

Environmentally Safe Fire Retardants for Polymeric Materials - I. Silica Gel - Potassium Carbonate Additive.

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ABSTRACT

We report here that silica gel combined with potassium carbonate is an effective fire retardant for a wide variety of common polymers such as polypropylene, nylon, polymethylmethacrylate, poly (vinyl alcohol), cellulose, and to a lesser extent for polystyrene and styrene-acrylonitrile. The rate of heat release, RHR, is reduced by up to 68% without increasing the smoke or carbon monoxide levels during the combustion.

KEYWORDS: Char, Silica gel, Flammability.

1. INTRODUCTION

An alternative to the use of halogenated fire retardants, which control flammability by changing the chemistry in the flame (1), is to control polymer flammability by manipulating the condensed phase chemistry. Additives that increase the amount of charcoal-like residue or carbonaceous char that forms during polymer combustion are very effective fire retardants (2). However, very little is understood about the detailed structure of char or how it forms. Our research efforts focus on reducing polymer flammability by promoting char formation through manipulation of the condensed phase decomposition chemistry. Char formation reduces the amount of small volatile polymer pyrolysis fragments, or fuel, available for burning in the gas phase; this, in turn reduces the amount of heat released and feedback to the polymer surface. The char also insulates the underlying virgin polymer, due to the char's low thermal conductivity. It also traps decomposition products and reradiates energy away from the polymer. The physical structure of the char is important in this role. Foamy char structure appears to be more fire resistant than brittle, thin char. This char enhancing approach is most successful when the polymer chars rapidly and early in the burning process (3). To be useful

the charring process must be designed so that it occur between the processing temperature and the polymer's T_{dec} . Our approach to char promotion is to investigate additives which enhance charring and to gain a fundamental understanding of the additives mechanism of char formation with the goal of optimizing the additives performance. Recent studies of the flammability of polymers containing silicon based materials have shown these materials to be promising fire retardants, either as additives, in blends with organic polymers or in copolymers (4,5). This paper reports on the effect that silica gel and potassium carbonate additives have on polymer flammability.

2. EXPERIMENTAL

Polymers and additives (6): Silica gel (Fisher Scientific Co., 28-200 mesh), potassium carbonate, K_2CO_3 (Mallinckrodt, granular) polypropylene, PP (Scientific Polymer Products, Inc., $M_w = 240,000$ g/mole), polystyrene, PS (Scientific Polymer Products, Inc., $M_w = 45,000$ g/mole), styrene-acrylonitrile, SAN (GE Polymers), polymethymethacrylate, PMMA (Du Pont, Elvacite), poly(vinyl alcohol), PVA (Scientific Polymer Products, Inc., $M_n = 86,000$ g/mole, $M_w = 178,000$ g/mole, 99.7% hydrolysed via $NaOH_{aq}$ method), nylon 6,6 (Rhône Poulence) and alpha cellulose (Sigma Chemical Co., fiber, 99.5%) were all used as received. Limiting Oxygen Index, LOI: Oxygen index tests were carried out on 50 mm long by 3 mm diameter rods. The polymers and additives were mixed in powder form in a blender and were extruded from a three stage lab scale (100g) extruder. Cone Calorimeter: Evaluation of polymer and polymer/additive flammability was done using the Cone Calorimeter. Rate of heat release and heat of combustion data can be expected to be good to within 5%, the CO and soot yield data can be expected to be good to within 10%. The additives were mixed with the polymers by grinding the powders together in a mortar and pestle. Cone samples were prepared by compression molding the powdered samples (40-55g) into 75 mm x 7-8 mm disks. A Carver press with a heated mold was used (~22 MPa (10 tons) held for 3-5 minutes at 150°C or T_g).

3. RESULTS AND DISCUSSION

3.1 Polypropylene. Polypropylene like PE and polystyrene, PS, when ignited burn rapidly, completely and leave little or no char (7). Reducing the flammability of these inherently non-charring polymers through char enhancement presents a particular challenge. In the process of systematically evaluating additives expected to enhance char formation, we found that silica gel when combined with potassium carbonate not only increased char yields but also reduced the flammability of a variety of aliphatic polymers. Figure 1 shows rate of heat release data, i.e., the R.H.R. curve for PP and a PP/silica gel/ K_2CO_3 (90/6/4) mixture, from the Cone Calorimeter. The R.H.R. has been shown to be the most important parameter for predicting fire hazard (8). The presence of the silica gel/ K_2CO_3 additives reduces the peak R.H.R. by 58% and reduces the total heat released by 28%. The R.H.R. curve shows the double maxima characteristic of a material that forms a char layer during combustion.(4,9) The presence of the silica gel/ K_2CO_3 additives in PP produces a residue yield of 19%. The residue is at least 47% carbonaceous material if we assume that all the additives survived the combustion in the Cone calorimeter and are contained in the residue. The yield of carbonaceous char therefore is ~ 10% (see Table 1).

The fact that the CO yield and soot (specific extinction area) are not significantly effected by silica gel /K₂CO₃ additives supports this view. The CO yield results are shown in figure 3, and indicate an advantage these additives may have relative to halogenated and phosphorous based additives, which commonly tend to increase CO yield and soot but are used in higher concentrations to obtain similar results. The Cone Calorimeter results for PP are summarized in Table 1 along with the data for several other polymers we examined.

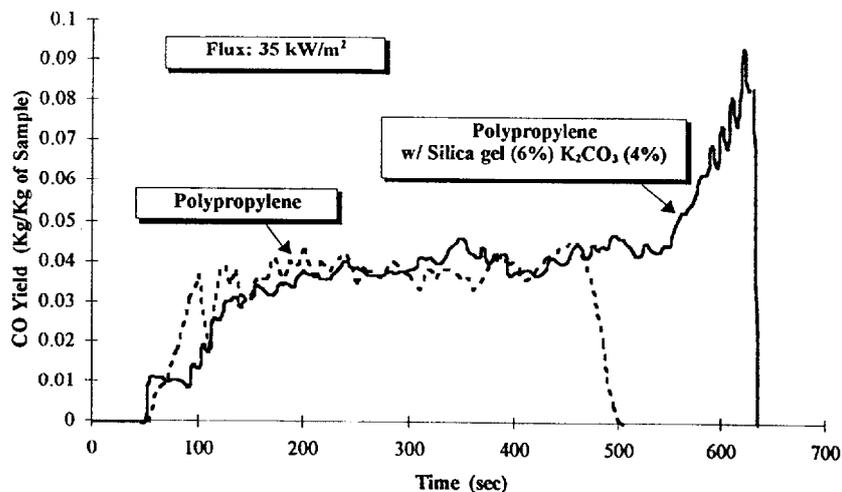


Fig. 3. The carbon monoxide yields for PP (at 35kW/m²) and PP/silica gel /K₂CO₃ (90/6/4 ratio) are very similar except at the end of the combustion where very small mass losses may be artificially raising the CO level, or since the sample surface is not completely covered by the flame the hot char residue may be generating CO through incomplete oxidation.

3.2 Polystyrene. The effect that silica gel/K₂CO₃ has on the flammability of polystyrene, PS, is shown in Table 1. The results are similar, but reduced in magnitude, to those for PP. The silica gel /K₂CO₃ additives cause the otherwise non-char-forming PS to have a char yield of 6% (16% residue yield). The additives reduce the rate of heat release by 31%, reduce the total heat release by 11% and, as was the case for PP, had little effect on the CO yield and smoke.

3.3 Polymethylmethacrylate. The Cone calorimeter results for PMMA are also shown in Table 1. PMMA is an inherently non-char-forming thermoplastic polymer, however, using less than half the usual amount of additives, the reduction in flammability was comparable to PP and PS. Even at this low level (3% silica gel, 1% K₂CO₃) the additives generated a 15% carbonaceous char (24% residue yield). The rate of heat release was reduced by 42%, the total heat release was reduced by 28%, and like PP and PS there was no effect on smoke. The CO yield, however was somewhat higher in the presence of the additives. It is reasonable to expect that if the additives were used at the loadings used for PP and PS then the reduction in PMMA's flammability would meet or exceed that of PP.

The efficacy of the additives in each of these inherently non-char-forming thermoplastic polymers (PP, PS, and PMMA) depends on the polymer (PP ≈ PMMA > PS). It is not clear what polymer property is responsible for the different behavior. This is also true for the

inherently char-forming polymers we examined (PVA > cellulose > SAN) (see below).

Table 1. Cone Calorimetry Data

Sample disk 75mm x 8mm	Char Yield (%)	LOI (%)	Peak RHR (Δ) (kW/m ²)	Mean RHR (kW/m ²)	Mean Heat of Combustion (MJ/kg)	Total Heat Released (MJ/m ²)	Mean Ext. Area (m ² /kg)	Mean CO yield (kg/kg)
PP	0	-	1,761	803	37.9	357	689	0.04
PP w/ 6%SG & 4%PC	10	-	736 (58%)	512	33.1	297	710	0.04
PS	0	18	1,737	1,010	24.6	277	1,422	0.07
PS w/ 6%SG & 4%PC	6	24	1,190 (31%)	725	24.7	246	1,503	0.07
PMMA	0	18	722	569	23.1	319	210	0.01
PMMA w/ 3%SG & 1%PC	15	25	420 (42%)	246	20.9	231	199	0.05
PVA	4	-	609	381	17.0	221	594	0.03
PVA w/ 6%SG & 4%PC	43	-	194 (68%)	114	12.4	101	201	0.03
Cellulose	4	-	310	161	11.3	101	27	0.02
Cellulose w/ 6%SG & 4%PC	32	-	149(52%)	71	5.3	34	20	0.04
SAN	2	-	1,499	837	25.2	197	1,331	0.07
SAN w/ 6%SG & 4%PC	3	-	1,127 (25%)	772	23.0	169	1,301	0.06
Nylon 6, 6	1	30	1,131	640	23.2	108	234	0.02
Nylon 6, 6 w/ 3%SG & 2%PC	5	33	526 (53%)	390	22.0	105	171	0.02
Nylon 6, 6 w/ 6%SG & 4%PC	6	30	546 (52%)	370	23.5	102	185	0.02

SG = Silica Gel, PC = K₂CO₃

3.4 Poly(vinyl alcohol). PVA is one of the few linear non-halogenated aliphatic polymers that has a significant char yield (3-5%) when burned. The flammability properties of PVA, the structure of the char and the processes by which it forms have been studied previously in our group (10). The Cone calorimeter results for PVA are shown in Table 1. Silica gel/ K₂CO₃ has a stronger effect on the flammability of PVA than on any of the other polymers we studied. The additives generated a 43% carbonaceous char (49% residue yield). The peak RHR was reduced by 68% and the total heat release was reduced by 54%. Furthermore, in contrast to the results for PP, PS, and PMMA: the heat of combustion was reduced by 27%; the CO yield was unchanged and the smoke was reduced by 66%!

3.5 Cellulose. Cellulose like PVA gives a measurable char yield when combusted (3-4%) and in view of the promising results seen for PVA, and since cellulose is a commercially important polymer, we examined the effect silica gel/ K₂CO₃ additive had on cellulose flammability properties. The results are shown in table 1. Cellulose, in the presence of the additives, like

PVA showed a significant increase in the amount of carbonaceous char, 32% (39% residue yield). The peak RHR was reduced by 52%, and the total heat release was reduced by 66%. Again, in contrast to the results for PP, PS, and PMMA: the heat of combustion was reduced by 53%. The CO yield was increased by ~50%; and the smoke was decreased by 26%.

3.6 Styrene acrylonitrile. The Cone calorimeter results for styrene acrylonitrile, SAN, are also shown in Table 1. The effect of the additives on the flammability of SAN was only moderate, much the same as PS. This was somewhat surprising since SAN is an inherently char-forming polymer. For the SAN we studied the char yield was ~2% for the combustion of the pure polymer and only ~3% in the presence of the additives. As we observed here and in other cases controlling the flammability of styrene and styrene copolymers is difficult.

3.7 Oxygen Index. We also measured the effect of the additives on the oxygen index of PMMA, PS and nylon 6,6. The results, similar to those found for PMMA and PS using the Cone calorimeter, are shown in Table 1.

3.8 Mechanism. A discussion of the original approach proposed for this additive system may shed some light on how these additives reduce polymer flammability. Our original intention in using silica gel with K_2CO_3 was to devise methods of *in situ* formation of silicon based fire retardants, during the combustion. The reaction of silica gel and organic alcohols in the presence of metal hydroxides has been shown to give multicoordinate organosilicate compounds (11). Instead of synthesizing these materials and then combining them with various polymers to evaluate their effect on polymer flammability properties, we envisioned the reaction occurring during the combustion, i.e., in the condensed phase of the pyrolyzing polymer beneath the burning surface, by combining a polyhydroxylic polymer, e.g. PVA or cellulose, with silica gel and K_2CO_3 (a weaker base but a more palatable additive than a metal hydroxide). If the indicated reaction occurred between the polymer and the additives it should crosslink the polymer, as shown in figure 4., and might assist in forming a silicon-oxy-carbide, SiOC, type protective char during combustion.

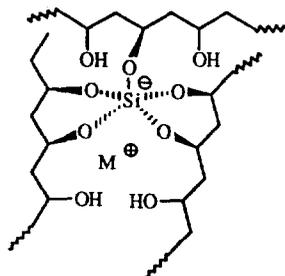


Fig. 4. Pentacoordinate organosilicate crosslinked PVA.

It is not likely, however, that this is how the additives affect flammability reduction in the non-hydroxylic polymers such as PP, PS, SAN, and PMMA.

An alternative mechanism of action for these additives is through the formation of a potassium