CORRELATION BETWEEN FRSS CHARACTERISTICS OF PLASTICIZED PVCs AND THEIR CHAR MORPHOLOGY

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INTRODUCTION

Polymeric materials on burning result in the formation of carbon, which may either be in solid phase (char) or in the gaseous phase (smoke or oxides of carbon). A major fire hazard of synthetic polymers is that on burning they generate large volumes of smoke and toxic gases. Flame retardants although known to improve fire performance may increase the smoke generation by polymers[1,2]. Since smoke and combustion gases are the major cause of fire related deaths, the use of flame retardant smoke suppressants (FRSS) has emerged as the optimum solution to the problem of improving fire retardance of polymeric materials.

Though the effect of FRSS complexes on fire behaviour is normally studied by different standard tests, indirect methods such as thermal analysis are also used as supporting tool to understand the behaviour of FRSS modified polymers. Electron microscopic techniques although finding application in dispersion studies of additives[3] and their effect on soot formation from polymers[4], have not been used for correlating char morphology with FRSS characteristics of polymers. In the present communication an attempt has been made to establish such a correlation.

MATERIALS

Plasticized PVC samples were prepared according to the recipe :

PVC	100	phr
Plasticizer	50	phr
Processing aids	2	phr
FRSS additive	3	phr

Ingredients were milled for ten minutes on a two- roll mill at 165-170°C followed by compression moulding at 175°C. FRSS additives used included MoO_3, V_2O_5, $ZrOCl_2$, and acetylacetonates of molybdenum (MoO acac), vanadium (VO acac), zirconium (Zr acac) and chromium (Cr acac).

FLAMMABILITY AND SMOKE GENERATION

To ensure reliable char comparisions, all samples investigated were subjected to an identical condition of forced burning in a Stanton Redcroft FTA for three minutes at oxygen concentrations of 2% higher than the LOI. This ensured optimum combustion of the material exposed.

Weight of char was measured in terms of backbone char percentage calculated after Kroenke[5]. Smoke measurements were carried out by a dynamic method developed by Sharma et al[6] where samples are burnt in an oxygen enriched atmosphere. Oxygen levels were maintained at 2% above the LOI (limiting oxygen index) values of respective samples. Intimate structural variations of char obtained were investigated by scanning electron microscope (SEM). The effect of additives on the substrat was recorded in terms LOI (for flame retardancy) and SSI (smoke suppression index).

Table 1 summarises the results of LOI and SSI for different specimens investigated. Higher values of LOI and SSI indicate better flame retardancy and smoke suppression.

TABLE 1. FLAME RETARDANT AND SMOKE SUPPRESSANT BEHAVIOUR OF MODIFIED PLASTICIZED PVC

Additive	LOI	SSI
MoO_3	27.9	21.80
V_2O_5	28.8	29.66
$ZrOCl_2$	26.8	25.25
MoO acac	33.20	58.08
VO acac	32.80	33.95
Zr acac	27.00	-24.36
Cr acac	32.10	58.75

LOI Limiting oxygen index ; SSI Smoke suppression index, calculated with reference to the corresponding unmodified samples. Negative value indicate increase in smoke generation

MORPHOLOGY OF CHAR

The final residue left after degradation of a polymer is very rich in carbon having the character of metallurgical coke in some cases e.g. PVC. However when compared to coke, the char residues have a higher bulk density often being very cohesive and rigid. Char from rigid PVCs has been reported to be swollen, rigid and brittle with numerous pores having a honeycombed appearance while that from plasticized PVCs is vitreous, when observed through an optical microscope[7]. In the present investigations char obtained from plasticized PVC samples, modified with different additives was found to be different.

A 'Phillips 501' scanning electron microscope was used for the present studies 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 masked with gold dust for SEM studies.

RESULTS AND DISCUSSION

Promotion of carbonisation i.e. char formation which preserves the structural integrity (matrix retention) of the polymer, is one of the most efficient method of reducing the flammability of a polymer. MBOs (metal based organic additives) produce carbon by promoting chain stripping. If smoke production increases from the polymeric system (PVC) containing an organomettalic compound, its action is to enhance chain scission reaction at the expense of chain stripping. It would be useful to consider the data (SEM micrographs) reported herein in the aforesaid context.

The SEM micrographs pertaining to the plasticized PVC are shown in Fig. 1. The figure reveals predominant matrix retention reminiscent of incomplete combustion of the carbonaceous matter. Evidently, the combustion has not reached a state of total incineration i.e. ash formation. This was to be expected since a fire retardant plasticizer (TCP) was used in preparing the PVC sample.

On adding molybdenum oxide (MoO_3) to the plasticized PVC it is observed that the matrix retention occurred to a lesser extent and some char formation is clearly revealed (Fig. 2). In the presence of vanadium oxide (V_2O_5) mixed features were seen, comprising matrix retention, 'honeycombing'(Fig. 3) and char formation. Addition of zirconium oxychloride ($ZrOCl_2$) to the PVC samples induced 'least' matrix retention especially in comparison to the three earlier instances. The residue predominantly comprised char (Fig. 4).

Addition of molybdenum based complex (MoO acac) reveals more pore openings in the matrix than hitherto observed (Fig. 5). Its general appearance resembled the one shown in Fig. 2 namely that obtained with MoO_3. The extent of charring is more than the one observed with oxide additives. The micrographs of PVC impregnated with the acetylacetonate of vanadium are also similar to those obtained with V_2O_5 addition, the predominant features being matrix retention (Fig. 6), 'honeycombing' and char formation (Fig. 7). Micrographs when zirconium based complex (Zr acac) was used resemble those obtained with $ZrOCl_2$ additive. PVC samples with the complex of chromium (Cr acac) reveal 'honeycombing' and partial matrix retention, char formation being the other predominant feature (Fig, 8).

In order to understand the data reported through the micrographs it would be necessary to understand the process(es) responsible for polymer degradation when subjected to fire conditions. The net process(es) of burning may be summed up as comprising:

(1) melting (resulting in matrix retention),
(2) inhibited burning (resulting in matrix retention) and the formation of char, soot, smoke and other combustion products,
(3) burning (resulting in little char and mainly ash formation).

Having thus provided the necessary frame work to understand the burning processes, it would now be relevant to assess as to how such an information can be used to comment upon the flame retardant / smoke suppressant behaviour of materials. In so far as the flame retardance is concerned, the preference would be for higher matrix retention and/or char formation. From the point of view of smoke suppression, it is once again favourable to attain matrix retention and/or a higher char content.

On the basis of this discussion it is now possible to analyse the observations made earlier (Table 2). A perusal of Figs. 1 - 8 and Table 2 leads us to the following conclusions:

TABLE 2. 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 (Matrix retention)*
5	Molybdenum acac	- Matrix retention with pore openings (Char)*
6	Vanadium acac	- Matrix retention (Char)*
7	Vanadium acac	- Honeycombing
8	Chromium acac	- Matrix retention, Flakes, Honeycombing

* additional information not given in micrographs

(1) When inorganic additives are used, three prominent features are observed - matrix retention, matrix retention +char, char + honeycombing. Honeycombing results from smouldering and represents combustion of

char. This leads to the evolution of carbon monoxide, carbon dioxide and the formation of ash. As reported by Bert et al[8] such a situation results in low smoke generation and controlled/ restricted 'flame retardance'. The most preferred condition from flame retardance point of view is matrix retention or inhibited burning followed by matrix retention + char and/ or char alone. From smoke suppression point of view matrix retention followed by charring + honey- combing are the preferred options. These inferences duly corroborate the data given in Table 1.

(2) Addition of acetylacetonates of different metals to the plasticized PVC produces less smoke and the predominant feature observed is char. Additionally, matrix retention is also observed and this indicates flame retardance at a second level (lower level) because the process of burning is inhibited but not during early stages i.e. initially charring occurred which prevented further burning by acting as a heat shield. Thus acetylacetonates are flame retardants which act by char formation mechanism and are also good smoke suppressants. Acetylacetonates used in the present study are found to be efficient FRSS, particularly those of cobalt, molybdenum and chromium - in that order (Table 1-2).

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 polymeric materials. It may be used for studies involving post fire investigations.

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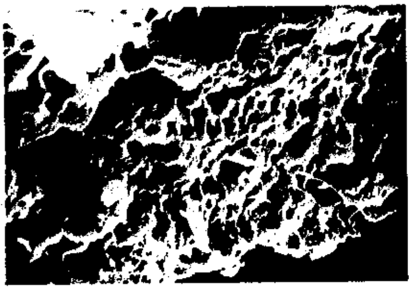
FIG. 1


FIG. 2


FIG. 3

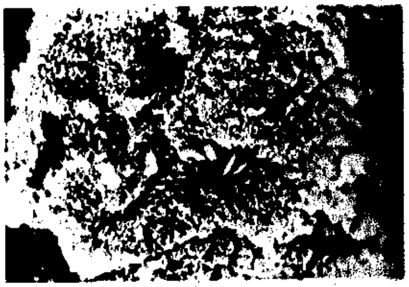
FIG. 4


FIG. 5


FIG. 6


FIG. 7

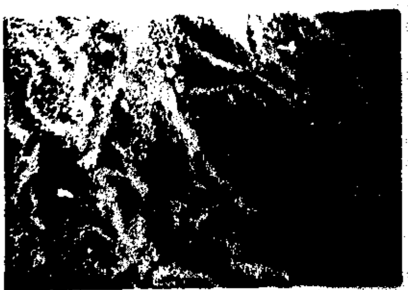
FIG. 8

SEM MORPHOLOGY