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Metal-based organic complex as fire retardant and smoke suppressant for polyvinyl chloride

Sunil K Sharma
Fire Research Laboratory, Central Building Research Institute, Roorkee, UP 247 667, India

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Use of a transition metal-based organic (MBO) complex, Tris (2, 4 Pentanediono) Chromium III has been examined as fire retardant and smoke suppressants for plasticised PVC. The effectiveness of the FRSS is described in terms of smoke release, time of ignition, heat release and generation of other gaseous combustion products at two irradiance levels using a cone calorimeter. The MBO was used at 0, 0.5, 1, 2 and 3 phr (parts per hundred parts of resin) loadings. Two fillers were used and their effect on smoke generation was observed. Results were compared with those for a commercially available fire retardant (FR) PVC. The MBO was found more effective when used at one phr with magnesium hydroxide as the filler and the modified PVC was superior to the FR PVC in terms of rate of heat release and smoke generation.

Poly vinyl chloride finds a wide range of applications in industrialized fields because of its many outstanding properties. Although it is intrinsically flame retardant, large quantities of smoke and toxic gases are evolved when it is forced to burn[1].Smoke poses danger to human life, due to disorientation and reduction in visibility leading to panic and irrational behaviour which makes escape difficult.

Comprehensive reviews on smoke suppression of polymeric materials have been published[2,3]. Smoke inhibition of polymers is achieved through use of fillers, additives, surface treatments and structural modifications. Fillers dilute the organic contents of the compound but affect physical properties of the polymers adversely. Surface coatings insulate the polymer substrate from direct attack of fire. Change in pyrolysates as well as the rate of combustion and pyrolysis can be achieved by polymer modification. Additives function both in gas and condensed phase processes, causing catalysis of soot oxidation and char formation.

Ferrocene, the first metal based organic (MBO) complex smoke suppressant, increases char formation but has the disadvantage of high vapour pressure and colour. Oxides and other compounds of transition metals are some of the smoke inhibitors used in PVC[4]. Bert *et. al.* have given a general discussion on smoke retarding PVC with a large variety of different metal compounds[5]. In assessing the relative merit of smoke inhibitor systems, the overall improvement of burning behaviour must be considered and hence the development of flame retardant smoke suppressants (FRSS) is an obvious solution. Polymer combustion involves thermal degradation of the solid materix to gaseous and liquid components. The gaseous components include combustion gases and smoke. The reaction of FRSS additives takes place at the interphase of the formation of volatile decomposition products. MBOs cause incandescence of char residue left after dehydrochlorination in the temperature range of 350-450°C causing formation of carbon monoxide and carbon dioxide which are normally formed at temperatures higher than 500°C for pure PVC[6]. An organic complex of chromium, was used as FRSS in the present study.

Experimental Procedure

Materials

All materials used were made in Japan unless specified.

(i) Virgin polyvinyl chloride resin
(ii) Dioctyl Azelate (DOZ)

Additives

(i) Complex lead stabiliser
(ii) Dibutyl tin dilaurate
(iii) Stearic acid (Merck, Germany)

Fillers

(i) Magnesium hydroxide
(ii) Calcium carbonate

Tris (2, 4 Pentanediono) Chromium III was synthesised using merck chemicals by standard method[7] and used as FRSS for the plasticised PVC used in the present study. Chemical compositions used for making PVC samples included: PVC (100 phr), DOZ (40 phr), complex lead stabiliser (3 phr), DBTDL (0.5 phr) and stearic acid (0.1 phr). In Set I magnesium hydroxide was used at 70 phr with the FRSS loadings of 0, 0.5, 1, 2 and 3 phr. The Set II had 50 phr of magnesium hydroxide and 20 phr of calcium carbonate as the filler, FRSS loading was the same as in Set I. Milling was done at 165-170°C followed by compression moulding at 175°C. Specimens of 100 mm × 100 mm were prepared and conditioned. Specimens were subjected to test conditions as per International Standardisation Organisation (ISO)[8] in horizontal orientation.

Results and Discussion

Specimens of plasticised PVC prepared as described earlier and a commercial fire retardant (FR) PVC were exposed to the irradiance levels of 30 and 40 KW/M^2 in a cone calorimeter. The effect of FRSS was studied on the Ignition time and Burning Rate, Heat Release and Generation of Combustion Products. The mixture of combustion gases in the duct was analysed for carbon monoxide, carbon dioxide, hydrocarbons and smoke.

Time of Ignition and Burning Rate—External ignition of specimens was accomplished by a spark plug located 13 mm above the center of the specimen. Time of ignition of different specimens indicate that ignition occurred earlier at 40 KW/M^2 than at 30 KW/M^2. Fire retardant PVC took considerably longer time for ignition to occur. The effect of FRSS on the time of ignition was small.

FRSS seems to have influenced the rate of burning of PVC. In Set I, at 30 and 40 KW/M^2, when magnesium hydroxide was used as filler along with 0.5 phr of FRSS the rate of burning was lowered by 20 and 33 per cent respectively. At 2 phr loading the rate of burning was further lowered; by a maximum of 43 per cent; at 40 KW/M^2. A maximum reduction of 45 per cent in burning rate was observed at 1 phr in Set II at an irradiance level of 40 KW/M^2. Thus the effect of FRSS in lowering the burning rate was more appreciable at higher irradiance level.

Heat Release—Heat release is a fundamental property of fire which is used for file hazard assessment. Rate of heat release (RHR) and the total heat release (THR) by the specimens were estimated. The results reported in Fig. 1 represent THR and the RHR of various compositions. At 30 KW/M^2, in Set I, THR increased with the increase in FRSS concentration upto 2 phr. In Set II the trend was reverse i.e. THR decreased continuously with increase in FRSS upto 2 phr and than increased at 3 phr. THR was nearly the same between 1 and 2 phr

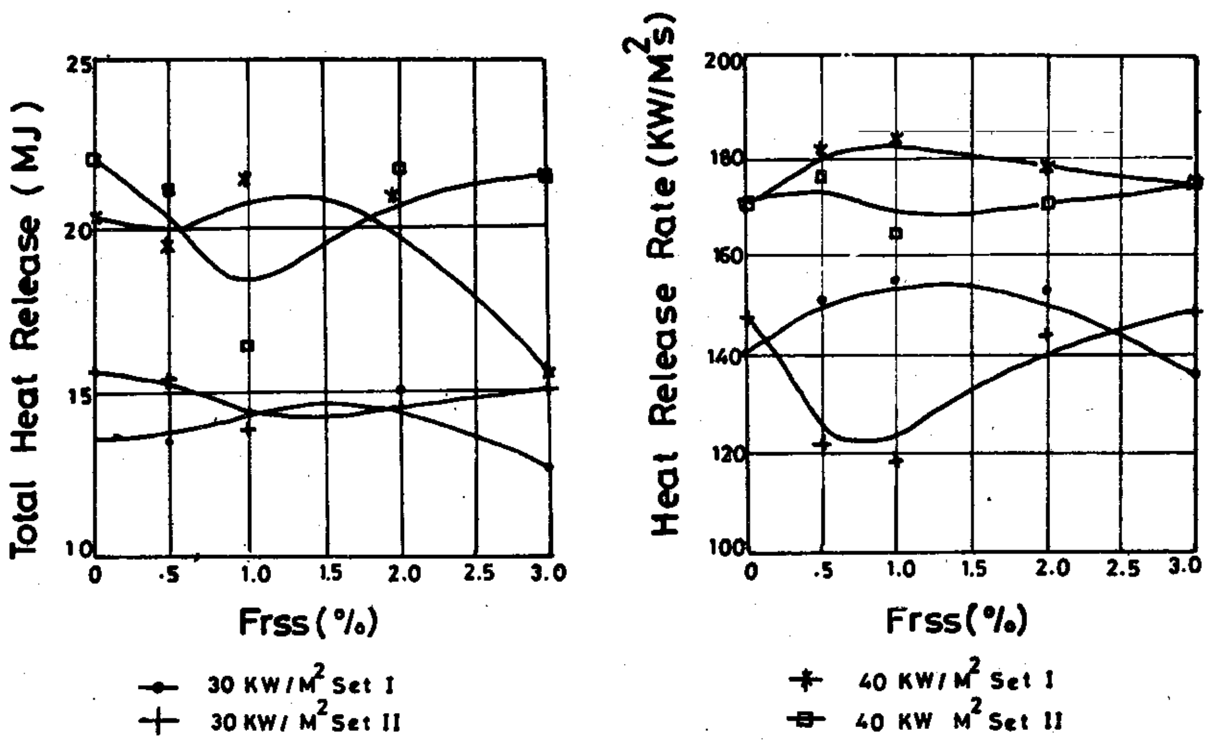

Fig. 1—Effect of FRSS on heat release

irrespective of the filler used. A similar trend was observed at 40 KW/M^2 though the THR in each case was comparatively higher as expected. Lowest RHR and THR were observed for 1 phr of FRSS in Set II for both the irradiance levels. It was observed that the type of filler used also had an influence on the heat release, $CaCO_3$ causing a lower RHR and THR. The heat release from FR PVC is given in (Table 1).

Gaseous Combustion Products and Smoke Generation—The gaseous combustion products monitored during combustion of specimens included oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2) and hydrocarbons (HC) (Figs 2a, b & c). The yield of combustion gases and smoke density (Fig. 2d) reported here are the 'peak values' obtained. Results of FR PVC are compared with the best results for Set I & II (Table 1).

The level of CO generated were of the order of 100 parts per million (ppm). The variations with respect to the FRSS loading and irradiance level were insignificant. At 30 KW/M^2 a steady decrease of 18.5 per cent in CO_2 was observed with increase in FRSS levels upto 3 phr for specimens of Set I, while in Set II a decrease of 28 per cent was observed at 0.5 phr but further addition of the FRSS caused a steady increase. The increased level of CO_2 in Set II may be attributed to the presence of $CaCO_3$. At 40 KW/M^2—a reduction of about 15 and 5 per cent for Set I and Set II respectively at 1 phr FRSS followed by a slow increase.

At 30 KW/M^2 oxygen level increased by about 50% upto 1 phr but than decreased slowly upto 3 phr of FRSS for Set I. However in Set II a decrease of about 20 per cent upto 1 phr was followed by an increase to the original level at 3 phr. The variations were minor for both the sets at 40 KW/M^2, i.e. a decrease from 3470 ppm to 3360 ppm for Set I, and a change from 3585 ppm to 3595 ppm in Set II.

Hydrocarbons showed a minimum value of around 46 ppm at 1 phr loading at 30 KW/M^2. At 40 KW/M^2 the values were nearly double (at 1 phr) which increased with FRSS loading for Set I but decreased in Set II (Fig 2).

Low values of smoke were observed when 1 phr of FRSS was used. However, the trends were slightly different for the two sets. At 30 KW/M^2 smoke density in Set I continuously decreased by 31% upto 2 phr followed by a slight increase at 3 phr. In Set II the decrease was by 16 per cent at 1 phr but a further addition of FRSS caused an increase in smoke density. Maximum smoke suppression at 30 KW/M^2 and 1 phr of FRSS in the two Sets was 21 and 16 per cent of FRSS.

Table 1—Comparative performance

Parameter	Irradiance level	FR PVC	Set I*	Set II*
Heat release rate	30 KW/M^2	176.7	154.4	118.2
(KW/M^2.s)	40 KW/M^2	165.6	182.3	164.0
Total heat release	30 KW/M^2	8.64	14.27	13.86
(MJ)	40 KW/M^2	8.03	21.36	16.29
Carbon monoxide	30 KW/M^2	250	99	150
(ppm)	40 KW/M^2	280	160	180
Carbon dioxide	30 KW/M^2	2000	2100	1800
(ppm)	40 KW/M^2	1700	2000	2600
Oxygen (ppm)	30 KW/M^2	3471	3000	2400
	40 KW/M^2	3300	3400	3400
Hydrocarbons	30 KW/M^2	199.6	46	46
(ppm)	40 KW/M^2	227	83	92
Smoke density	30 KW/M^2	6.54	1.59	1.86
(M^{-1})	40 KW/M^2	7.74	2.70	3.32

FR PVC Fire retardant poly (vinylchloride)
KW/M^2.s Kilowatt per meter square seconds
MJ Mega Joules
ppm Part per million
M^{-1} Meter inverse
* 1 phr of FRSS

At 40 KW/M^2 higher levels of smoke density were obtained for specimens of both sets. However, maximum smoke suppression was once again achieved at 1 phr for both the sets.

Conclusion

Chromium based MBO can be used as an effective FRSS at a loading of 1 phr. It was found to have given desirable results in terms of ignition time, burning rate, heat release, combustion gases as well as smoke density when used at this loading. Lower levels of smoke were obtained when $Mg(OH)_2$ was used alone as a filler. When compared to a commercially available FR PVC, though the FRSS caused a two fold increase in heat release it proved effective in generating lower levels of combustion products and upto 4.5 times lower smoke density.

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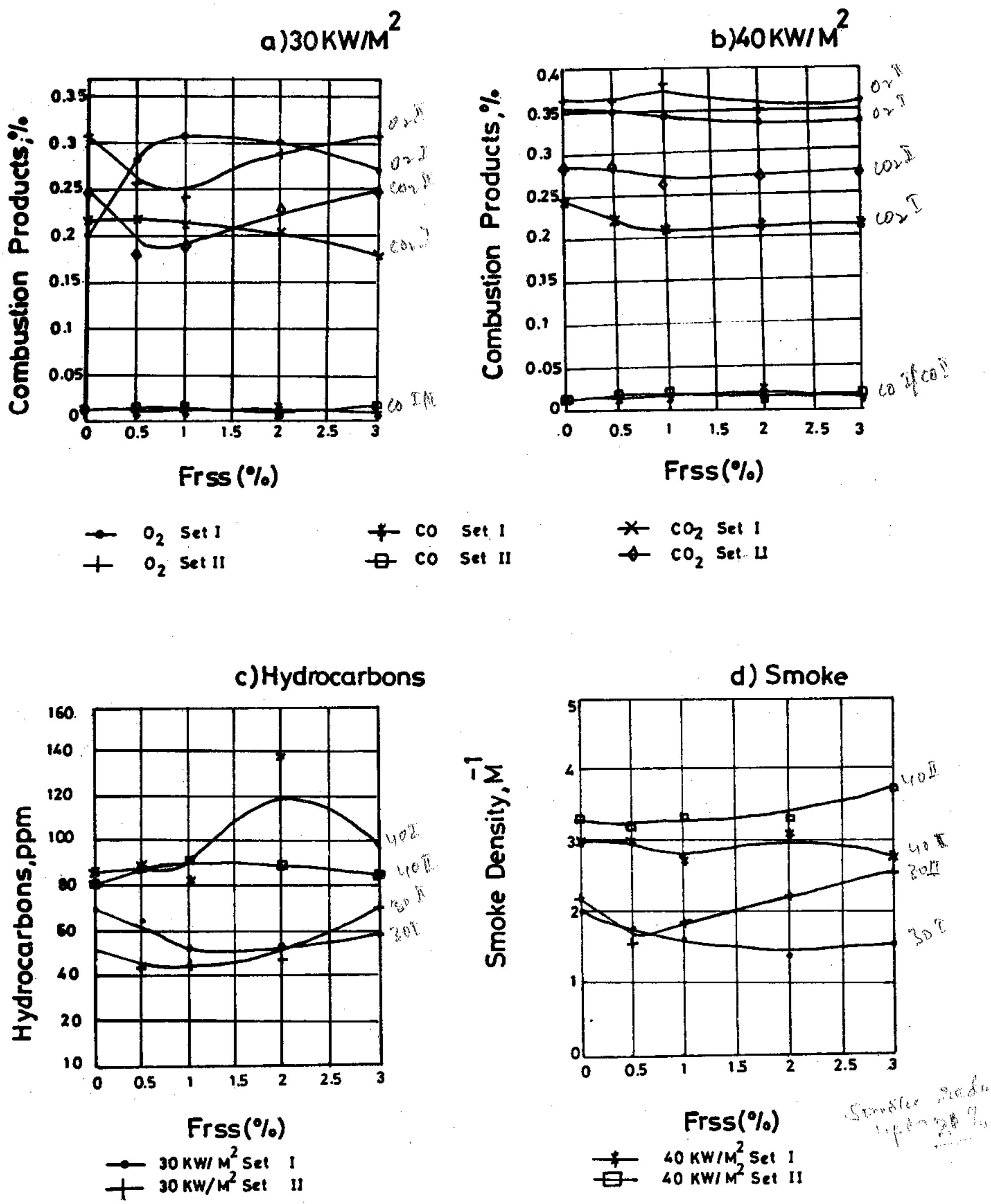

Fig. 2—Effect of FRSS on combustion products

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