Oxidative Thermal Decomposition of Poly(vinyl Chloride) Compositions

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Synopsis

"Pure" poly(vinyl chloride) resin and four compositions containing poly(vinyl chloride) were subjected to oxidative thermal degradation in air at ~400°C both in a quiescent and a flow system. The volatiles formed were identified and quantitatively determined on a gram-per-gram basis. Hydrogen chloride was the main product found. The nature and relative concentration of the produced organic chlorinated species appeared to be dependent not only on the poly(vinyl chloride) constituent but also on the other ingredients. All the compositions contained phthalate ester plasticizers. In the dynamic system, these distilled largely unchanged, whereas under static conditions transformation into phthalic anhydride occurred.

INTRODUCTION

Poly(vinyl chloride) compositions are widely employed, notably in underground mining operations, owing to their flame resistance and low cost. These applications, among others, include conveyor belts, hose conduits, ventilation pipe, and brattice cloth. In the latter case, poly(vinyl chloride) is usually employed as a laminate in conjunction with nylon or another fiber which provides the strength and tear resistance required for the given end use. Thermal degradations of poly(vinyl chloride) resins have been studied very widely both in inert and oxidizing media.[1-12] The current investigation was undertaken with the specific aim to determine quantitatively, both under quiescent and dynamic conditions, the type of products formed on thermal oxidative degradation (in the absence of combustion) of poly(vinyl chloride) compositions used specifically in mines.

EXPERIMENTAL

The samples tested are listed in Table I. The quiescent investigations were conducted using a 2000-ml calibrated sealed volume which included a bulb and a fingerlike projection wherein the sample was placed. The system was filled with air at pressure somewhat below 1 atm (usually 400 mm), and the sample was heated at 370°C for 30 min by immersing the finger in a preheated metal bath. After cooling to room temperature, the

TABLE I
List of PVC Compositions Studied

Material	Material description/manufacturer
Poly(vinyl chloride) "pure" resin-PVC	poly(vinyl chloride)resin/U.S. rubber
Poly(vinyl chloride)– nylon composition-6A	brattice cloth #1800y; nylon scrim, PVC layer/C. R. Daniels
Poly(vinyl chloride) composition-7A	hose conduit, O'Koseal 200/ O'Konite Cable (subsidiary of LTV)
Poly(vinyl chloride)– nylon composition-13A	brattice cloth, nylon-reinforced PVC/ Griffolyn
Poly(vinyl chloride)–nylon composition-9B	brattice cloth, nylon-reinforced PVC/ Johnston-Morehouse-Dickey

TABLE II
Experimental Data for Sealed-Tube Degradations of PVC Compositions

Sample	Sample wt, mg	Residue, %[a]	Oxygen consumed		Total volatiles, %[c]
			mg	%[b]	
PVC	611	32.9	46.1	12.3	88.1
6A	637	38.1	35.9	9.5	43.7
13A	628	36.8	25.4	4.0	63.4
7A	632	35.4	16.1	4.3	66.7
9B	625	30.1	52.2	14.2	67.1

[a] Per cent of weight of starting material; this is only the solid, removable portion of the residue and does not include the tars and oils deposited on the sides of the tube.

[b] Per cent of oxygen available.

[c] Per cent of total products expected based on sample weight loss and oxygen consumed.

liquid nitrogen volatiles (O_2, N_2, CO, CH_4) were collected in a Sprengel pump, measured, and determined by mass spectrometry. The room-temperature volatile $-196°C$ condensibles were fractionated in vacuo through traps held at $-23°$, $-78°$, and $-196°C$. Each of the fractions was measured and weighed and then subjected to infrared and mass spectroscopy, gas chromatography (using 8 ft $\times$ $1/8$ in. stainless steel Porapak Q column programmed from $50°$ to $220°C$ at $8°C$/min employing thermal conductivity detector), and wet analysis (for hydrogen chloride). The solid carbonaceous residue left in the finger of the bulb was removed and weighed, whereas the involatile oils and tars deposited on the wall were examined by infrared spectroscopy. The experimental details are summarized in Table II.

For the dynamic studies, a stagnation burner arrangement previously described[13,14] was employed. In the past, the burner was used as an open system; in the current work all the outlets but one were closed. The

TABLE III
Experimental Data for Stagnation Burner Degradations of PVC Compositions

Sample	Sample wt, mg	Residue		Condensible volatiles		RT[b] involatiles	
		mg	%[a]	mg	%[a]	mg	%[a]
PVC	968	344	35.5	744.0	76.9	64.6	6.7
6A	1035	373	36.0	475.3	45.9	192.2	18.6
13A	1038	363	34.9	550.4	53.0	159.2	15.3
7A	1230	433	35.2	401.6	32.7	174.4	14.2
9B	1001	265	26.5	329.1	32.8	209.2	20.9

[a] Per cent of weight of starting material.
[b] Room temperature.

open outlet was connected to three traps: the first at $-78°C$; the other two, at $-196°C$. The cooling was sufficiently effective to condense most of the air flowing over the sample. Both the air and heating block were at $400°C$; the sample's residence in the stagnation burner was 15 min. After the completion of the experiment, the traps were evacuated while cooling in liquid nitrogen. Subsequently, the room temperature volatiles were fractionated and analyzed in the same manner as the products from the quiescent degradation, whereas the involatiles (oils) were examined by infrared spectroscopy. The experimental details are given in Table III.

RESULTS AND DISCUSSION

In Tables IV and V are compiled the identified and quantitated products of the degradations performed on the poly(vinyl chloride) compositions given in Table I. Comparing Tables IV and V, it is apparent that no large differences exist between the product mix obtained under quiescent and dynamic conditions. (The lower values of hydrogen chloride found in the stagnation burner tests are due to partial loss of the hydrogen chloride caused by the large metal surface area of this apparatus.) It should be mentioned that once glow or combustion occurs, the product mix changes drastically as was evidenced in the neoprene investigations.[15] The vacuum line fractionation was found very effective. The $-196°C$ fraction consisted mainly of hydrogen chloride; in the case of the "pure" resin, it amounted to above 90%. The total hydrogen chloride evolved amounted to 94.4% of theory. The $-78°C$ fractions usually consisted of organic materials admixed with the aqueous solution of hydrogen chloride. In the case of the "pure" resin, the major organic component was benzene, with just traces of other materials. However, the other compositions afforded a variety of products.

Thus, in the case of material 6A, benzene no longer was the main hydrocarbon product; actually, the amount found was lower than would be deduced from the evolved hydrogen chloride assuming the latter to be derived from the poly(vinyl chloride) component only. On the other

TABLE IV
Decompositions Products of PVC Compositions (Sealed-Tube Studies)

Products	PVC, mg/g	6A, mg/g	13A, mg/g	7A, mg/g	9B, mg/g
CO	19.7	4.84	5.02	5.65	8.91
CH$_4$	0.80	0.20	0.54	0.55	0.85
HCl	550.6	174.2	253.7	263.5	205.8
CO$_2$	12.1	29.1	18.1	19.0	32.4
SO$_2$	0.38	0.25	0.37	—	—
COS	—	0.16	—	—	—
CS$_2$	—	—	—	0.36	—
C$_x$H$_y$[a]	1.51	1.71	6.14	2.87	2.18
Isoprene	—	—	—	—	0.66
C$_6$H$_6$	47.5	5.12	26.7	25.4	35.8
C$_6$H$_{12}$	—	1.05	—	—	—
C$_6$H$_5$CH$_3$	0.61	0.57	1.51	0.84	0.42
C$_6$H$_4$(CH$_3$)$_2$	0.08	0.03	0.08	0.11	0.02
CH$_3$Cl	0.44	3.75	3.19	T	0.72
C$_2$H$_3$Cl	0.05	—	—	0.05	—
C$_2$H$_5$Cl	0.03	1.10	20.7	T	0.34
(CH$_2$Cl)$_2$	0.10	—	0.81	—	—
C$_4$H$_5$Cl	0.56	0.02	0.19	—	—
C$_6$H$_{13}$Cl	0.10	0.16	—	0.11	0.35
C$_6$H$_5$CH$_2$Cl	0.03	—	—	T	—
CH$_3$OH	0.03	0.03	0.05	0.06	0.05
C$_2$H$_5$OH	0.02	T	1.10	0.28	4.88
n-C$_3$H$_7$OH	0.03	0.23	0.43	0.02	1.18
i-C$_3$H$_7$OH	0.07	—	T	0.08	0.40
HCHO	?	?	?	?	?
CH$_3$CHO	0.13	T	0.02	0.09	—
(CH$_3$)$_2$CO	0.07	0.64	0.03	1.44	2.82
HCOOH	—	T	—	—	0.16
CH$_3$COOH	0.06	0.23	0.30	0.03	0.72

[a] C$_x$H$_y$ denotes hydrocarbons C$_2$ through C$_4$.

hand, methyl chloride produced was about an order of magnitude higher than in the "pure" poly(vinyl chloride). The mass-spectral analyses of the $-78°$C fraction showed mainly the presence of a C$_6$ skeleton derived compounds both cyclic and linear, pointing to nylon 66 as the component of this poly(vinyl chloride)–nylon composition. It should be added that under the somewhat more drastic stagnation burner conditions, a portion of the C$_6$ compounds was transformed into benzene (compare Tables IV and V).

Based on mass-spectral evidence, materials such as tolualdehyde (m/e = 119, 120) appear to have been also produced together with higher aromatics (naphthalenes), C$_3$- and C$_4$-substituted benzenes, and possibly chlorinated aromatics (m/e = 155, 140, 126, 120, 119, 118). The m/e 126 peak has been ascribed to benzyl chloride. This compound was also found by Boettner et al.[8] on thermal oxidative degradation of poly(vinyl chloride)

TABLE V
Decomposition Products of PVC Compositions (Stagnation Burner Studies)

Products	PVC, mg/g	6A, mg/g	13A, mg/g	7A, mg/g	9B, mg/g
HCl	421.4	168.6	184.4	146.9	155.4
CO_2	49.2	23.2	22.6	31.6	24.0
SO_2	0.43	0.12	0.40	—	—
COS	—	0.11	—	—	—
C_xH_y[a]	1.92	0.65	3.03	0.90	0.33
C_6H_6	39.4	16.0	33.3	17.6	32.0
C_6H_{12}	—	0.73	—	—	—
$C_6H_5CH_3$	0.40	0.48	0.02	0.09	0.50
$C_6H_4(CH_3)_2$	0.20	0.02	T	T	T
CH_3Cl	0.36	3.31	2.49	0.51	0.13
C_2H_3Cl	—	0.16	0.15	—	—
C_2H_5Cl	T	0.50	12.4	0.24	0.03
$C_6H_{13}Cl$	—	—	0.05	—	2.11
$C_6H_5CH_2Cl$	—	0.01	—	—	—
CH_3OH	0.01	0.03	0.04	0.03	0.04
C_2H_5OH	—	T	7.22	0.38	0.05
$n\text{-}C_3H_7OH$	T	0.04	0.48	T	T
$i\text{-}C_3H_7OH$	0.01	0.02	0.06	0.01	T
HCHO	?	?	?	?	?
CH_3CHO	0.16	—	0.77	—	—
$(CH_3)_2CO$	0.01	0.15	0.59	1.26	0.02
HCOOH	0.10	—	—	—	—
CH_3COOH	0.01	0.04	0.47	0.38	0.14
$HCOOC_2H_5$	—	—	0.56	0.02	—
4-Methylcyclohexanone	—	—	—	—	2.08

[a] C_xH_y denotes hydrocarbons C_2 through C_4.

compositions. All these materials seemed to be present in very small quantities, at least in the room-temperature volatiles. The $-23°C$ fractions consisted mainly of water admixed with alcohols and organic acids.

The oily involatiles (with the exception of the "pure" resin, where hardly any were present) were found to consist, in the quiescent system, of a mixture of phthalate esters and phthalic anhydride; whereas in the dynamic studies, mainly the phthalate esters were observed. This would tend to indicate that under the flow conditions, the plasticizer evaporates mostly unchanged and is immediately swept out of the reaction zone; whereas in the quiescent system, being exposed to heat treatment for a considerable period of time, it is transformed into phthalic anhydride and other products.

Comparing the data given in Tables IV and V for the various poly(vinyl chloride) compositions, it would appear that production of chlorinated organic species is not necessarily dependent upon the material's poly(vinyl chloride) content (assuming that hydrogen chloride is derived only from the poly(vinyl chloride) component and that no other chlorinated compounds are present). This is in particular evident in material 7A (compare

ethyl chloride content), materials 6A and 13A (compare methyl chloride content), and material 9B (compare chlorohexane content). Consequently the data obtained from a given "pure" composition insofar as the nature and relative product concentration are concerned can be used as a guideline but not as an absolute measure regarding the expected production of individual species from a composite.

Controversy exists regarding the formation of hydrogen cyanide from polyamides. Based on the degradations of nylon 610 in air at ca. 550°C conducted by Thinius et al.,[3] the products formed are carbon monoxide, carbon dioxide, saturated and unsaturated hydrocarbons, acetaldehyde, ammonia, butylamine, and hexamethylenediamine. No hydrogen cyanide was detected using the sensitive Draeger tubes. Similar findings were reported by Hagen.[4] The publication by Oettel and Hofman[11] also stresses that polyamides do not evolve hydrogen cyanide below 400°C. Only on burning (above 500°C) was HCN observed.

On the other hand, Gross et al.,[7] Dufour,[16] and Bott[17] do report hydrogen cyanide formation from polyamides. We have observed hydrogen cyanide in the −196°C fraction of materials 6A and 9B as shown by the infrared absorption at 14.05 μ. The values based on infrared absorption in case of material 6A are ~0.3 mg/g for the sealed tube studies and ~0.4 mg/g for the stagnation burner investigation; the respective figures for material 9B are ~0.7 and 0.2 mg/g. Both of these compositions contain nylon. The surprising aspect of the current investigation is the lack of detection of amines among the volatiles. On the other hand, in the presence of hydrogen chloride, the formation of amine salts would be expected which would remain in the involatile oils and tars.

In none of the analyses have we been able to identify unequivocally the presence of formaldehyde and acrolein. Yet, based on definite identification of formic acid and its esters and the observation of m/e 30 in the mass spectra (assuming that this is not derived from amines, NO, or N_2O), we feel certain that formaldehyde is formed. Isolation of the C_3 alcohols and of acetone would indicate that acrolein is also produced. In a number of instances, we have detected sulfur dioxide, which originates most likely from sulfur-containing antioxidants and/or polymerization initiators.

For the poly(vinyl chloride) compositions, the main toxic species at the temperatures involved in the current investigations is undoubtedly hydrogen chloride; however, other components which cannot be ignored are benzene, phthalates, aldehydes, and carbon monoxide. The latter, as can be seen from the sealed tube data, does not really pose a great danger. Based on TLV[18] values, benzene (TLV, 25 ppm), which is produced in a larger quantity than carbon monoxide(TLV, 50 ppm), has to be rated as a greater hazard.

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