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Vinyl Chloride Formation from the Thermal Degradation of Poly(Vinyl Chloride)

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The volatile products from the thermal degradation of poly(vinyl chloride) (PVC) resins and compounds are shown to contain trace amounts of vinyl chloride. Data presented show the effect of temperature and resin type on the amount of vinyl chloride formed. At the maximum temperatures involved in PVC processing which may reach 210°C, vinyl chloride monomer (VCM) evolution amounts to less than 1 ppm (resin basis). A technique employing a thermogravimetric balance and charcoal adsorption of volatiles is described for studying thermal degradation of PVC. The volatiles are analyzed for vinyl chloride by gas chromatography. Peak identity was confirmed by mass spectrometry.

INTRODUCTION

Numerous studies and surveys have been published describing the thermal degradation and pyrolysis products of poly(vinyl chloride) (PVC). These studies have shown that at elevated temperatures essentially quantitative dehydrochlorination of PVC occurs, resulting in the formation of a complex mixture of aromatic and aliphatic hydrocarbons with benzene being the largest single component (1-8). Stromberg, *et al.* (1) studied the decomposition of PVC under vacuum at temperatures up to 400°C and measured the variations in the decomposition products as a function of temperature. They did not indicate the formation of any vinyl chloride monomer (VCM) under these conditions. Boettner, *et al.* (2) investigated the thermal degradation of PVC in air up to 600°C. Using infrared spectroscopy and gas chromatography-mass spectroscopy, they identified approximately 50 volatile degradation products and measured the rate of formation of the major products as a function of temperature. Their data indicate that up to 600 ppm of VCM is formed from PVC homopolymer and up to 3000 ppm from PVC compounds. Although no mention is made of residual VCM in the polymer, the bulk of the VCM was detected in the 280-430°C range and it is inferred that VCM is produced during the thermal decomposition. Woolley (3) reported low levels of VCM in PVC pyrolysis products but did not measure residual VCM, and it is not clear whether any VCM was actually formed during the decomposition. Lewis (4) has recently reported degradation studies of a homopolymer having a residual VCM content of < 0.5 ppm and found a maximum VCM formation of 35 ppm at 350°C.

The recent findings (9) of carcinogenicity on prolonged exposure of test animals to elevated concentrations of vinyl chloride in the air and of cases of angiosarcoma in vinyl chloride workers have caused serious concern about the effects on workers involved in all phases of PVC manufacture and fabrication. Although present day manufacturing processes have reduced the residual VCM content of PVC resins and compounds to very low levels (10), the possibility of forming VCM by degradation of the polymer during calendering, extrusion, and thermoforming operations is still a cause of concern.

There is very little likelihood of VCM formation during thermoforming of PVC for food packaging application since this operation is carried out under mild conditions(90-120°C for a few seconds). It has been demonstrated previously that no detectable VCM is formed in up to 1 h exposure at 130°C, using an analytical method capable of detecting 1 part per billion of VCM (10).

During calendering and extrusion operations, however, temperatures may reach the 175-210°C range for brief time periods. We know of no published information involving VCM formation under these conditions. Our present work involved the investigation of the thermal degradation of PVC over the 130-500°C temperature range with special emphasis on VCM formation at 210°C, the upper limit used in PVC fabrication.

EXPERIMENTAL

Thermal degradation studies were carried out using a duPont Model 950 thermal balance which provided a convenient method for accurately controlling the temperature and heating rates. Samples of 80-100 mg were placed in a platinum foil boat suspended on the thermal balance sample holder. The furnace tube surrounding

the sample was swept with clean air at 60 ml/min. Prior to starting the thermal degradation run, the sample was held at 130°C for 30 min with air flowing in the furnace tube. This procedure has been demonstrated to completely remove all residual VCM in the sample without causing any decomposition (10). After this conditioning period, the exit side of the furnace was fitted with a short glass U-tube immersed in a cracked ice bath. This served to cool the sweep gas prior to passing it through a standard NIOSH approved, charcoal personnel monitoring tube (SKC #226-01) to adsorb any VCM resulting from the degradation of the sample.

At the completion of the run the contents of the charcoal tube were transferred to a vial capped with a Teflon® lined septum (SKC 226-02-100). The vial was held in an acetone-dry ice bath and 1 ml of carbon disulfide injected through the septum. The vials were then allowed to stand at room temperature for 30 min to desorb the VCM.

Gas Chromatography

A Perkin Elmer Model 3920 gas chromatograph equipped with dual flame ionization detectors was used in this work. In view of the large number of products formed during the thermal degradation of PVC, and the additional degradation products formed from additives incorporated in PVC compounds, a variety of columns were screened to obtain optimum separation of the VCM peak. A combination column of a 10 ft × 1/8 in. Porapak P (Waters Associates) followed by a 10 in. × 1/8 in. Chromosorb 104 (Johns Manville) was finally selected for the separation. This column operated at 85°C with a helium carrier gas flow of 25 ml/min gave good separation of the VCM peak (retention time—6 min).

Initially, in order to definitely establish the identity of the "VCM" peak, exposed charcoal tubes were submitted to a commercial laboratory (11). Using the same GC column, samples of the carbon disulfide solutions were injected into a gas chromatograph-mass spectrometer instrument. Mass spectrometer scans made at three points on the VCM peak (peak maximum and leading and trailing portions) identified the peak as being entirely VCM. The VCM peak from the thermal degradation of certain PVC compounds prepared with sulfur-containing stabilizers, however, showed the presence of sulfur dioxide. This interference was eliminated by placing a 2-in. tube packed with Mallcosorb (Mallinckrodt Chemical Works) immediately before the carbon adsorption tube. The Mallcosorb tube was shown to have no effect on VCM recovery by passing known amounts of VCM through the tube and analyzing the effluent gas.

Ten microliter aliquots of the carbon disulfide solution were injected into the gas chromatograph. Peak areas were determined using a Spectra-Physics Model 6300 digital integrator. The VCM produced was calculated by comparing the VCM peak area of the sample to the areas produced by injecting known gas standards (Alltech Associates). The minimum amount of VCM which could be detected was 0.1 nanogram, equivalent to 0.1 ppm of VCM from the 100 mg resin sample.

Thermal Degradation

Initial studies involved thermal degradation of PVC over the 130 to 500°C range using a heating rate of 10°C/min. A variety of PVC resins from different producers were tested for total VCM evolution over this temperature range to determine if resin type or manufacturing source has any effect on the amount of VCM produced. A few commercial compounds were similarly tested to determine the effect of stabilizers and other additives on VCM evolution.

Thermal Degradation at PVC Fabrication Temperatures

In order to determine if any exposure danger exists for workers involved in PVC fabrication operations, a series of polymers, compounds and PVC sheets were tested for VCM formation during 5 and 30 min heating periods at 210°C the maximum temperature which would be employed in PVC processing.

Effect of Temperature on VCM Formation

VCM formation as a function of temperature was determined on a homopolymer sample over the range of 200-450°C at a heating rate of 3°/min. The charcoal tubes were changed at 25° intervals during the heating cycle and analyzed individually for VCM content. The corresponding thermogravimetric analysis (TGA) curve was recorded at the same time to provide a comparison of weight loss with VCM formation.

RESULTS

The total amounts of VCM evolved from the thermal decomposition of a variety of PVC homopolymers and PVC-PVAC copolymers are listed in *Table 1*. Samples are included from six different producers. A consistently low level of VCM amounting to 15-30 ppm (based on

Table 1. VCM Formation from Thermal Degradation of PVC (130-500°C)

Resin	VCM, ppm (resin basis)
Homopolymers	
Suspension low mol wt	19
Suspension low mol wt	23
Suspension medium mol wt	22
Suspension high mol wt	18
Suspension high mol wt	20
Dispersion	21
Dispersion	20
Dispersion	19
Dispersion	16
Dispersion	22
Dispersion	19
Blending	19
Blending	15
Blending	31
Solution Polym.	21
Copolymers	
Type 1	20
Type 2	25
Type 3	20

resin) was found in the volatile decomposition products from all of the samples tested, regardless of resin type or manufacturing source. To insure against a possible catalytic effect from the platinum boat, two homopolymer and one copolymer samples were run using a glass boat. The levels of VCM produced were identical to those obtained using the platinum boat.

Results obtained from the degradation of typical PVC compounds containing the most commonly used commercial stabilizers are shown in *Table 2*. Again, low levels of VCM were found for all samples, indicating that the presence of stabilizers and other additives in the compounds does not inhibit the formation of VCM.

The effect of temperature on VCM formation from homopolymer is shown in *Table 3* and in *Fig. 1*. Programming a 100 mg sample from 200 to 450°C at 3°/min resulted in the formation of a total of 23.2 ppm of VCM, the major portion being generated in the 275-350° region. The corresponding weight loss curve shows that dehydrochlorination occurs most rapidly in the 250-275°C temperature interval. During this period only 2.3 ppm of VCM is formed. Under the conditions employed in these studies, the major amount of VCM is formed after dehydrochlorination is essentially complete, leaving a dark-colored residue.

Programming the same homopolymer at 10°/min and finishing with a 30 min hold at 450°C, also resulted in the formation of 23 ppm of VCM.

A primary objective of this study was the determination of the levels of VCM to be expected at PVC fabrication temperatures. This was carried out by holding samples at 210°C, the upper limit of the fabrication temperature range, for periods of 5 and 30 min. As shown in *Table 4*, only traces of VCM are formed under these conditions amounting to a maximum of 0.5 ppm (resin basis) after 5 min exposure and a maximum of 1.2 ppm after 30 min exposure. This is particularly significant since it demonstrates that workers involved in PVC fabrication are not exposed to dangerous concentrations of VCM, and that VCM levels in fabrication areas are well below the limits established by OSHA and EPA standards.

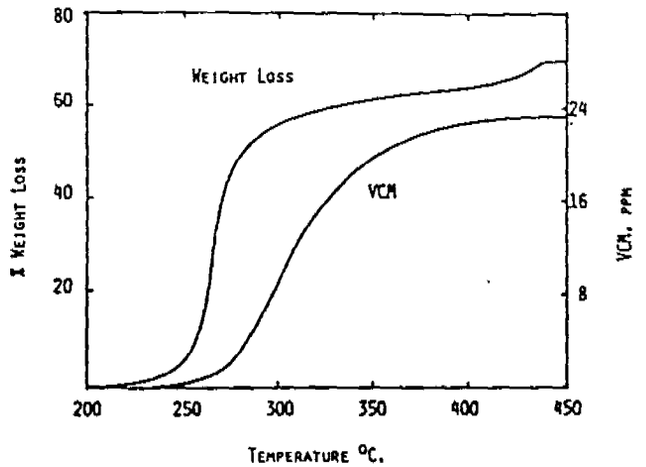

Fig. 1. PVC degradation and VCM formation as a function of temperature.

Table 2. Formation of VCM from Degradation of PVC Compounds Heated from 130 to 500°C at 10°C/min

Compound type	Stabilizer type	VCM, ppm (compound basis)
Filled flexible	Pb	27
Filled rigid	Pb	13
Flexible	Unknown	40
Flexible	Butyl tin	27
Flexible	Unknown	27
Flexible	Ba, Cd, Zn, P	52

Table 3. Effect of Temperature on VCM Formation from Homopolymer

Temperature, °C	Total VCM formed, ppm (resin basis)	Weight loss, percent by weight
200	N.D.	N.D.
225	N.D.	0.5
250	N.D.	5
275	2.3	46
300	8.6	57
325	15.4	60
350	19.4	62
375	21.4	63
400	22.4	64
425	23.2	66
450	23.2	72

Sample size = 100 mg.
Temperature programming = 3°/min.
N.D. = none detected, < 0.1 ppm.

Table 4. Vinyl Chloride Formation at PVC Fabrication Temperature (210°C)

Sample	VCM, ppm (resin basis) 5 Minute heating	30 Minute heating
Homopolymers		
Suspension Low Mol. Wt.	N.D.	0.3
Suspension Medium Mol. Wt.	N.D.	0.4
Suspension Medium Mol. Wt.	N.D.	0.4
Suspension High Mol. Wt.	N.D.	0.3
Blending	N.D.	0.5
Blending	0.5	1.2
Dispersion	N.D.	0.2
Copolymers		
Type 1	N.D.	0.1
Type 2	N.D.	0.3
Films		
Flexible	N.D.	N.D.
Flexible	N.D.	N.D.
Rigid	N.D.	N.D.
Rigid	N.D.	N.D.
Flexible	N.D.	N.D.
Compounds		
Flexible	N.D.	0.1
Flexible	N.D.	0.1
Filled flexible	N.D.	N.D.
Rigid	N.D.	N.D.

N.D. = none detected, < 0.1 ppm.

The amounts of VCM detected during thermal degradation of PVC resins and compounds in this study are in good agreement with those published by Lewis (3).

A recent paper by Hoffman, *et al.* (12) describes the detection and determination of low nanogram levels of VCM in the smoke from tobacco. Their data suggest that the total inorganic chloride in tobacco is the determining factor for the amount of VCM in the smoke, the necessary organic radical being generated by the burning of the tobacco products. A similar mechanism may account for the low levels of VCM observed in our work.

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