethylbenzene (120), naphthalene (128) and methylnaphthalene (142). The organochlorine compounds were not detected due to extremely small quantities in this TG-MS system. The TG-MS selected ion chromatogram of the major products in the degradation of PVC at heating rate of 4 °C/min is shown in Figure 3. The formation of HCl started at 220 °C and finished nearly at 370 °C, and had two peaks of 280 °C and 320 °C during the dehydrochlorination. This result supports that the dehydrochlorination proceeds by two stage reactions. The two satge production of HCl is caused by different type bond of PVC like a both of Head-head and Head-tail.

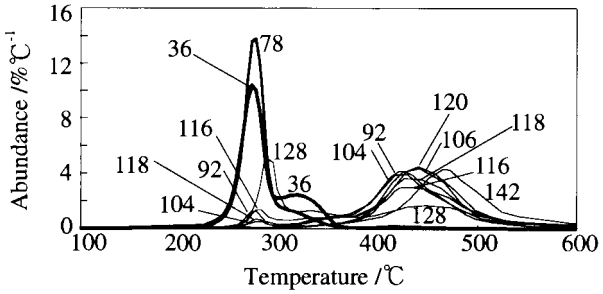

Figure 3. Selected Ion Chromatogram of the major products in the thermal degradation of PVC at 4 ℃/min. [36:hydrogen chloride, 78:benzene, 92:toluene, 104:styrene, 106:xylene or ethylbenzene, 116:indene, 118:indan, 120:propylbenzene or ethylmethylbenzene, 128:naphthalene, 142:methylnaphthalene.]

Benzene was formed during the first dehydrochlorination stage, but hardly in the second dehydrochlorination stage. This supported the fragmentary results of Bockhorn and Blazso et al. by TG-MS and Pyrolysis-MS.[6,7] It is well known that aromatic compounds such as benzene are formed due to break down of polyene chains by bimolecular addition and coiling. Therefore, it is considered that polyene decomposition occurs in the first dehydrochlorination stage. On the other hand, naphthalene forming stared at the same temperature that the second dehydrochlorination stage started, and its rate reached maximum 290 °C.

The other aromatic compounds were formed mainly after the dehydrochlorination stages over 370 °C gave peaks between 420 and 470 °C, whereas have no strong peak during the dehydrochlorination stages. This result indicates the aromatic compounds except benzene and naphthalene are produced by breakdown of polyene-aromatic network.

The result of present paper clearly showed that the dehydrochlorination of PVC up to 650 °C under He was divided into three degradation stages, namely two dehydrochlorinations and a breakdown of polyene-aromatic network. In the first stage, benzene was formed with HCl. In the second stage, dehydrochlorination occurred predominately, benzene and naphthalene were produced a little. In the third stage, breakdown of polyene-aromatic network occurred and various aromatic hydrocarbons expect benzene formed predominately.

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