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Smoke suppression for poly(vinyl chloride) by iron–organic polymer systems

Katuhiro Sekigawa [a], Hajime Yasuda [a,*], Hisashi Tamai [a], Akio Hiwara [b], Akira Nakamura [b], Hiroshi Sakai [c]

[a] Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724, Japan
[b] Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka 560, Japan
[c] Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima 724, Japan

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Abstract

Polyvinylferrocene mixed with poly(methyl methacrylate) or polystyrene (9 : 1 weight ratio) and 1,1'-dibenzylferrocene were found to exhibit efficient smoke-suppressing properties for low filler plasticized poly(vinyl chloride) at the 0.3–3.0 wt.% loading level of Fe. On heat treatment under argon, poly(vinyl chloride) homogenized with polyvinylferrocene produced predominantly α-Fe particles together with carbonization product, whereas in air α-Fe_2O_3 was formed preferentially without the formation of carbonization product.

Keywords: Poly(vinyl chloride); Smoke suppression; Iron particles; Poly(vinylferrocene)

1. Introduction

Smoke development in accidental fires is of importance as more human lives are lost in fire disasters through the effects of smoke and gas evolution than flame action. Pronounced flame-retardant and smoke-suppressing properties of ferrocene for a number of polymeric materials such as poly(vinyl chloride) (PVC) and polyurethane have been reported [1–4]. More recently, poly(ferrocene-1,1'-methylene) containing a ferrocene-1,3-methylene unit was found to exhibit good smoke-suppressing properties towards PVC and to reduce the smoke density by 25–85% at a 3% loading level [5]. These results indicate that polymeric ferrocene should be more effective than simple ferrocene as a smoke suppressant because these polymeric materials are hardly sublimed from the surface of resins on heat treatment of the sample. However, there has been no report on the smoke-suppressing properties of pendant-type polymeric ferrocene. In this work, we investigated the smoke-suppressing effects of several iron–organic polymers towards PVC.

2. Results and discussion

Polyvinylferrocene (itself and a 1 : 9 w/w mixture with poly(methyl methacrylate) or polystyrene), ferrocene, 1,1'-dibenzylferrocene, 1-hydroxyethylferrocene, (1,4-diphenylbutadiene)$Fe(CO)_3$ and iron phthalocyanine were tested as smoke suppressants for high or low plasticized PVC. These materials were mixed well in a Plast-Mill at 170°C to give iron contents of 0.3–1.0 wt.%. A mixture of poly(methyl methacrylate) (poly(MMA)) or polystyrene (poly(St)) with polyvinylferrocene could be efficiently homogenized with PVC because of their good miscibility, whereas homogenization of ferrocene and iron phthalocyanine failed because fine crystals separated out when the samples were cooled to ambient temperature.

The amount of smoke emitted was measured directly by weighing the char adsorbed on the glass filter used for smoke capture. On the supposition that in an accidental fire commercial samples are heated prior to starting the fire, all the samples were burned after preheating to 600°C.

The results of the smoke suppression are summarized in Table 1 for a variety of iron-containing resins that were burned after preheating at 600°C for 10 s. The use

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[*] Corresponding author.

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Table 1
Smoke suppression by iron compounds

Fe additive	Amount of smoke ($mg\ g^{-1}$ PVC)
poly(MMA)–polyvinylferrocene/(9 : 1)	25
1,1′-Dibenzylferrocene	26
poly(St)–polyvinylferrocene/(9 : 1)	32
1-Hydroxyethylferrocene	35
Ferrocene	38
$(PhCH{=}CHCH{=}CHPh)Fe(CO)_3$	41
Polyvinylferrocene	42
Iron phthalocyanine	50
None	90

Fe 0.3%, burned after holding the sample at 800°C for 10 s.

of a mixture of poly(MMA) with polyvinylferrocene, a mixture of poly(St) with polyvinylferrocene and 1,1′-dibenzylferrocene were found to be more effective than ferrocene and iron phthalocyanine for reduction of smoke generation. The amount of smoke emitted varies depending on the preheating period and is decreased by prolonging the preheating period (Fig. 1).

After heating for 30 s, the chlorine content decreased to 3% in the case of PVC mixed with polyvinylferrocene, whereas for metal-free PVC it decreased to 35%. Hydrogen chloride gas evolves in this step. The ratio of hydrogen chloride to chlorine was 92 : 8, as revealed by the mass spectrum.

In order to elucidate the mechanism of the smoke suppression, carbonization yields for the iron-containing PVC (1 wt.%) were measured at 400 and 1000°C in air or argon with heat treatment for 4 h. In argon at 400°C, the carbonization yield for iron-free low filler plasticized PVC was 26% whereas those for iron-containing materials increased to 35–41% with increase in iron content (Fig. 2). This means that the carbonization is accelerated by the catalytic action of the generated iron component. At 1000°C, the carbonization yield for iron-free low filler plasticized PVC was 16% whereas those for iron-containing PVC, especially PVC containing a mixture of poly(MMA) or poly(St) with polyvinylferrocene, increased to 20–23% in proportion to the iron content (0.3–3.0%) (Fig. 3). With respect to the effect of the iron component on the carbonization yield, the catalytic action of ultrafine α-Fe particles in graphitizing the carbon has already been reported in the pyrolysis of polyacrylonitrile [6,7]. Thus, the order of carbonization yields observed at 1000°C is comparable with the degree of smoke suppression by iron-containing samples. This result suggests that the larger the carbonization yields become, the greater is the smoke suppression that occurs in an argon atmosphere.

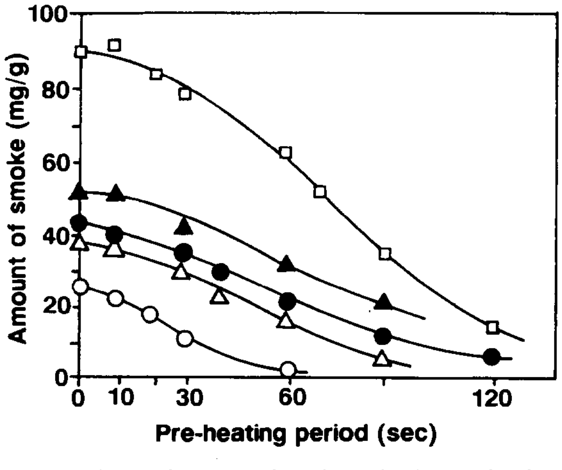

Fig. 1. Dependence of amount of smoke emitted on preheating time at 600°C at 0.3% loading level. (○) Poly(MMA)–polyvinylferrocene (9 : 1); (△) ferrocene; (●) polyvinylferrocene; (▲) iron phthalocyanine; (□) no additive.

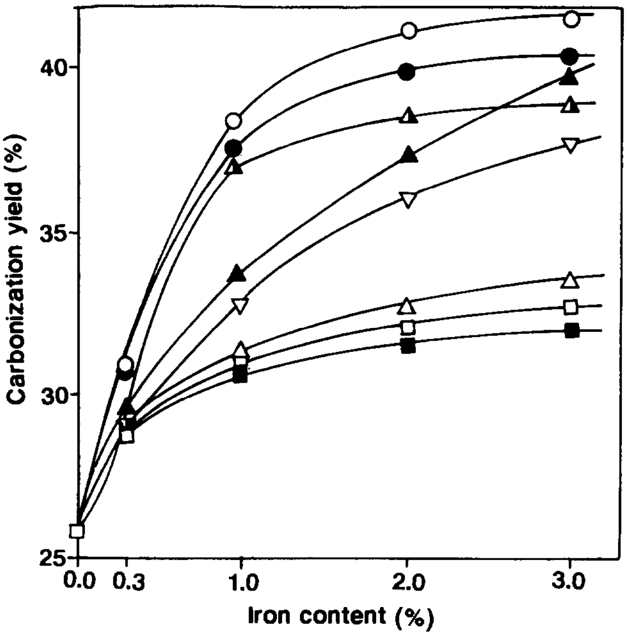

Fig. 2. Carbonization yield of PVC containing iron derivatives (1.0 wt.%) in argon at 400°C. (∅) Poly(MMA)–polyvinylferrocene; (●) poly(St)–polyvinylferrocene; (▲) iron phthalocyanine; (▲) 1-hydroxyethylferrocene; (▽) 1,1′-dibenzylferrocene; (△) ferrocene; (□) polyvinylferrocene; (■) $(PhCH{=}CHCH{=}CHPh)Fe(CO)_3$.

X-ray analysis of the carbonaceous product resulting after heat treatment of PVC containing a mixture of poly(MMA) and polyvinylferrocene (1 wt.%) at 1000°C in an argon revealed the formation of α-Fe, Fe_3C and a ferrocene derivative in the ratio 8 : 1.5 : 0.5, whereas the ratio obtained from the Mössbauer spectrum was 7 : 1 : 2; this difference may arise from the formation of an amorphous ferrocene derivative, which is detectable by Mössbauer spectroscopy. At 400°C, the formation of $FeCl_2 \cdot 4H_2O$ and $FeCl_3$ was detected by X-ray spectrometry, with a ratio of 3 : 1, whereas the Mössbauer spectrum indicated the remaining ferrocene moiety and $FeCl_2 \cdot 4H_2O$–$FeCl_3$ in a ratio of 9 : 1.

A similar phenomenon was also observed in the case of high filler plasticized PVC containing polyvinylferrocene (1 wt.%) in argon. The carbonization yield at 400°C (24%) was larger than the 21% observed with low filler plasticized PVC and the carbonization yield at 1000°C (19%) was larger than the 16% observed for low filler plasticized PVC. The addition of polyvinylferrocene and ferrocene to the resin (1 wt.%) resulted in an increased carbonization yield (22–24%) at 1000°C, whereas the order was reversed at 400°C, with the formation of the carbonaceous products in 20% yield from the high filler plasticized PVC mixed with $(PhCH{=}CHCH{=}CHPh)Fe(CO)_3$ and iron phthalocyanine.

In contrast to the result of heat treatment in argon, pyrolysis in the air for 30 min resulted in lower carbonization yields. At 400°C, the low filler plasticized PVC containing 3% polyvinylferrocene gave only a 12.8% carbonization yield whereas iron-free low filler plasticized PVC produced 28.7% carbonaceous material.

These results indicate that the iron component accelerated the evolution of volatiles from the PVC surface in air at 400°C, that is, the PVC surface exposed to air decomposed quickly by releasing volatile components. At 1000°C, the carbonization yield of iron-containing PVC was only 1.0% whereas that of metal-free PVC was as low as 0.01%. The X-ray analysis of the air-oxidation products at 400 and 1000°C shows α-Fe_2O_3 in line with Mössbauer spectral analysis.

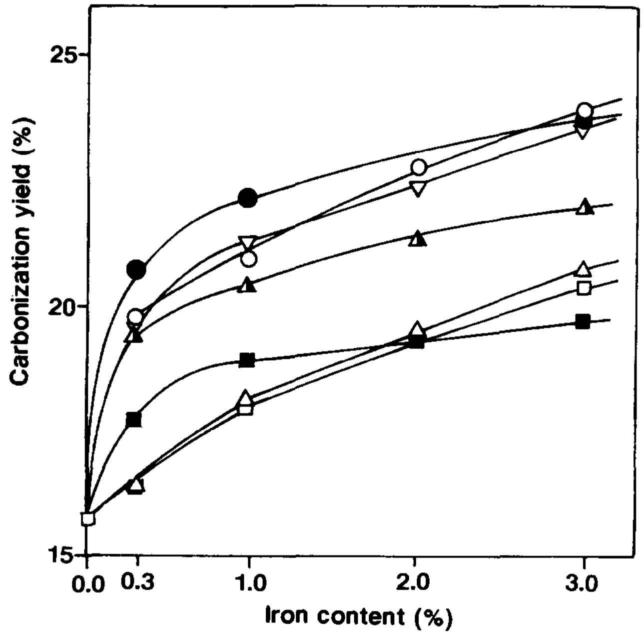

Fig. 3. Carbonization yield of PVC containing iron derivatives (1.0 wt.%) in argon at 1000°C. (○) Poly(MMA)–polyvinylferrocene; (●) poly(St)–polyvinylferrocene; (▽) iron phthalocyanine; (▲) 1-hydroxyethylferrocene; (△) ferrocene; (□) polyvinylferrocene; (■) $(PhCH{=}CHCH{=}CHPh)Fe(CO)_3$.

Table 2

Smoke suppression effect of poly(methyl methacrylate)–poly(vinylferrocene) (9:1 ratio) for various polymers

Polymer	Smoke suppression (%)
poly(vinyl acetate) (M_n = 185 000)	73
poly(vinyl chloride) (M_n = 38 000, low filler)	71
poly(vinyl alcohol) (M_n = 31 000)	70
polyacrylonitrile (M_n = 86 000)	50
Poly(1,2-butadiene) (M_n = 25 000)	39
ABS resin (16:32:52 ratio)	35
Poly(1,4-butadiene)(*cis*, M_n = 250 000)	20
AB resin (acrylonitrile 31%)	12
Polystyrene (atactic, M_n = 55 000)	5

Fe content of each polymer = 0.3 wt%.

On the basis of these results, we can conclude that the inner part of PVC is carbonized by the action of α-Fe particles and the surface of the PVC evolves gaseous products by the action of the iron component releasing α-Fe_2O_3, resulting in smoke suppression.

As an extension of the present method, the smoke-suppressing properties of a 9:1 mixture of poly(MMA) with polyvinylferrocene (0.3 wt.%) was measured for a variety of polymer materials. The smoke suppression (%) is represented by the ratio of char deposited through burning the iron-containing PVC to that of iron-free PVC. Poly(MMA)–polyvinylferrocene was again effective for the smoke suppression of poly(vinyl alcohol), poly(vinyl acetate) and polyacrylonitrile but was ineffective for poly(St) and AB resin (Table 2).

3. Experimental

Polyvinylferrocene was prepared by using azobisisobutyronitrile as initiator in toluene at 70°C (M_n = 45 000) and was mixed with poly(methyl methacrylate) (M_n = 51 000) or polystyrene (M_n = 55 000) in a ratio of 1:9. Ferrocene and iron phthalocyanine (Aldrich) were purchased from Wako Pure Chemicals and used without furthur purification. ^{57}Fe Mössbauer spectra were taken in standard transmission geometry at 77 K in vacuo with ^{57}Co in a Rh source. Data acquisition was performed with a microcomputer, and the resulting spectra were best fitted with lorentzian curves. X-ray diffraction data were collected on a Rigaku RAD-R diffractometer at 1.2 kW with graphite monochromatized Cu Kα radiation.

The carbonization yield was calculated as the weight ratio of residual carbon material after heat treatment to the initial polymer. The chlorine content of the polymeric material was determined by the AgCl method at the Analytical Centre, Osaka University.

3.1. Low filler plasticized PVC

This resin was purchased from Sunallow Chemical in powder form and thoroughly homogenized with the various of iron materials using a double screw-type mixer (Toyo Seiki Plast-Mill) at 170°C for 1 h, the concentration of the latter being 0.3, 1.0 and 3.0% by weight of resin. The contents of resin were PVC 100, dioctyl phthalate 1.0, MBS 3.0, dibutyltin dialkylmaleate 3.0 and aliphatic ester 0.3 wt.%. The individual batches were compression moulded into flat sheets of nominally 1.5 mm thickness and cut into small strips (200 mg). An iron-free polymeric material was prepared identically as described above.

3.2. High filler plasticized PVC

The resin containing PVC 100, dioctyl phthalate 70, calcium carbonate 20, antimony oxide 200, and dibutyltin dialkylmaleate 6 wt.%, purchased from Sunallow Chemical, was homogenized with the iron compound using the Plast-Mill at 150°C for 15 min. Individual batches were compression moulded by the same method as described above.

3.3. Capture of smoke

The char adsorbed on a glass filter (Advantec GF) of diameter 75 mm was weighed after burning the sample (100 mg). The filter was set in a filter holder and exhausted at the rate of 4 ml min^{-1}. The sample was placed in a flat alumina boat and the combustion tube was preheated to 600°C. Then all the samples were burned.

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