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FIRE RETARDANT ADDITIVES FOR POLYMERIC MATERIALS - I. CHAR FORMATION from SILICA GEL - POTASSIUM CARBONATE

Jeffrey W. Gilman,* Steven J. Ritchie, Takashi Kashiwagi
Materials Fire Research Group, Building and Fire Research Laboratory,
National Institute of Standards and Technology, Gaithersburg, Maryland 20899
and
Sergey M. Lomakin
Institute of Biochemical Physics,
Russian Academy of Sciences, Moscow, Russia

ABSTRACT

Silica gel combined with potassium carbonate is an effective fire retardant for a wide variety of common polymers (at only 10 wt. % total additive) such as polypropylene, nylon, polymethylmethacrylate, poly (vinyl alcohol), cellulose, and to a lesser extent polystyrene and styrene-acrylonitrile. The peak heat release rate is reduced by up to 68% without significantly increasing the smoke or carbon monoxide levels during the combustion.

INTRODUCTION

An alternative to the use of halogenated fire retardants, which control flammability by changing the chemistry in the flame¹ 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 retardants². 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 process³. To be useful the charring process must be designed so that it occur between the processing temperature and the polymer decomposition temperature. Our approach to char promotion is to investigate additives which enhance charring and to gain a fundamental understanding of the additive's mechanism of char formation with the goal of optimizing the additive's 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.

EXPERIMENTAL

Polymers and additives⁶: Silica gel (Fisher Scientific Co., 28-200 mesh), potassium carbonate, K₂CO₃ (Mallinckrodt, granular) polypropylene, PP (Scientific Polymer Products, Inc., Mw = 240,000 g/mole), polystyrene, PS (Scientific Polymer Products, Inc., Mw 45,000 g/mole), styrene-acrylonitrile, SAN (GE Polymers), polymethylmethacrylate, PMMA (Du Pont, Elvacite), poly(vinyl alcohol), PVA (Scientific Polymer Products, Inc., Mn = 86,000 g/mole, Mw = 178,000 g/mole, 99.7% hydrolysed via NaOHaq method), nylon 6,6 (Rhone Poulence) and alpha cellulose (Sigma Chemical Co., fiber, 99.5%) were all used as received.

Cone Calorimeter: Evaluations of polymer and polymer/additive flammability were done using the Cone Calorimeter⁷. Rate of heat release and heat of combustion data are good to within 10%. The

carbon monoxide and soot yield data are good to within 10%. The tests were done at an incident heat flux of 35 kW/m² using the cone heater. 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 g-55 g) into 75 mm x 7-8 mm disks using a Carver press with a heated mold (~22 MPa (10 tons) held for 3-5 minutes at 150 °C or at T_g).

Gasification apparatus: Figure 5 is a schematic diagram of a radiative gasification apparatus. This facility is physically similar to the Cone calorimeter (identical samples, cone heater system, etc.) except that the tests are carried out in a controlled, oxidized-free (nitrogen) atmosphere. This apparatus allows study of the condensed-phase processes decoupled from the influence of gas phase combustion and heat feedback. This is achieved using fire-like incident heat fluxes of 20 to 70 kW/m² from the cone heater. In a typical experiment thermocouples are imbedded into the exposed and backside sample surfaces to monitor the temperatures at which the pyrolysis and decomposition processes are occurring. A load cell gives mass loss rate data which can be compared to that from the Cone calorimeter experiments.

Nuclear Magnetic Resonance (NMR): Solid State ¹³C NMR characterization utilized techniques of cross polarization ⁸ (CP) and magic angle spinning (MAS) (25 MHz, 4kHz MAS, 1 ms CP time, 3 sec rep. time). In the interrupted decoupling experiments the decoupler was turned off for 40 ms prior to acquisition with decoupling ^{9,10}.

Oxygen Index, OI: 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 (100 g) extruder.

RESULTS AND DISCUSSION

CONE CALORIMETER

Thermoplastic Polymers

Polypropylene

Polypropylene, like PE and polystyrene, PS, when ignited burns rapidly, completely and leaves little or no char¹¹. Reducing the flammability of 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 heat release rate data for PP and a PP/silica gel/K₂CO₃ (90/6/4) mixture, from the Cone Calorimeter. The peak heat release rate has been shown to be the most important parameter for predicting fire hazard. The presence of the silica gel/K₂CO₃ additives reduces the peak heat release rate by 58% and reduces the total heat released by 28%. The rate of heat release curve shows the double maxima characteristic of a material that forms a char layer during combustion¹². The presence of the silica gel/K₂CO₃ 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). All char yields in Table 1 and in the following discussion are corrected for the presence of additive in this manner and are therefore carbonaceous char yields. It appears that the char that forms during the combustion reduces the rate at which fuel is released into the gas phase, this reduction in mass loss rate reduces the rate of heat release.

Unlike halogenated additives silica gel /K₂CO₃ does not significantly effect the specific heat of combustion when added to PP, as seen in figure 2. Furthermore, the CO yield and soot (specific extinction area) are not significantly effected by silica gel /K₂CO₃ additives. This indicates that these additives most likely act primarily in the condensed phase not in the gas phase.

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 and are typically 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.

Polystyrene

The effect that silica gel/ K_2CO_3 has on the flammability of PS is shown in Table 1. The results are similar, but reduced in magnitude, to those for PP. Use of silica gel / K_2CO_3 additives cause the otherwise non-char-forming PS to produce 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 similar to PP, had little effect on the CO yield and smoke.

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% K_2CO_3) 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 \approx PMMA > PS). It is not clear what polymer property (Mw, functionality, decomposition mode, etc.) is responsible for the different behavior. This is also true for the inherently char-forming polymers we examined (PVA > cellulose > SAN). These results are discussed below.

Char Forming Polymers

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 previously¹³. The Cone calorimeter results for PVA are shown in Table 1. Silica gel/ K_2CO_3 has a stronger effect on the flammability of PVA than on any other polymer studied. The additives generated a 43% carbonaceous char (49% residue yield). The peak heat release rate 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%!

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, its flammability properties were examined in the presence of silica gel/ K_2CO_3 additive. 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 heat release rate 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%, primarily from incomplete oxidation at the end of the combustion (ca. Fig. 3); and the smoke was decreased by 26%.

The results for PVA and cellulose indicate a combination of condensed phase mechanisms of

action. In addition to the enhanced charring effect and the resulting reduction in mass loss rate, the additives may also be increasing the rate of H₂O elimination from cellulose and PVA. This dilution of the combustible gases may be responsible for the reduction in the specific heat of combustion.

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 studied the char yield was ~2% for the combustion of the pure polymer and only ~3% in the presence of the additives. As seen here and in other cases controlling the flammability of styrene and styrene copolymers is difficult.

OXYGEN INDEX

We also measured the effect of the additives on the oxygen index of PMMA, PS and nylon 6,6. The results are shown in Table 1. The trend in oxygen index response for these polymers is similar to the trend in the peak and average heat release rate data from the Cone calorimeter. Costa and Camino report similar results in their comparison between Cone calorimeter and traditional tests (oxygen index, glow wire test, etc.) for polypropylene with additives or fillers¹⁴.

RADIATIVE GASIFICATION

Figure 6 shows the mass and mass loss rate data for an experiment aimed at determining the influence of the additives on the decomposition processes. The slope of the mass loss curve for PMMA w/ silica gel and K₂CO₃ (95:4:1) first begins to differ from that for pure PMMA at ~ 80 sec. A video of the pyrolysis experiment reveals that the PMMA begins to char at this time. The thermocouple embedded in the top surface of the sample shows that the temperature is 360 °C - 440 °C at this time. This data shows that the silica gel/ K₂CO₃ additives affects charring of the PMMA early in the decomposition process and at temperatures as low as 360 °C. This is similar to the results of Benbow where fumed silica reduced the smoke by forming a sintered silica surface layer at temperatures as low as 447 °C¹⁵.

CP/MAS ¹³C NMR CHARACTERIZATION

The chars of PVA with silica gel / K₂CO₃ (90:6:4) and PVA with silica gel only (90:10) isolated following the combustion in the Cone calorimeter, were analyzed using several solid state ¹³C NMR techniques. The spectra are shown in Figures 7 and 8 for the PVA with silica gel only (90:10) char and for the PVA with silica gel / K₂CO₃ (90:6:4) char, respectively. The normal CP/MAS ¹³C NMR, shown in the middle of Figure 7, contains a broad resonance in the aromatic-olefinic region from 110 ppm to 150 ppm and two weaker broad signals in the aliphatic region, one centered at 20 ppm and the other at 35 ppm. This spectrum shows that the ratio of aromatic-olefinic (sp²) carbon to aliphatic (sp³) carbon is ~ 3:1. However, due to the uncertainty associated with quantitative measurements of the intensities of ¹³C signals in CP/MAS experiments of hydrogen depleted carbonaceous materials and of materials which may contain significant concentrations of paramagnetic centers (e.g., unpaired electrons, ie., free radicals) this spectrum may only be representative of a fraction of the carbons present in the char^{16,17}. Carbons which are less than 0.5 nm from protons make the largest contribution to this signal. Within this limitation, the fraction of the cross-polarized signal arising from protonated versus non-protonated carbons can be analyzed quantitatively. An interrupted decoupling (ID)-CP/MAS spectrum of this char, shown in the bottom spectrum in Figure 7, reveals only the non-protonated carbons which have cross-polarized. Comparison of the ID-CP/MAS spectrum (bottom) to the normal CP/MAS spectrum (middle) reveals that the downfield shoulder in the CP/MAS spectrum, centered at 135 ppm, is due to non-protonated aromatic-olefinic carbons. The result of subtracting the appropriate intensity of the ID-CP/MAS spectrum from the CP/MAS spectrum, so that the downfield shoulder is removed, is shown in the top of Figure 7. This difference spectrum (top) reveals that the narrower upfield portion of the aromatic-olefinic resonance, at 110 ppm -135 ppm, is due to protonated carbons. The ratio of non-protonated to protonated aromatic-olefinic carbons in the cross-polarized signal of this char sample is approximately 1 to 1. Comparison

of the set of NMR data above with that for the char resulting from the pyrolysis of pure PVA reveals that the non-protonated to protonated aromatic-olefinic carbon ratio is 1:1 in both cases and that the chars appear to have almost identical structure¹⁸. However, the presence of silica gel in PVA reduces the peak heat release rate from 609 kW/m², for pure PVA, to 250 kW/m². The presence of silica gel also increases the char yield from 5% to 27%. It appears that the silica gel does not change the type of char formed, since the chars have similar structure, but it does change the rate that it forms since the char yield is higher and the flammability is lower.

A similar series of spectra of the char from PVA with silica gel and K₂CO₃ (90:6:4) is shown in Figure 8. The normal CP/MAS spectrum (middle) contains the sharp carbonate resonance at 162 ppm and a broad resonance in the aromatic-olefinic region from 115 ppm to 150 ppm. In contrast to the spectra for PVA only or for PVA with silica gel (10%) there is little evidence of any aliphatic (sp³) carbon. Comparison of the ID-CP/MAS spectrum (bottom) to the normal CP/MAS spectrum (middle) reveals, as was observed for pure PVA and for PVA with silica gel, that the downfield shoulder in the CP/MAS spectrum, centered at 135 ppm, is due to non-protonated aromatic-olefinic carbons. The result of subtracting the appropriate intensity of the ID-CP/MAS spectrum from the CP/MAS spectrum, so that the downfield shoulder is removed, is shown in the top of Figure 8. The difference spectrum (top) reveals that the upfield portion of the aromatic-olefinic resonance, at 115 ppm -135 ppm, is due to protonated carbons. The ratio of non-protonated to protonated aromatic-olefinic carbon in the spectrum of this char sample is approximately 1.5 to 1, i.e., this char contains a greater fraction of non-protonated aromatic-olefinic carbons than the char formed in the absence of K₂CO₃. To the extent that the cross-polarized signals in these materials reflect the sample-wide chemistries, this data indicates that the presence of the K₂CO₃ has increased the extent of carbon-carbon bond formation and therefore of crosslinking in the char. This may be the reason for the even lower flammability (peak heat release rate: 609 kW/m² for pure PVA; 250 kW/m² for PVA with silica gel; and 194 kW/m² for PVA with silica gel and K₂CO₃) and for the higher char yield in the presence of K₂CO₃ (char yield: 5% for pure PVA; 27% for PVA with silica gel; and 43% for PVA with silica gel and K₂CO₃).

MECHANISM

A discussion of the original approach envisioned for this additive system may shed some light on how these additives reduce polymer flammability. The original intention in using silica gel with K₂CO₃ was to devise a method 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 organosiliconate compounds¹⁹. 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 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 K₂CO₃ (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. It is not as 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 silicate glass during the combustion. In earlier work on fire retardants, silicates were claimed to be quite effective²⁰. The pertinent phase diagrams do not show potassium silicate formation until 725 °C. However, if sodium salts are present this temperature drops to 400 °C - 500 °C²¹. Other work on inorganic glass forming fire retardants examined an analogous borate/carbonate system; B₂O₃/MCO₃. These formulations were found to form an inorganic glassy foam as a surface barrier which insulated and slowed the escape of volatile decomposition gasses. Unfortunately relatively high loadings of these additives, 40 phr - 100 phr (parts per hundred parts of resin), were required to realize

significant improvement in fire retardant performance and the loss of mechanical properties precluded application of this system²².

CONCLUSIONS

The results presented here demonstrate that the flammability of a wide variety of polymers is dramatically reduced in the presence of relatively small concentrations of silica gel and K_2CO_3 . We see that these additives appear to act in the condensed phase but we have only just begun to gain insight into how these additives change the polymer pyrolysis. Future efforts to understand this system will include evaluation of the effect of other types of basic materials and of particle size and internal pore size of the silica gel. We are also characterizing the residues formed from the combustion of the polymers discussed above using solid state 1H , ^{29}Si , single pulse (more quantitative) ^{13}C NMR, and other techniques. This information should help us understand how this additive system increases the char yield and reduces the flammability of such a wide variety of polymers.

ACKNOWLEDGMENTS

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17. Single pulse (SP) MAS ^{13}C NMR experiments which avoid the problems inherent in CP/MAS experiments were attempted; however, suitable signal-to-noise levels were not obtained in either the normal (90°) SP/MAS or in the interrupted decoupling (ID) SP/MAS experiments. This may be due to very long ^{13}C T_1 relaxation times relative to the pulse repetition delay we were able to employ.
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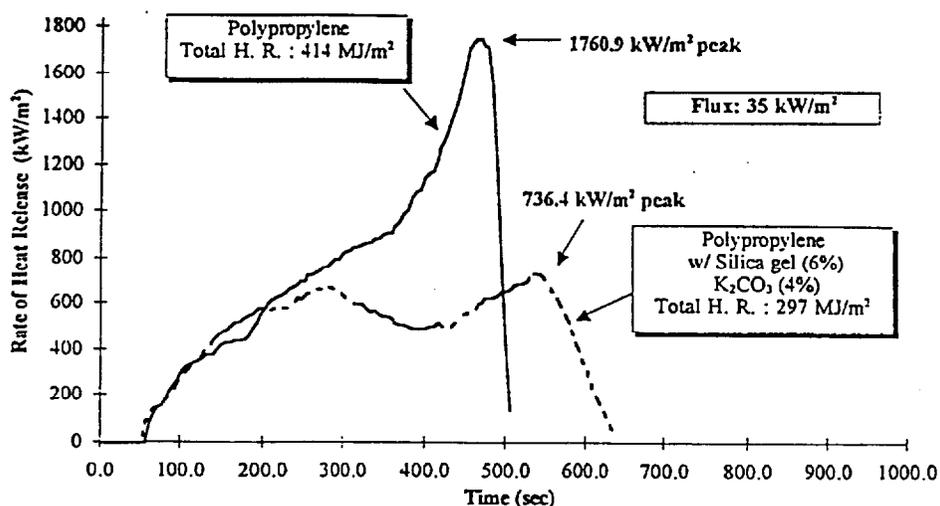


Fig. 1. Rate of Heat Release (RHR) curve for PP (35kW/m^2) (75 mm x 7mm disk) and PP/silica gel / K_2CO_3 (90/6/4 ratio, 75 mm x 10 mm disk) with a 58 % reduction in peak RHR and a 28% reduction in total H.R. in the presence of the additives.

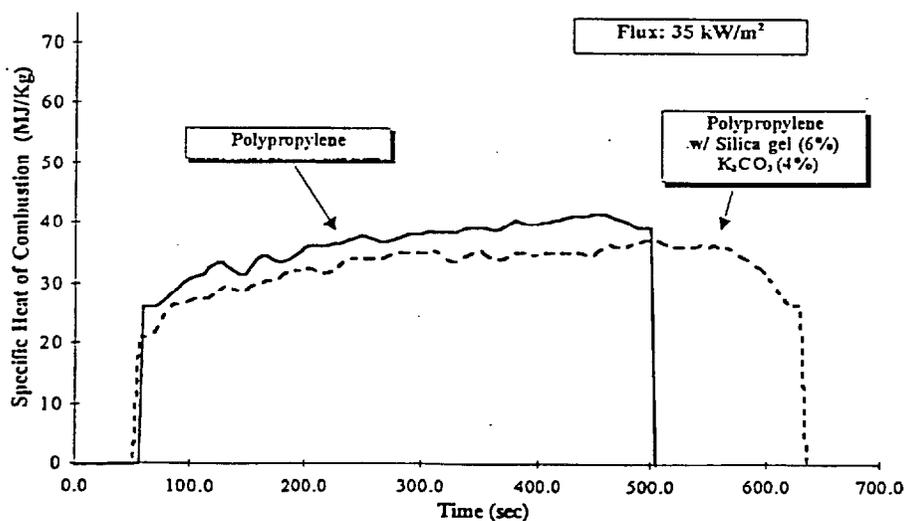


Fig. 2. Specific heat of combustion for PP (at 35kW/m^2) and PP/silica gel / K_2CO_3 (90/6/4 ratio) showing only a slight reduction in the presence of the additive. This indicates silica gel / K_2CO_3 is acting in the condensed phase not in the gas phase as halogenated fire retardants do.

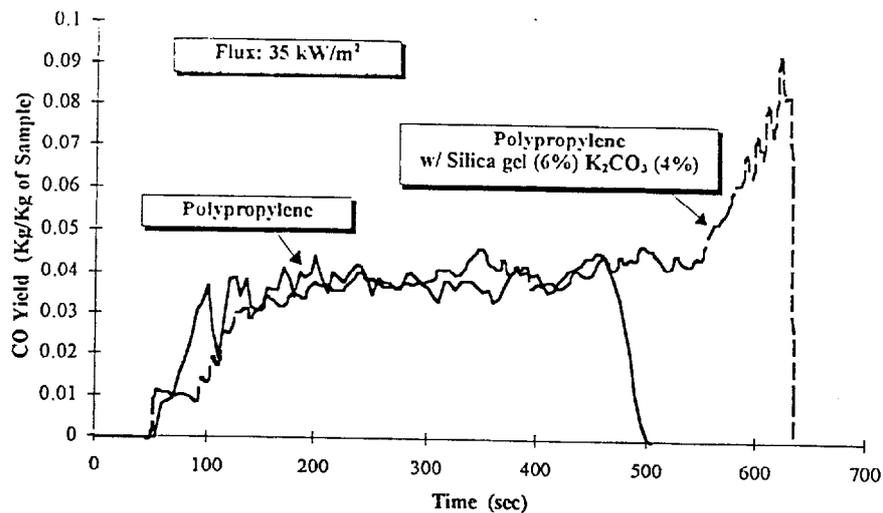


Fig. 3. The carbon monoxide yields for PP (at 35kW/m²) and PP/silica gel /K₂CO₃ (90/6/4 ratio) are very similar except at the end of the combustion where very small mass losses may be artificially raising the CO level, or since the sample surface is not completely covered by the flame the hot char residue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

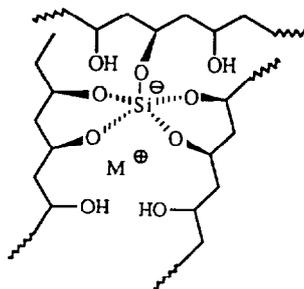


Fig. 4. Pentacoordinate organosilicate crosslinked PVA.

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

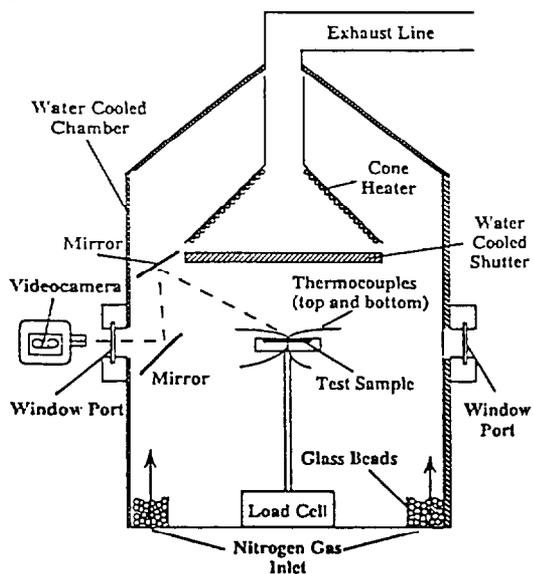


Fig. 5. Gasification apparatus. Allows study of condensed phase processes in the absence of combustion.

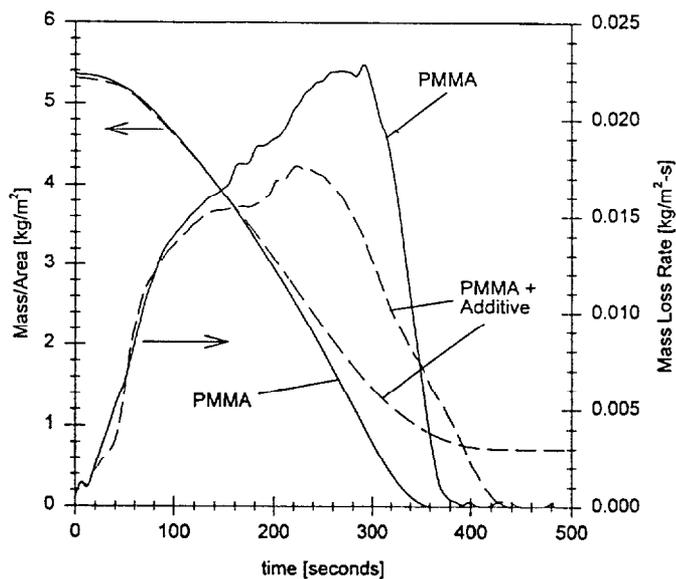


Fig. 6. Gasification experiments for PMMA and PMMA with silica gel / K_2CO_3 (95:4:1)

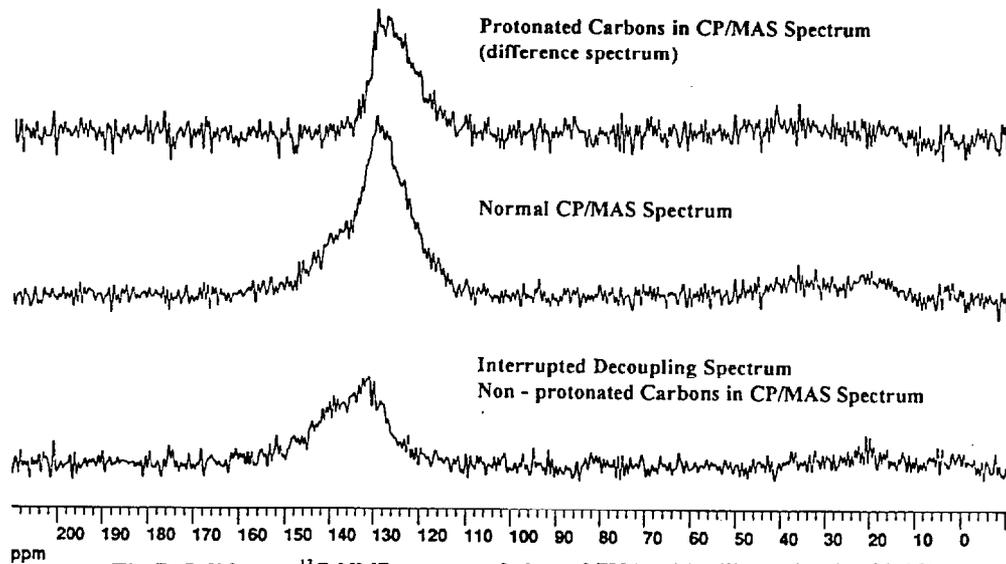


Fig. 7. Solid state ^{13}C NMR spectra of char of PVA with silica gel only (90:10).

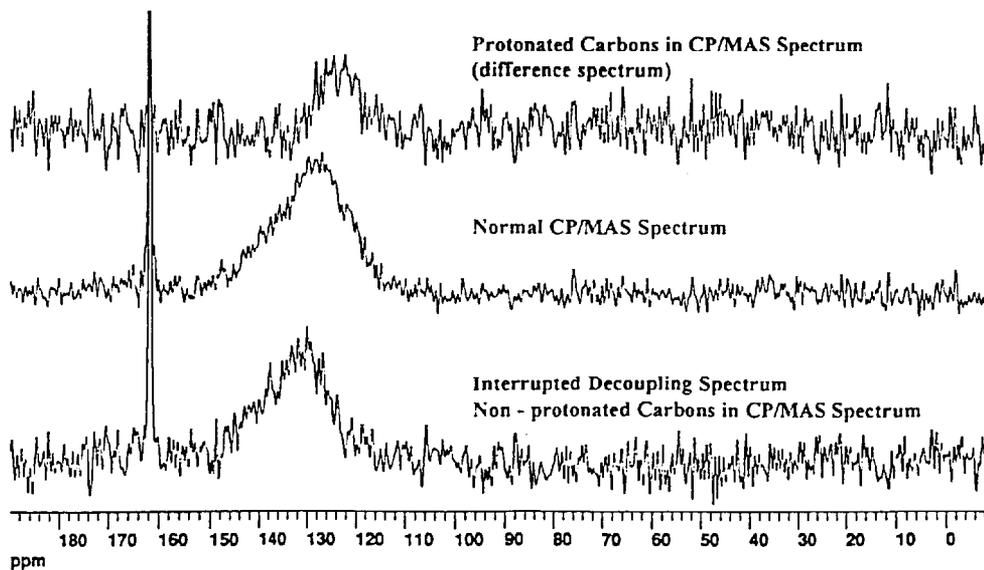


Fig. 8. Solid state ^{13}C NMR spectra of char of PVA with silica gel / K_2CO_3 (90:6:4).

Discussion

Henri Mitler: I noticed that you used 6% and 4% additions. If there a reason?

Jeffrey Gilman: We haven't explore optimizing that ratio.

Richard Lyon: Did you plan on trying it on systems that would really benefit from something like this like epoxies that have terminal pendant groups that would really benefit from that boost of charge.

Jeffrey Gilman: We are in the process of doing that now.

Richard Lyon: What about moisture sensitivity?

Jeffrey Gilman: We are going to look at other sources of bases and other types of bases and other sources of potassium which seems to be very important.

END: March 19, 1996