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An iron–organic polymeric smoke suppressant for poly(vinyl chloride)

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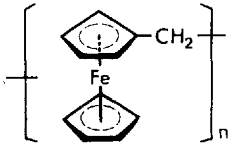
The incorporation of a poly[ferrocene-1, 2 (1, 3: 1, 1′)diylmethylene] fraction with $\bar{M}_n = 2100$ as a smoke suppressant additive into both unplasticized and di(2-ethylhexyl)phthalate-plasticized, calcium carbonate-filled poly(vinyl chloride) (PVC) compositions entails appreciable reductions in smoke evolution during combustion tests relative to unmodified formulations. Best results, with smoke density reductions in the range 25–80%, are obtained at the 3% loading level, with higher additive concentrations causing no further improvements. The findings of this study may have implications on the design of other polymeric engineering materials exposed to potential fire hazards.

Keywords: Polyferrocene, smoke suppressant, poly(vinyl chloride), PVC, smoke density, maximal optical density

INTRODUCTION

The catalytic properties of ferrocene (dicyclopentadienyliron) and some of its simple derivates in oxidation processes have been utilized for decades in the control of the combustion of industrial and aerospace fuels.[1] More recent reports in the literature[2a–f] describe pronounced flame-retardant and smoke-suppressing properties of ferrocene in a number of polymeric engineering materials such as poly(vinyl chloride) (PVC) or polyurethanes. The problem of smoke development in accidental fires is increasingly attracting public attention in the light of the finding that more human lives are lost in fire disasters through the effect of smoke and gas evolution than by flame action. A problem associated with the use of ferrocene and its low-molecular derivatives as smoke-suppressant additives is their tendency to diffuse through the material and evaporate from the surface [2e, 3] on long-term storage or under conditions of slow build-up of a high-temperature environment as realized in certain fire situations, which may lead to additive depletion in the most critical phase of pyrolytic degradation and combustion.

As part of a comprehensive program to develop ferrocene-containing smoke suppressants possessing structures incapable of migration and volatilization in hot environments, the present study is concerned with the incorporation of a polymeric ferrocene compound 1 into PVC compositions and an evaluation of its smoke-suppressing properties.



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RESULTS AND DISCUSSION

On account of its halogen content, unplasticized PVC is a material of inherently low flammability and thus resists both ignition and flame spreading. However, once exposed to a flame front it will emit smoke and gas and will ultimately conflagrate, especially when in contact with other combustibles.[4] The elimination of gaseous HCl with concomitant formation of polyene structures represents the first step of degradation (~170–250°C). Smoke evolution sets in at this early stage. Fission of polyene chains and intramolecular cyclization reactions immediately lead to the generation of benzene, further increasing smoke development. Partial hydrogenation of polyene segments in the condensed phase and additional rearrangements give rise to the formation of alkylaromatics at further elevated temperatures, wheres the remaining unsaturated hydrocarbon structures stepwise consolidate to carbonaceous chars. At even higher temperatures (600°C) these ultimately undergo incandescent and flaming combustion.[5]

The effects of ferrocene in PVC combustion comprise (i) catalysis of dehydrochlorination, (ii) reduction of benzene evolution and promotion of crosslinking reactions, leading to char formation as benzenoid ring structures consolidate to solid-state graphitic material (char) and (iii) catalysis of char oxidation in the final stage of combustion.[2b–e] It is largely the second step involving char formation from benzene aromatics which is considered to be responsible for the smoke-suppressant effect of ferrocene or, perhaps, more accurately, its degradation products.[6] The ferrocene derivative selected for the present project from a large number of candidate compounds investigated in earlier work[7] was the polymeric compound **1**, poly[ferrocene-1, 2 (1, 3: 1,1′)diylmethylene],[8] possessing a number-average molecular mass, $\bar{M}_n$, of 2100. This choice was based on the following considerations: (i) the polymer shows excellent PVC compatibility without detrimental effects on the material's mechanical properties; (ii) the polymer possesses an optimal content of ferrocene, with only a single carbon atom contained in the bridging link (the 'ferrocene only' type of polymer, poly-1,1′-ferrocenylene,[9] lacks the chain flexibility required for acceptable compatibility with PVC stock); and (iii) the polymer possesses a molecular mass large enough entirely to preclude diffusion through, and volatilization from, the compounded PVC.

Polymer **1**, prepared by a known polycondensation method,[8] was compounded with both an unplasticized PVC formulation (loading levels 1–7% by wt of PVC resin) and two different plasticized and calcium carbonate-filled PVC compositions (loading levels 1–7% by wt of total composition), the latter representing typical low-filler (7%) and high-filler (58%) cable-grade recipes containing di(2-ethylhexyl) phthalate plasticizer and chloroparaffin extender. The compression-molded samples, together with additive-free standards, were subjected to smoke evolution tests performed in a previously described[10] smoke chamber at temperatures ranging from 400 to 700°C, and the specific optical density,[11] D_s, was determined as a function of temperature (see the Experimental section). The results are compiled in Tables 1 and 2 for the unplasticized and the plasticized compositions, respectively. The first table, for comparison, includes an entry for an unplasticized PVC formulation containing 3% of (monomeric) ferrocene in place of **1**.

Inspection reveals a good-to-excellent smoke suppression effect of **1**. A loading of 3% in the three different formulations clearly represents an optimum, further increased additive concentrations causing no additional improvements. For the unplasticized compositions this is graphically shown in Fig. 1, in which the overall percentage smoke suppression at the two critical temperatures of 475 and 550°C (*vide infra*) is plotted against the additive concentration. In Fig. 2 the smoke evolution curve (plot of D_s versus smoke chamber temperature) for the unplasticized PVC with a 3% content of **1** is juxtaposed to that of an additive-free standard. The latter (curve (a)) gives a density maximum at 475°C corresponding to the end of the smoldering phase. At higher temperatures the volatiles liberated on degradation are capable of self-ignition, and smoke emission is diminished, although there emerges a second, weaker maximum near 550°C where non-flaming and flaming modes coexist. The additive-containing PVC (curve (b)) causes the same primary maximum at 475°C to appear. However, the appreciably lowered ordinate value indicates a reduction by some 40% in smoke evolution at this point.[12] More outstanding still (80%) is the reduction in the early stage of the flaming mode at 550°C, where a maximum no longer appears. It is also apparent that at the 3% loading level the monomeric ferrocene additive is inferior to the polymeric derivative **1** even under the chosen test conditions involving high heating rates, where additive depletion should be minimal.

Organic plasticizers of the phthalate ester type are known to enhance flammability and smoke emission quite considerably during the smoldering phase of combustion. Typical cable-grade fillers, such as calcium carbonate, tend to offset the detrimental action of the plasticizer. These effects are clearly reflected in the data of Table 2 for the plasticized formulations, as these are compared with those of Table 1. It is seen that the modification with additive again caused distinct reductions in smoke evolution, although, because of the high plasticizer contents, these were not as pronounced as with the unplasticized material. Figure 3 represents the smoke evolution curves for the high-filler, plasticized PVC

Table 1 Specific optical density as a function of chamber temperature for unplasticized PVC modified with **1**

PVC composition[a]	Chamber temperature (°C)[b] 400	450	475	500	550	600	650	700	750
UPVC–0	0.5	2.0	2.5	1.1	1.5	1.1	1.0	0.7	0.6
UPVC–1	0.08	1.7	2.1	0.45	0.7	0.7	0.8	0.7	0.7
UPVC–3	0.06	1.2	1.5	0.2	0.3	0.4	0.4	0.4	0.5
UPVC–5	—	1.3	1.6	0.2	0.4	0.3	0.3	0.4	0.5
UPVC–7	—	—	1.8	—	0.4	—	—	—	—
UPVC–Fc	0.25	1.4	1.6	0.5	1.0	0.6	0.6	0.7	0.6

[a] UPVC, unplasticized PVC; dash numbers refer to the percentage concentration of additive **1**. UPVC–Fc, unplasticized PVC containing ferrocene additive (3%). [b] — Not measured.

Table 2 Specific optical density as a function of chamber temperature for plasticized PVC modified with **1**

PVC composition[a]	Chamber temperature (°C)[b] 400	450	475	500	550	600	650	700	750
HFPVC–0	1.8	2.2	3.1	0.4	0.3	0.3	0.4	0.4	0.5
HFPVC–1	1.1	1.8	1.8	0.7	0.2	0.3	0.15	0.4	0.4
HFPVC–3	1.1	1.8	1.8	0.8	0.2	0.2	0.3	0.24	0.2
HFPVC–5	1.6	2.0	2.0	0.45	0.1	0.2	0.2	0.3	0.3
HFPVC–7	1.1	1.8	2.0	1.6	0.25	0.1	0.2	0.2	0.2
LFPVC–0	—	—	3.4	—	0.8	—	—	—	—
LFPVC–1	—	—	3.0	—	0.45	—	—	—	—
LFPVC–3	—	—	2.3	—	0.4	—	—	—	—
LFPVC–5	—	—	2.3	—	0.57	—	—	—	—
LFPVC–7	—	—	2.4	—	0.55	—	—	—	—

[a] HFPVC, high-filler, plasticized PVC (58% $CaCO_3$); LFPVC, low-filler, plasticized PVC (7% $CaCO_3$); dash numbers refer to the percentage concentration of additive **1**. [b] — Not measured.

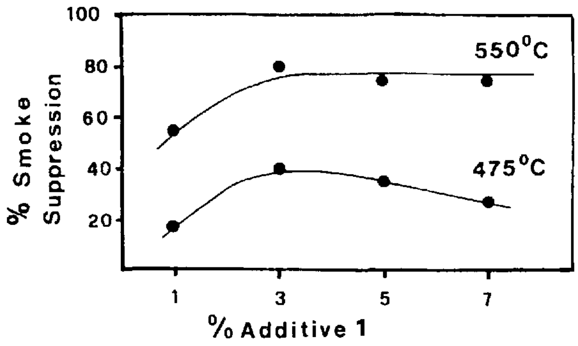

Figure 1 Percentage smoke suppression vs additive concentration in unplasticized PVC.

standard (curve (a)) and for the respective material containing a 3% loading of additive **1** (curve (b)). The reduction in smoke generation at 475°C brought about by the additive approaches 42%, and in the temperature region of the flaming mode above 600°C, reduction values range from 25 to 60%. Neither curve shows a maximum at 550°C. The faint maximum of curve (b) near 650°C is probably an artifact and has no significance, as a comparison of the data at the 1% and 5% loading levels suggests.

In summary, the modification of both unplasticized and plasticized PVC compositions

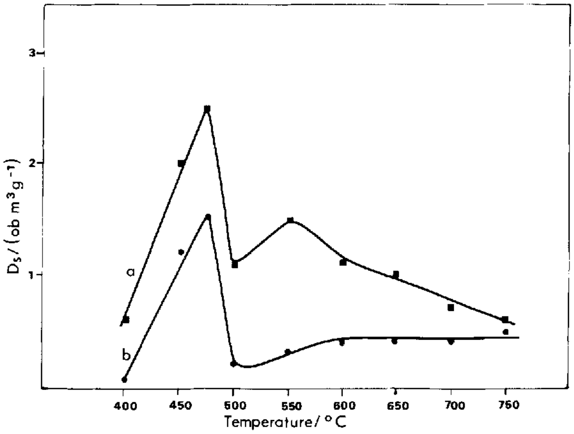

Figure 2 Specific optical density, D_s, vs combustion temperature for unplasticized PVC. Curve (a), unmodified (standard); curve (b), modified with 3% of **1**.

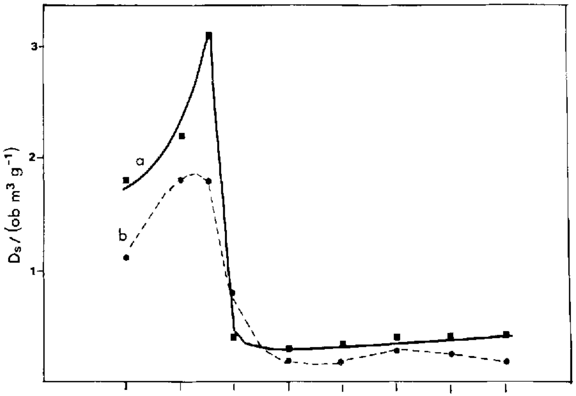

Figure 3 Specific optical density, D_s, vs combustion temperature for high-filler, plasticized PVC. Curve (a), unmodified (standard); curve (b), modified with 3% of **1**.

with the methylene-bridged ferrocene polymer additive **1** in concentrations up to 3% causes an appreciable suppression of smoke emission in combustion experiments. It will be of interest to examine the smoke-suppressant effects of **1** and similar macromolecular additives in polyurethane foam and other polymeric building and insulation materials required to conform to stringent specification of low smoke emission limits.

EXPERIMENTAL

Poly[ferrocene-1,2(1,3:1,1′)diylmethylene](1)

The additive **1** was prepared[8] by $ZnCl_2$-catalyzed melt polymerization of ferrocene with dimethoxymethane (formaldehyde dimethylacetal), followed by reprecipitation from toluene solution by methanol. A major fraction of precipitated polymer with $M_n = 2100$ was selected for the present study.

Analysis: Found: Fe, 27.73. Calc. for $(C_{11}H_{10}Fe)_n$ (**1**: ferrocenyl end-group neglected): Fe, 28.20%.

PVC compounding

Unplasticized PVC

Suspension-grade PVC in powder form (Aldrich, Code 18 261-3), $\eta_{inh} = 126\,cm^3\,g^{-1}$, was thoroughly homogenized with **1**, concentrations of the latter being 1, 3, 5 and 7% by wt of resin. The individual batches were compression-molded at 170°C into flat sheets of nominally 1.5 mm thickness and cut into small (200 mg) strips. An additive-free material was prepared identically as a standard. These samples were labeled UPVC.

Plasticized PVC

A low-filler, plasticized base stock of cable grade was prepared as described[7] from (parts by weight): a suspension-grade PVC resin, Corrie S 6617 (100); di(2-ethylhexyl)phthalate (26); chloroparaffin, Plasticlor 52 L (26); tribasic lead sulfate stabilizer (4); and calcium carbonate filler, Omya BCH (7). The pre-gelled, rolled, and pelletized base stock was recompounded[7] with **1**, the latter added in concentrations of 1, 3, 5 and 7% by wt of total compound and, after compression-molding into flat sheets of nominally 1.3 mm thickness, was cut into 200-mg strips. An additive-free standard material was prepared as before. The samples were labeled LFPVC. In an analogous fashion, formulations possessing a high filler content (calcium carbonate, 58% by wt of resin) were prepared and were labeled HFPVC.

Smoke density measurements

These were performed in the accumulation mode by the method, and with the aid of instrumentation, described elsewhere.[10] The amount of smoke emitted is expressed in terms of specific optical density, $D_s = VD_mL^{-1}w^{-1}$, where D_m is the maximal optical density, V is the volume of the chamber (m^3), L is the path length (m), and w is the initial mass of material (g). The unit of D_s is given as ob $m^3 g^{-1}$, where ob (obscura) represents the smokiness of an ambient atmosphere when the measured light attenuation is one decibel per meter of smoke path.[11]

Acknowledgements: The authors are indebted to AECI Ltd for the generous donation of materials and for permission to use their compounding facilities for the preparation of the plasticized PVC compositions.

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