The Effects Of Fillers On The Dehydrochlorination And Smoke Properties Of Rigid PVC

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ABSTRACT

In the light of recent health and environmental issues, halogen containing polymers have come under intense scrutiny. In particular, polyvinyl chloride (PVC) has been a matter of public concern. The emission of hydrochloric acid gas (HCl) has been indicted due to its corrosivity and potential toxicity. The use of fillers and additives are being considered as potential acid gas scavengers. Alumina trihydrate (ATH) and Calcium carbonate ($CaCO_3$) have long been used as fillers for PVC, as have been a variety of clays.

This paper offers acid gas evolution and smoke data for the typical non-halogen flame retardant fillers, $CaCO_3$, ATH and Magnesium hydroxide ($Mg(OH)_2$), as well as a new developmental filler, HYSAFE™ 150, compounded in a rigid PVC pipe formulation. Specifically, the effects of loading upon induction time, rate of dehydrochlorination and smoke properties, as measured in the NBS Smoke Chamber, are reported.

INTRODUCTION

The rapidly growing use of plastic components has challenged formulators and compounders to reduce the overall fire hazard associated with these materials. The scientific community is currently responding to this pressure with new, more advanced testing procedures[1] and a plethora of polymer additives. A common approach to flame retardancy has been to interfere with the combustion process by introducing volatile gaseous components directly into the burning matrix. The organo-halogen compounds act synergistically with antimony oxide to impart flame retardancy in this manner. Recent health and environmental issues have caused many halogen/antimony systems to come under intense scrutiny.[2]

An alternate method of imparting flame retardancy to a polymer is by loading the resin system with a filler designed to release fire suppressing volatiles during the pyrolysis process. These volatiles serve to interrupt the burning process. Alumina trihydrate functions in this way and has gained acceptance as a flame retardant filler.[3] The degradation temperature of ATH (~400°F), however, has precluded its use in many applications that require higher processing or end-use temperatures.

Recently, a new developmental filler, HYSAFE 150, was introduced as a flame retardant additive for thermosets requiring high end-use temperatures.[4] An extension of that work has led to the development of a new line of non-halogenated, inorganic fillers. When these materials are incorporated into thermoset resins they afford filled systems that are lower in smoke properties, and are flame retardant in nature. An advantage of the HYSAFE fillers is their ability to withstand higher processing and end-use temperatures than ATH. A comparison of the thermal gravimetric analysis curves for HYSAFE, $Mg(OH)_2$ and ATH (Figure 1) illustrates the difference in thermal stability of the three fillers. This work is aimed at evaluating the filler interaction with rigid PVC which could change or alter the evolution of HCl and smoke properties.

Many methods for the analysis of HCl from PVC are available,[6,7,11] however, a modification of the method by Chan[8] was used. Studies on the dehydrochlorination of PVC[7,9] and the dehydrohalogenation of other compounds[10] clearly indicate that a kinetic approach to the filler interaction with PVC is sound and the comparison of induction times and rate constants adequately describe the thermal stability of halogenated polymers.

DEVELOPMENTAL

1. Raw Materials

Four types of inorganic fillers were evaluated in this study. Three of the fillers are commercially available, and the remaining one represents a developmental product currently being offered to the plastics industry.[5] The commercially available fillers are calcium carbonate, alumina trihydrate and magnesium hydroxide. The developmental filler is inorganic in nature, whose chemistry is based on aluminum. A comparison of some key physical properties of the fillers used in this work appears in Table 1.

The resin chosen for this work consists of a rigid PVC UL conduit formulation. The formulation is 100 phr rigid PVC,[12] 5 phr impact modifier,[13] 0.4 phr tin stabilizer,[14] 1.1 phr paraffin wax,[16] 1.0 phr TiO_2,[17] and 10, 25, 50 phr of the various fillers.

2. Compounding Procedure

The formulation is initially mixed in three steps using a Henschel 10 liter heater mixer. Part A (PVC, impact modifier, tin stabilizer) is mixed @ 3400 rpm and heated to 77°C. Part B (waxes are added and mixed @ 3400 rpm until 93°C is reached. Part C (TiO_2, filler) is added and mixed @ 3400 rpm until 110°C is

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reached. The material is then cooled via the water jacket @ 800 rpm until 49°C is reached. The material is removed from the mixer and allowed to stand for one hour (minimum). The samples were compounded further on a Farrel 6"x13" heated 2 roll mill @ 199°C-202°C for five minutes after fusion. A portion of each sample was compression molded in a 9"x8"x1/8" mold @ 20,000 psi and 177°C.

3. Preparation of Test Specimens

The test specimens (3"x3"x1/8") needed for smoke evaluation were cut from the compression molded sample using a 12" band saw equipped with a fine-tooth blade. Care was taken not to force the sample through the blade in order to prevent scalloping of the edges.

The samples for dehydrochlorination evaluation were granulated for ease of handling.[18]

4. Measurement of the Rate of Dehydrochlorination

The sample size of the filled PVC sample was varied so as to always contain 0.5g of PVC resin. The sample was placed in a Coors porcelain boat #60032 (70mm x 11mm x 8mm). The boat was placed into a 1" I.D. quartz tube held at isothermal conditions in a clam shell furnace.[19] the evolved HCl was carried by air (200cc/min) through a 24/40 heated (160°C) quartz bubbler (coarse frit). The evolved HCl was absorbed by 765 ml of 0.1M NaNO3 solution in a modified one liter Wolff flask. The concentration of HCl was detected by a Orion 96-17-00 combination chloride electrode (SIE) via an Orion 701A Ionalyzer. An Omega chromel-alumel thermocouple (1/16"x12") with an Omega Cold Junction Compensator CJ was used to monitor sample temperature. The chloride electrode and thermocouple responses were recorded with time using a Leeds and Northrup flat bed 2 channel recorder Model XL 620 at 150 cm/min. The boat was withdrawn from the apparatus after 30 minutes reaction time, and the weight recorded. A detailed drawing of the dehydrochlorination apparatus is found in Figure 2.

The thermal decomposition of the filled PVC samples was carried out at 250°C as the filler loading level was varied from 0 to 50 phr. The temperature effects were measured at a constant loading level (50 phr) for all fillers. The temperatures studied were 230°C, 250°C, 270°C and 290°C.

The induction time (T_i) is the time of HCl evolution as predicted by the specific ion electrode response plot (Figure 3). The time is calculated by regression analysis of the following equation:

$$T = m[EMF-EMF_o] + T_i$$

EMF - SIE response in chart units above base line

EMF_o - SIE response in chart units - base line

m - slope

The first order kinetic plot[10] of the dehydrochlorination is found in Figure 4 (Unfilled and 50 phr HYSAFE 150). The linear portion after the onset of HCl evolution is used and is found to obey the following equation:

$$\log \frac{x}{a-x} = k_i t - C$$

x = millimoles of HCl evolved

a = millimoles of HCl in sample calculated from the formulation.

The rate constant for HCl (k_i) is in min^{-1}; t is in minutes; and C, the integration constant, is dimensionless. R is the correlation coefficient.

5. NBS Smoke Chamber Evaluation

Smoke Obscuration data was collected on all of the filled PVC samples using a Super Pressure Smoke Density chamber developed at the National Bureau of Standards. The samples were evaluated in both the flaming and non-flaming mode in accordance with ASTM standard E-662. Carbon monoxide levels were determined on smoke samples at the maximum specific optical density (D_m) by diverting a gas stream to a Hach-Carle Series 400 AGC Gas Chromatograph.

RESULTS AND DISCUSSIONS

1. Effect of Fillers on Induction Time and Rate Constants

An "idealized" acid scavenging filler would affect PVC in such a way so that $T_i \rightarrow \infty$ and $k_i \rightarrow 0$, and be operable at all temperatures. However, this filler does not yet exist. Comparisons of the induction time and dehydrochlorination rate constants of filled PVC can serve as an evaluation of a filler's behavior as an acid gas scavenger. A comparison of the induction time and rate constants at 250°C for various filler loadings is found in Table 2.

The induction time for the filled PVC is increased somewhat for $CaCO_3$, ATH and $Mg(OH)_2$ as compared to unfilled PVC. The induction time of filled PVC is increased significantly for HYSAFE 150, such that at 50 phr loading, the induction time is approximately three times that of the other filled samples. The rate constants for dehydrochlorination are decreased somewhat for $CaCO_3$, and significantly for ATH and HYSAFE 150. The rate constants for $Mg(OH)_2$ filled samples do not exhibit this behavior.

The overall effect of filling PVC is to retard the beginning of HCl evolution (increased T_i), and to change the rate of evolution of HCl as measured by the rate constant. HYSAFE 150 and ATH show the lowest rate constants. The filler effect for all the fillers appears linear.

2. Effect of Temperature on Induction Time and Rate Constants

The temperature effects on unfilled and 50 phr filled PVC are found in Table 3. Decreasing temperature expressed as degrees Kelvin shows an increase in induction time and reduction in the rate constants. HYSAFE 150 shows the best performance, having the greatest induction time and the lowest rate constant at 503°K (230°C). The data consists of linear plots of log k_i vs 1/T and log T_i vs T(°K).

Arrhenius Activation Energies (E_A) and frequency factors for unfilled and 50 phr filled PVC are found in Table 4. HYSAFE 150 shows the largest activation energy and smallest frequency factor than any other filler evaluated.

3. Smoke Properties of Filled PVC

The smoke obscuration data was collected in both the flaming and non-flaming mode in accordance with ASTM standard E-662. The evaluations were carried out until a maximum specific optical density value D_m, to a gas chromatograph.

As expected, the unfilled control exhibited the highest smoke value in most cases. In the non-flaming mode, all of the inorganic fillers had similar smoke properties. Exceptions to this trend were

noted in the $Mg(OH)_2$ filled PVC (50 phr) which exhibited a lower smoke value than the rest of the fillers evaluated.

The flame mode data clearly indicate a reduction in smoke evolution for all the fillers, at each loading level studied. ATH filled (10 phr level) exhibited a lower smoke value than the other fillers studied at this loading level. At higher loadings (50 phr), all the fillers studied exhibited similar smoke properties.

Complete NBS smoke chamber data can be found in Tables 5, 6, and 7.

CONCLUSIONS

The technique involving the use of the specific ion electrode can easily detect and evaluate both the induction time and rate constants for the dehydrochlorination of rigid PVC and could be effectively extended to semi-rigid and flexible PVC.

The use of fillers in rigid PVC increases the induction time as compared to unfilled PVC, with HYSAFE 150 having the best performance. This effect is linear with loading. The rate constants are also affected to a lesser degree, with HYSAFE 150 and ATH showing the better performance.

Temperature effects upon unfilled and filled PVC are somewhat surprising. Decreasing temperature increases the induction time and lowers the rate constant for all samples studied. HYSAFE 150 displays the best performance, having the lowest rate constant and the greatest induction time @ 503°K (230°C).

The data clearly indicates that HYSAFE 150 can be used in rigid PVC conduit, and should afford the compounder with longer times to HCl evolution and lower rates of evolution. This could perhaps translate to higher through-put rates and much lower maintenance costs.

All fillers studied acted to lower the overall smoke properties of rigid PVC in both the flaming and non-flaming modes. Smoke properties were significantly lower at higher filler loadings (50 phr).

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[4]Tarquini, M. E. and Andrews, C. R., "A Novel Flame Retardant Additive for Thermosets Requiring High End-Use Temperatures", presented at 42nd Annual Conference and Expo '87 of The Society of the Plastics Industry (1987).

[5]The HYSAFE product line is being offered by the Chemicals Division of the J. M. Huber Corporation, P. O. Box 310, Havre de Grace, Maryland 21078.

[6]Smith, G. F., Journal of Vinyl Technology, Vol. 9, No. 1, March 1987, p. 18-21.

[7]Jenkins, A.D., ed. "Polyvinyl Chloride Degradation", Polymer Science Library 3, Elsevier, New York, 1985, p. 228.

[8]Chan, H.S.O., Journal of Fire Science, Vol. 2, March/April, 1984, p. 106.

[9]Bertelo, C. A., Carrol, W. F., Jr., Hirschler, M. M., Smith, G. F., "Fire Safety Science - Proceeding of the First International Symposium, 1986.

[10]Larsen, E. R., Journal of Fire Sciences, Vol. 4, July/August, 1986, p. 261.

[11]Military Specification, Cable and Cord, Electrical, Low Smoke, For Shipboard Use, MIL-C-24643, 28 Sept., 1984, p. 69, 104.

[12]Rigid PVC, Pipe Grade Georgia Gulf 1091 obtained from the Georgia Pacific Corporation.

[13]Impact Modifier CPE 3615 obtained from Dow Chemical Corporation.

[14]Tin Stabilizer 7711 obtained from Cardinal Chem Company.

[15]Paraffin Wax XL 165 obtained From American Hoeschst, Inc.

[16]Oxidized Paraffin Wax AC 629A obtained from Allied Chemical Corporation.

[17]Titanium Dioxide (TiO_2) R 900 obtained from DuPont Corporation.

[18]Wor-tex Granulator, Model JC-3, Hillsboro, Texas.

[19]Coulometrics, Inc., 1300 watt clam shell furnace fitted with an Omron E5T Programmable Temperature Controller.

BIOGRAPHY

Claude R. Andrews received a B.S. degree in Chemistry from Loyola College, Baltimore, Maryland, in 1958. He received a M.S. degree in chemistry from Villanova University, Villanova, PA, in 1960. He joined Davison Division of W. R. Grace in 1960 as an Analytical Chemist. He joined J. M. Huber Corporation as an Analytical Chemist in 1973. He is currently a Section Leader in Inorganic Research and Product Development.

Michael E. Tarquini received a B.S. degree in chemistry from Washington College in 1978. He was awarded a Ph.D. in inorganic chemistry, from the University of South Carolina in 1983. He joined the Chemicals Division of J. M. Huber, as a Research Chemist, in June of 1983. He was promoted to Senior Research Chemist in 1987. He currently is a Market Development Specialist with primary responsibilities for marketing products for the plastics industry.

FIGURE 1

TGA

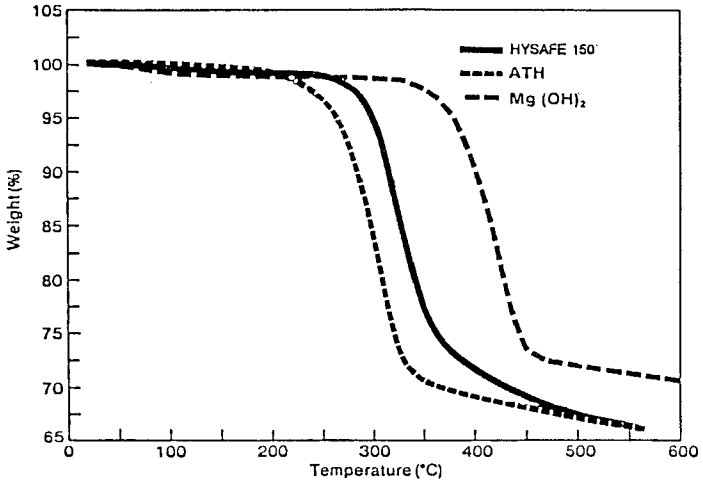

FIGURE 2

APPARATUS FOR THE DETERMINATION OF THE RATE OF DEHYDROCHLORINATION

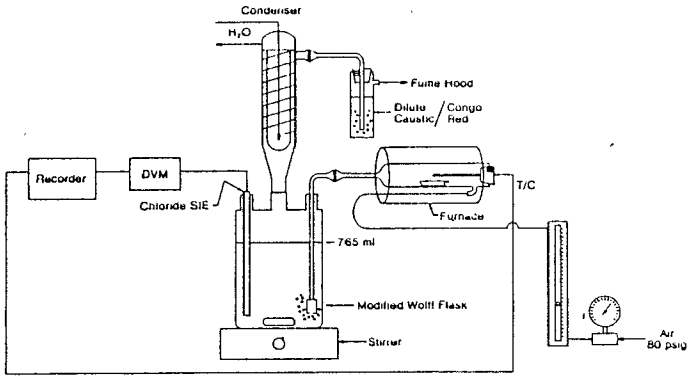

TABLE 1

PHYSICAL PROPERTIES OF FILLERS

Filler	Surface Area M^2/g	Oil Absorption cc/100 g	APS Microns	Pour Density g/cc	Pack Density g/cc	Gardner Brightness
ATH	13	28	2.6	0.56	0.87	94.9
$Mg(OH)_2$	21	47	2.2	0.31	0.57	95.4
HYSAFE 150	17	45	1.0	0.37	0.63	95.9
$CaCO_3$	2.4	22	3.7	0.68	1.09	88.5

RIGID PVC UL CONDUIT

Specific Chloride Electrode Response

Unfilled PVC

250°C

FIGURE 3

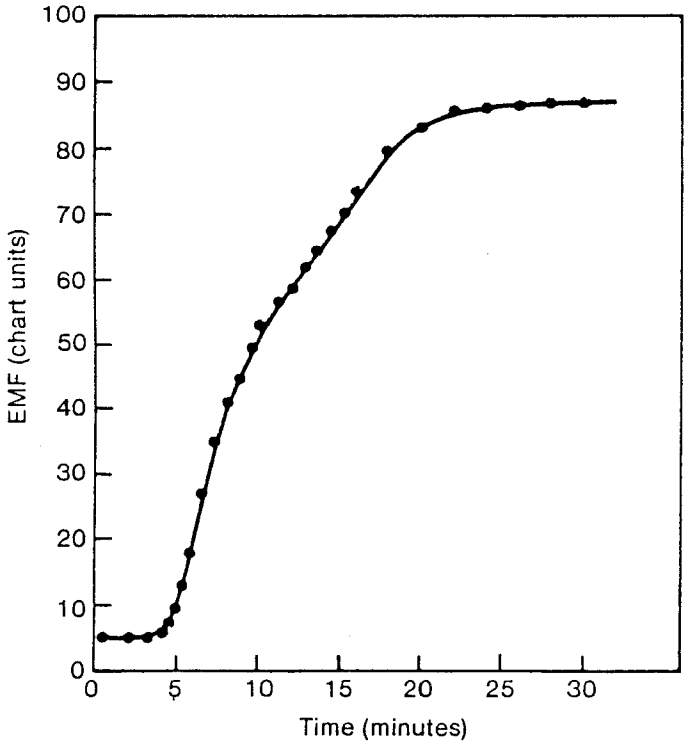

FIGURE 4

RIGID PVC UL CONDUIT

Rate of Dehydrochlorination

250°C

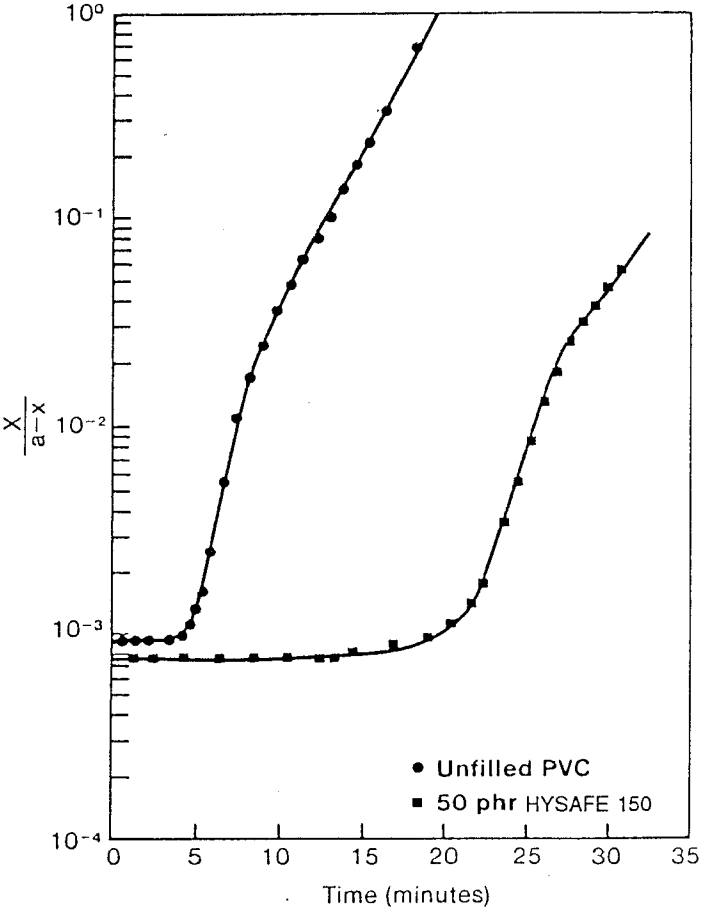

TABLE 2
RIGID PVC UL CONDUIT
Rate of Dehydrochlorination
Filler Loading Effect
250°C

Sample	Loading phr	Induction Time (min.)	Rate Constant $min.^{-1}$	Correlation Coefficient
Unfilled*	0	4.66±.41	0.349±.07	0.993±.005
$CaCO_3$	10	6.52	0.382	0.996
"	25	6.77	0.439	0.997
"	50	7.62	0.303	0.996
ATH	10	6.49	0.271	0.997
"	25	6.82	0.257	0.997
"	50	5.97	0.212	0.998
HYSAFE 150	10	9.42	0.305	0.996
"	25	13.18	0.435	0.990
"	50	20.71	0.212	0.998
$Mg(OH)_2$	10	5.94	0.568	0.996
"	25	6.58	0.492	0.993
"	50	6.87	0.420	0.991

* 7 determinations

TABLE 3
RIGID PVC UL CONDUIT
Rate of Dehydrochlorination
50 phr Filled PVC
Temperature Effects

Induction Time (min) T_i				
Sample	563°K	543°K	523°K	503°K
Unfilled	2.51	3.60	4.66	6.29
$CaCO_3$	3.24	5.05	7.62	10.19
ATH	3.43	4.86	5.97	6.80
HYSAFE 150	7.61	10.69	20.69	29.97
$Mg(OH)_2$	3.63	5.16	6.87	9.82

Rate Constants (min^{-1}) k_i				
Sample	563°K	543°K	523°K	503°K
Unfilled	0.950	0.634	0.349	0.236
$CaCO_3$	1.013	0.795	0.302	0.215
ATH	0.693	0.350	0.212	0.157
HYSAFE 150	1.518	0.665	0.212	0.099
$Mg(OH)_2$	1.396	0.840	0.420	0.228

TABLE 4
RIGID PVC UL CONDUIT
Dehydrochlorination Activation Energy
50 phr Filler

Sample	E_A (kcal)	A (min^{-1})	R
Unfilled	13.8	2.11×10^5	−.98
$CaCO_3$	15.0	7.08×10^6	−.97
ATH	13.8	1.47×10^5	−.98
HYSAFE 150	26.2	6.22×10^4	−.98
$Mg(OH)_2$	17.2	7.07×10^6	−.99

E_A – Arrhenius Activation Energy
A – Frequency Factor

TABLE 5
NBS SMOKE CHAMBER DATA
PVC
10 phr FLAMING AND
NON-FLAMING MODE

Sample	Mode	D_m	CO (ppm)
Control	NF	331	665
$CaCO_3$	NF	274	470
ATH	NF	298	924
$Mg(OH)_2$	NF	342	1070
HYSAFE 150	NF	324	715
Control	F	676	1162
$CaCO_3$	F	628	801
ATH	F	388	1241
$Mg(OH)_2$	F	500	874
HYSAFE 150	F	510	804

NF – Non-Flaming Mode
F – Flaming Mode

TABLE 6

NBS SMOKE CHAMBER DATA PVC 25 phr FLAMING AND NON-FLAMING MODE

Sample	Mode	D_m	CO (ppm)
Control	NF	331	665
$CaCO_3$	NF	478	683
ATH	NF	270	1155
$Mg(OH)_2$	NF	328	307
HYSAFE 150	NF	294	896
Control	F	676	1162
$CaCO_3$	F	482	673
ATH	F	430	794
$Mg(OH)_2$	F	581	898
HYSAFE 150	F	418	1090

NF – Non-Flaming Mode
F – Flaming Mode

TABLE 7

NBS SMOKE CHAMBER DATA PVC 50 phr FLAMING AND NON-FLAMING MODE

Sample	Mode	D_m	CO (ppm)
Control	NF	331	665
$CaCO_3$	NF	316	449
ATH	NF	308	1621
$Mg(OH)_2$	NF	118	219
HYSAFE 150	NF	275	1213
Control	F	676	1162
$CaCO_3$	F	412	635
ATH	F	416	1252
$Mg(OH)_2$	F	415	1112
HYSAFE 150	F	379	947

NF – Non-Flaming Mode
F – Flaming Mode