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The Effect of Flame Retardant Smoke Suppressants on the Char Morphology of Plasticized PVC

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Abstract

Char formation that preserves the structural integrity of the polymer is one of the most efficient methods of reducing its flammability. Enhanced char formation from polymers such as PVC may also be associated with a decrease in smoke production, as is observed when the polymer is modified by a flame retardant smoke suppressant (FRSS) complex. A correlation had been made between the FRSS characteristics and char morphology. The effect of different flame retardant smoke suppressants on char formation has been highlighted.

Introduction

Polymeric materials are widely applied because they have many inherently good qualities, but when they burn, many organic polymers can form carbon or carbon-based compounds. The resulting carbon may either be in the solid phase (char) or in the gaseous phase (smoke or oxides of carbon).[1] One of the major fire hazards from synthetic polymers like PVC is that when they burn, they can generate large volumes of smoke and toxic gasses. The problem of smoke formation from polymers, which poses a life hazard and hampers firefighting, particularly in enclosure fires, needs to be looked into. Although the use of flame retardants to improve the fire performance of materials has been practiced for quite some time, many flame retardant chemicals are known to increase the amount of smoke generated by polymers.[2,3] Since smoke and combustion gases are known to be the major cause of fire-related deaths, use of flame retardant smoke suppressants (FRSS) is the optimum solution to this problem.

The effect of FRSS complexes on fire behavior of polymeric materials is normally studied by different standard methods, e.g., limiting oxygen index (ASTM D 2863), cone calorimetry (ASTM E 1354), Steiner tunnel (ASTM D 84) and NBS smoke density chamber method (ASTM E 662). However, indirect methods, such as thermal analysis (DTA/DSC/TGA)[4] and microscopic techniques[5,6] are also used as supporting tools to understand the fire behavior of FRSS modified polymers. Electron microscopic techniques have been used for studies on dispersion of additives in the polymer matrix[7] as well as their effect on soot formation from polymers.[8] Sevecek and Dvorak[6] have reported using an optical microscope for analyzing char residue. They have commented on the macrostructure and anisotropy of char obtained from polystyrene, poly (vinylchloride), and polyamide. However, little work has been reported on correlating char morphology and FRSS characteristics of polymers. In this paper, we try to correlate the FRSS characteristic of plasticized PVC with the morphology of its char.

Materials

Poly (vinyl chloride) having degree of polymerization 1,300, VCM less than 0.1 and "Glass transition temperature" 78°C was used in the present study. Samples of plasticized PVC were prepared according to the recipe given in Table 1. Ingredients were milled for 10 minutes at 165-170°C on a two-roll mill followed by compression moulding at 175°C. Plasticizers used were Dioctyl phthalate (DOP) and tricresyl phosphate (TCP). FRSS additives used included MoO_3, V_2O_5, $ZrOCl_2$, and metal-based organic complexes (MBO), namely, acetylacetonates[9] including Dioxobis (2,4 Pentanediono) Molybdenum (VI), Bis (2,4 Pentanediono) oxo Vanadium(IV), Tris (2,4 Pentanediono) Chromium (III), Tris (2,4 Pentanediono) Cobalt (III) and Tetrakis (2,4 Pentanediono) Zirconium (IV). MBOs were used in the study for their known efficacy as FRSS in polymers due to their better miscibility.[10] The plasticizer used with inorganic additives and zirconium complex was dioctyl phthalate. All other samples were prepared by using tri cresyl phosphate.

Methodology

To ensure reliable char comparisons, all samples investigated were subjected to identical forced burning conditions in a Limiting Oxygen Index Apparatus (Stanton Redcroft FTA) for three minutes at oxygen concentrations 2% higher than the Limiting Oxygen Index (LOI) value. This ensured optimum combustion of the material exposed. Smoke measurements were carried out by a dynamic method,[11] where samples are burned in an oxygen-enriched atmosphere. Oxygen levels were maintained at 2% above the LOI values of respective samples. The FRSS effect of additives on the substrate was recorded in terms of LOI, for flame retardancy, and SSI, for the smoke suppression index. The smoke suppression index was calculated as[11]

$$SSI = \frac{A - A_t}{A} \times 10$$

where A = the area under the OD profile of the untreated sample/ weight of specimen consumed, and A_t = the area under the OD profile of the treated sample/weight of specimen consumed. Weight of char was calculated in terms of backbone char percentage ($BC\%$) as reported by Kroenke.[12]

TABLE 1
Recipe for Plasticized PVC

Ingredients	Loading
PVC	100 phr
Plasticizer	50 phr
Processing aids	2.0 phr
FRSS additive	3.0 phr

All quantities are in parts per hundred parts of resin (phr)

$$BC\% = \frac{\text{Weight of char}}{\text{Wt. of sample} - \text{Wt. of non PVC component} - \text{Wt. of HCl}} \times 100$$

Intimate structural variations of char obtained by forced burning of PVC samples were investigated by scanning electron microscope (SEM).

Morphology of Char

The final residue left after degradation of a polymer is very rich in carbon and has the character of metallurgical coke in some polymers, such as PVC. When compared to coke, however, the char residues have a higher bulk density, which is often very cohesive and rigid. Char from rigid PVC has been reported to be very swollen, rigid, and brittle, with numerous pores showing a honeycombed appearance, while char from plasticized PVC is vitreous when observed through an optical microscope.[6] In the present investigations, char obtained from plasticized PVC samples modified with different FRSS additives was found to be different.

Technique and Sample Preparation

The solid phase residue (char) that was left after the combustion of the FRSS-modified plasticized PVC samples was studied using Scanning Electron Microscopy (SEM). The technique uses an electron beam, which is made to impinge upon a specimen surface. Then the reflected "electron signals" are amplified and analyzed, mainly to ascertain surface topographical details. A large depth of focus is an inherent feature of SEM. A "Phillips 501" scanning electron microscope was used for this study, which was carried out at an operating voltage of 15 kV. The "solid residue," i.e., the char obtained after exposing the specimens in the flammability test apparatus (FTA), was collected and used as samples. These were dried for 24 hours at 100+5°C. The sample holders of SEM were first coated with an adhesive tape on which small amounts of the char samples were spread. These were then coated, or shadowed, with gold dust to make them conducive and thus, suitable for the study.

Results and Discussion

Carbon can be formed in two ways from a halogenated organic polymer such as PVC[13]: First, in the condensed phase, by stripping off most or all noncarbonaceous material from the polymer, leaving solid char residue, and second, by chain scission reaction in the condensed phase, leading to the formation of volatile low-molecular-weight compounds. These can then undergo dehydrohalogenation reaction, as in case of PVC, via polyacetylenes or polynuclear aromatic hydrocarbons in the gas phase to produce soot. Promotion of carbonization, i.e., char formation, which preserves the structural integrity (matrix retention) of the polymer, is one of the most efficient methods of reducing the flammability of a polymer. Enhanced char formation from a polymer may also be associated with a decrease in smoke production, as is observed when the PVC is modified by MBOs (Table 2). MBO additives are known to produce carbon by promoting chain stripping. However, if smoke production increases from the polymeric system containing an additive, it is a result of enhanced chain scission reaction at the expense of chain stripping. Table 2 summarizes the results of flammability (LOI), smoke suppression (SSI), and char formation, BC%, for different specimens investigated. Higher values of LOI and SSI indicate better flame retardancy and smoke suppression.

It would be useful to consider the data reported herein, in the form of SEM micrographs, in the aforesaid context. Flame retardant smoke suppressant behavior of polymers can be read in terms of four main morphological features and their combinations.[14] While the term "matrix retention" designates inhibited burning or incomplete combustion, "partial matrix retention" refers to char formation with preservation of structural entity, i.e., charring mainly of the top layer. The "lesser matrix retention" indicates concurrent presence of other features, such as char/ash, along with matrix. This technique, however, has a limitation that, at present, it can only be used for qualitative estimates.

In order to understand the data reported through the micrographs, it would be necessary to understand the processes responsible for degradation of the polymer when subjected to heat or fire. The net processes of burning may thus be summed up as comprising melting (resulting in matrix retention); inhibited burning (resulting in matrix retention) and the formation of char, soot, smoke, and other combustion products; and burning (resulting mainly in ash formation but little char).

Using this framework to understand the burning process, we can assess as to how such information can be used to comment on the flame retardant and smoke suppressant behavior of materials. Insofar as flame retardance is concerned, the

TABLE 2
Flame Retardant and Smoke Suppressant Behavior of Modified Plasticized PVC

Additive	LOI *	SSI	%BC
Molybdenum Trioxide (MoO_3)	27.9	21.74	79.80
Vanadium Pentaoxide (V_2O_5)	28.8	29.66	66.84
Zirconium Oxychloride ($ZrOCl_2$)	26.8	25.25	74.11
Dioxobis (2, 4 Pentanediono) Molybdenum (VI)	33.20	58.08	67.21
Bis (2, 4 Pentanediono) oxo Vanadium (IV)	32.80	33.95	58.73
Tetrakis (2, 4 Pentanediono) Zirconium (IV)	27.00	-24.36	46.77
Tris (2, 4 Pentanediono) Chromium (III)	32.10	58.75	57.79
Tris (2, 4 Pentanediono) Cobalt (III)	33.40	63.54	84.43

** Specimens were burnt at an oxygen level 2% higher than their LOI*

Definitions:

- *LOI, Limiting oxygen index*
- *SSI, Smoke suppression index, calculated with reference to the corresponding unmodified samples. A negative value indicates an increase in smoke generation.*
- *%BC, Backbone char percentage*

preference would be for higher matrix retention and/or char formation. From the point of view of smoke suppression, it is once again favorable to attain matrix retention and/or a higher char content.

The SEM micrographs pertaining to the plasticized PVC are shown in Figure 1. The figures reveal predominant matrix retention reminiscent of incomplete combustion of the carbonaceous matter. Evidently the combustion has not reached a state of total incineration, that is, ash formation. This was to be expected, since a fire retardant plasticizer (TCP) was used in preparing the PVC samples. On adding molybdenum oxide (MoO_3) to the plasticized PVC, it is observed that matrix retention occurred to a lesser extent, and some char formation is also clearly revealed (Figure 2). In the presence of vanadium oxide (V_2O_5), mixed features were seen comprising matrix retention, "honeycomb" formation (Figure 3), and char formation. The addition of Zirconium oxychloride ($ZrOCl_2$) to the PVC samples induced "least matrix retention," especially in comparison to the three earlier instances (Figure 4).

Addition of molybdenum based MBO reveals more pore openings in the matrix than hitherto observed (Figure 5). Its general appearance seems to resemble the one shown in Figure 2, namely that obtained with MoO_3. The extent of charring was more than that observed with the oxide additives (not shown in the micrograph) . The micrographs of PVC, modified with the MBO of vanadium, are also similar to those obtained with V_2O_5 addition, the predominant features

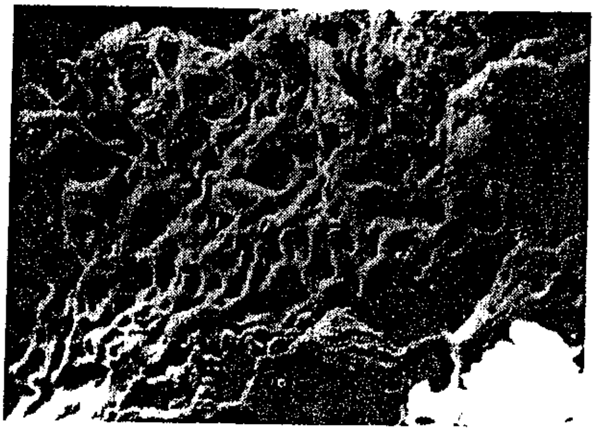

Figure 1. Plasticized PVC (predominant matrix retention).

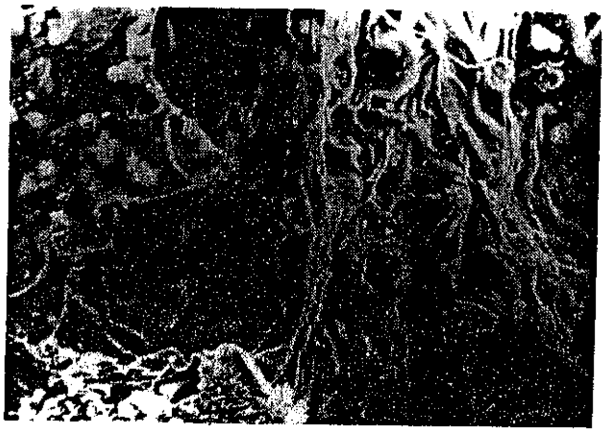

Figure 2. MoO_3 Modified PVC (lesser matrix retention plus char).

Figure 3. V_2O_5 Modified PVC (matrix retention plus char).

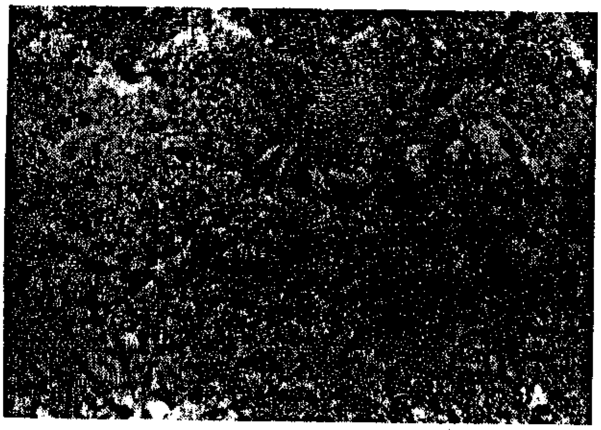

Figure 4. $ZrOCl_2$ Modified PVC (least matrix retention plus predominant char).

Figure 5. MoO acac Modified PVC (matrix retention with pore openings).

Figure 6. VO acac Modified PVC (matrix retention).

being matrix retention (Figure 6), honeycombing, and char formation. When zirconium-based complex was used (Figure 7), micrographs resemble those obtained with $ZrOCl_2$ additive. The predominant features are the matrix and char accompanied by the formation of ash specks. Incidentally, the results (Table 2) reveal that the char formation is lower than with the other MBOs used in the study. This could be possible because a significant quantity of char was formed, but due to incandescence (an important feature of MBOs), it was converted to CO and CO_2. This situation reflects good FRSS performance of the MBO. A second possibility is that char formation was actually lower, which would have been the case if the additive was not a good FRSS because all MBOs act through a condensed phase/char forming mechanism. Neither the incandescence phenomena nor an increase in combustion gases was observed, thus indicating poor perfor-

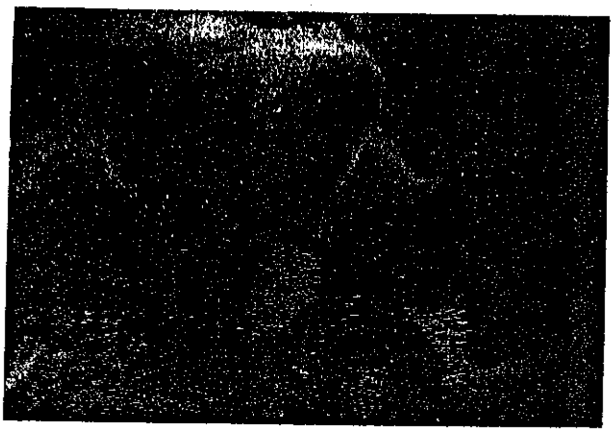

Figure 7. Zr acac Modified PVC (matrix retention plus flakes).

Figure 8. Cr acac Modified PVC (honeycomb plus partial matrix retention).

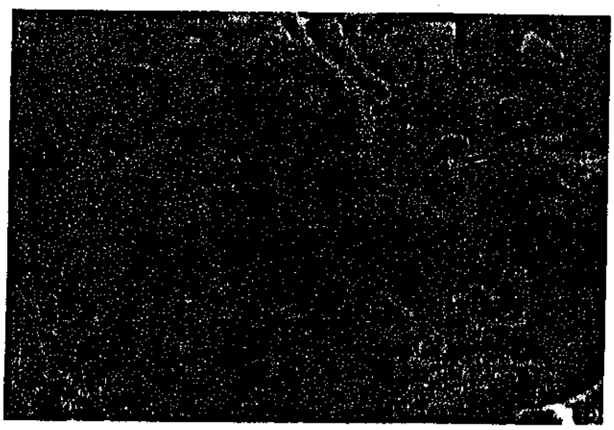

Figure 9. Co acac Modified PVC (char and matrix retention).

TABLE 3
SEM Observations on Char

Figure	Additive	Observations
1	Reference sample	• Matrix retention • Stray patches of ash
2	Molybdenum oxide	• Reduced matrix retention • Char
3	Vanadium oxide	• Honeycombing • Matrix retention, char*
4	Zirconium oxychloride	• Char • Minimum matrix retention*
5	Molybdenum acac	• Matrix retention with pore openings • Char*
6	Vanadium acac	• Matrix retention • Char* • Honeycombing*
7	Zirconium acac	• Char with minimum matrix retention
8	Chromium acac	• Honeycombing + flakes • Partial matrix retention
9	Cobalt acac	• Char with matrix retention

**Features observed in micrographs but not shown here*

mance of Tetra kis (2, 4 Pentanediono) Zirconium (IV) as an FRSS additive. Char samples obtained from specimens of PVC incorporating the chromium based MBO reveal honeycombing and partial matrix retention (Figure 8), char formation being the other predominant feature. When the cobalt-based MBO was used to modify PVC, the samples clearly indicate matrix (Figure 9) and charring .

On the basis of the above discussion, it is now possible to analyze the observations made earlier (Table 2). A perusal of Figures 1 through 8 and Table 2 leads us to conclude that when inorganic additives are used, three prominent features are observed: matrix retention, matrix retention plus char, and char plus honeycombing. Honeycombing results from smoldering and represents combustion of char. This leads to the evaluation of carbon monoxide, carbon dioxide, and the formation of ash. As reported by Bert *et al.* ,[10] such a situation results in low generation of smoke and controlled or restricted flame retardance. The preferred condition, from the point of view of flame retardance, is matrix retention or inhibited burning followed by matrix retention plus char or char alone. From a smoke suppression point of view, matrix retention followed by charring plus honeycombing are the preferred options. These inferences duly corroborate the data given in Table 2.

Furthermore, adding acetylacetonates of different metals to the plasticized PVC produces less smoke, and the predominant feature observed is char. Matrix retention is also observed. This indicates flame retardance at a second, lower level, but not during early stages because initial charring prevents further burning by acting as a heat shield. Thus, acetylacetonates are flame retardants that act by char formation mechanisms, and they are also good smoke suppressants. Acetylacetonates used in this study were found to be efficient FRSS, particularly for cobalt, molybdenum, and chromium, in that order (Table 2-3).

Conclusions

Emerging from this study, it can be concluded that SEM observations can be used as a qualitative tool for assessment of FRSS characteristics of plasticized PVC. It may be used for studies involving post fire investigations.

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