

Chapter 8

Char Enhancing Approaches to Flame Retarding Polymers

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ABSTRACT: Additives that increase the amount of charcoal-like residue or carbonaceous char that forms during polymer combustion are very effective fire retardants (FR) [1–3]. Our research efforts focus on reducing polymer flammability by promoting char formation. 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 their performance. 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 fed back to the polymer surface. The char also insulates the underlying polymer, due to its low thermal conductivity, and reradiates incident energy away from the polymer surface. The char must also function as a mass transport barrier, by physically delaying the volatilization of decomposition products and/or chemically reacting with decomposition products. The physical structure of the char is important in this role. Thick, foamy char appears to be more fire resistant than brittle, thin char [4]. This char-enhancing approach is most successful when the polymer chars rapidly and early in the burning process. To be useful, the charring process must occur at a temperature above the polymer processing temperature, but below the temperature where rapid gasification of the polymer to combustible fuel occurs. This chapter is an overview of several new char enhancing approaches to reducing the flammability of polymers.

8.1 Introduction

Current efforts in our laboratory focus on several different char enhancing, inorganic-additive systems. All of these systems entail the use of inorganic materials as additives to organic polymers, such as commodity polymers, engineering polymers, thermoplastics and thermosets‡. Under a class of additives best described as metal

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oxides, we have looked at the mechanism of flammability reduction when silica gel is used as an additive, both with, and without, K_2CO_3 [5]. We have also investigated the effect that zirconium oxide and ammonium pentaborate have on polymer flammability [6]. We are also actively pursuing two new approaches where the combination of organic polymers with inorganic materials not only improves the flammability properties, but also improves various other physical properties. One approach involves blends of preceramic polymers and organic polymers [7]. The second approach utilizes polymer-layered-silicate nanocomposites which employ montmorillonite as the inorganic [8]. This second approach will be covered in a separate chapter in this book (Chapter 14).

8.2 Silica gel with K_2CO_3 flame retardant studies

Recent studies of the flammability of polymers containing silicon based materials have shown these materials to be promising fire retardants, either as additives, or in blends with organic polymers [9]. The original intention in using silica gel with K_2CO_3 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 organosilicate compounds [10]. 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. We attempted to accomplish this by combining a polyhydroxylic polymer, e.g. poly(vinyl alcohol) (PVA) or cellulose, with silica gel and K_2CO_3 . If the indicated reaction occurred between the polymer and the additives it should crosslink the polymer, as shown in Fig. 8.1. This multicoordinate organosilicate compound of the type shown might form a silicon-oxy-carbide, SiOC, type protective char during combustion.

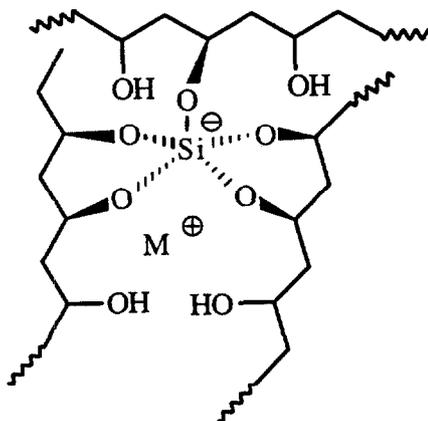


Fig. 8.1 Pentacoordinate organosilicate crosslinked PVA. Pyrolysis of materials like this may produce silicon-oxy-carbide type char.

The flammability properties of the system were characterized using the cone calorimeter [11]. Indeed, we found that silica gel combined with K_2CO_3 increased the char yield, and reduced the flammability of polyhydroxylic polymers, such as, PVA (Fig. 8.2) and cellulose. These additives are also effective in reducing the flammability of poly(methyl methacrylate) (PMMA), polypropylene (PP) and, to a lesser degree even nylon-6,6, polystyrene (PS), and poly(styrene acrylonitrile) (SAN) without increasing the smoke or carbon monoxide yields (see Table 8.1) [5].

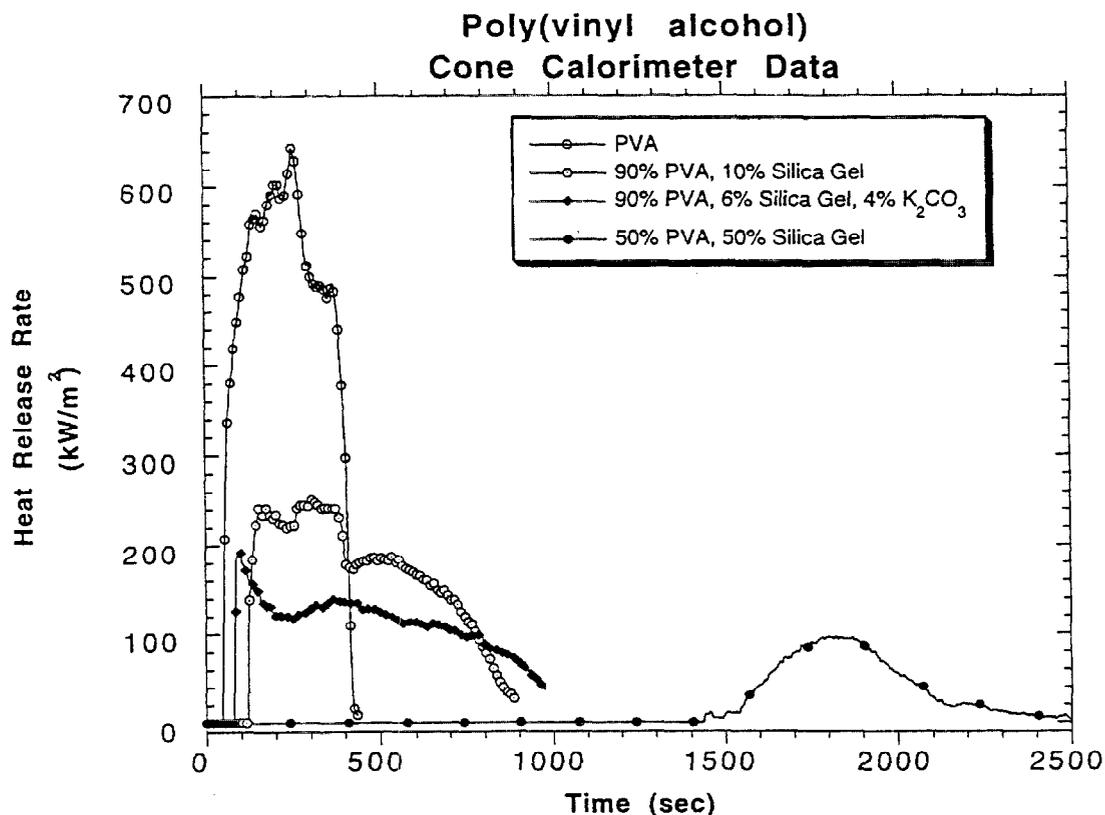


Fig. 8.2 Heat release rate (HRR) vs. time plot for PVA with silica gel and K_2CO_3 .

It is not as likely, however, that silicon-oxy-carbide char formation is responsible for the 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 effective. The pertinent phase diagrams do not show potassium silicate formation until $725^{\circ}C$. However, if sodium salts are present this temperature drops to $400-500^{\circ}C$. Other work on inorganic glass-forming fire retardants examined an analogous borate/carbonate system; B_2O_3/MCO_3 [12]. These formulations were found to form an inorganic glassy foam as a surface barrier which insulated and slowed the escape of volatile decomposition gases. It should be noted that Weil *et al.* [3] have proposed that K_2CO_3 acts as a flame retardant for acrylonitrile-butadiene-styrene, ABS, by base catalysed oxidative crosslinking of the butadiene block of the terpolymer. This mechanism may be

Table 8.1 Cone calorimeter data for silica gel/ K_2CO_3 system.

Sample	Peak HRR (Δ) (kW/m ²)	Mean HRR (kW/m ²)	Mean H_c (MJ/kg)	Total heat released (MJ/m ²)	Mean SEA (m ² /kg)	Mean CO yield (kg/kg)
PP	1761	803	38	357	689	0.04
PP w/ 6%SG and 4%PC	736 (58%)	512	33	297	710	0.04
PS	1737	1010	25	277	1422	0.07
PS w/ 6%SG and 4%PC	1190 (31%)	725	25	246	1503	0.07
PMMA	722	569	23	319	210	0.01
PMMA w/ 3%SG and 1%PC	420 (42%)	246	21	231	199	0.05
PVA	609	381	17	221	594	0.03
PVA w/ 10%PC	322 (47%)	222	17	145	571	0.03
PVA w/ 10%SG	252 (57%)	173	15	131	361	0.03
PVA w/ 6%SG and 4%PC	194 (68%)	114	12	101	201	0.03
Cellulose	310	161	11	101	27	0.02
Cellulose w/ 6%SG and 4%PC	149 (52%)	71	5.3	34	20	0.04
SAN	1499	837	25	197	1331	0.07
SAN w/ 6%SG and 4%PC	1127 (25%)	772	23	169	1301	0.06
Nylon 6,6	1131	640	23	108	234	0.02
Nylon 6,6 w/ 6%SG	558 (51%)	365	24	111	164	0.02
Nylon 6,6 w/ 6%SG & 4%PC	546 (52%)	370	24	102	185	0.02

Incident heat flux = 35kW/m²; HRR = heat release rate; H_c = heat of combustion; SEA = specific extinction area; SG = silica gel; PC = K_2CO_3 ; Uncertainties: $\pm 5\%$ for HRR and H_c data, $\pm 10\%$ for the carbon monoxide and specific extinction area (SEA) data.

important for PVA and cellulose, since they decompose to give condensed phase olefinic products.

Analysis of the combustion chars using solid state silicon-29 NMR indicates that the majority of the original silanol (SiOH) structure of the silica gel remains intact during the combustion. This data raises the possibility that silica gel itself is directly affecting the flammability, either chemically, in a catalytic process, or physically.

To study this issue we recently carried out an investigation of the effect of silica gel structure on the flammability properties of PP. In this study the effects of three silica gel characteristics were examined; pore volume, particle size and surface silanol concentration. Polypropylene was used as the base resin, and polypropylene-graft-maleic anhydride was used as a dispersing agent for the additives. A full-factorial design-of-experiment set of formulations was compounded using a twin screw extruder. The heat release rate plot, shown in Fig. 8.3, reveals the dramatic effect of silica gel pore volume on the flammability of PP. The flammability data from the cone calorimeter reveals that the primary reason for the lower HRR for PP, with large pore volume silica gel added, is the reduced mass loss rate (see Fig. 8.4); that is, the rate at which fuel is released into the gas phase for combustion.

Furthermore, the cone data also show that the silica gel is not affecting the gas phase combustion processes, since the heat of combustion, H_c , carbon monoxide yield

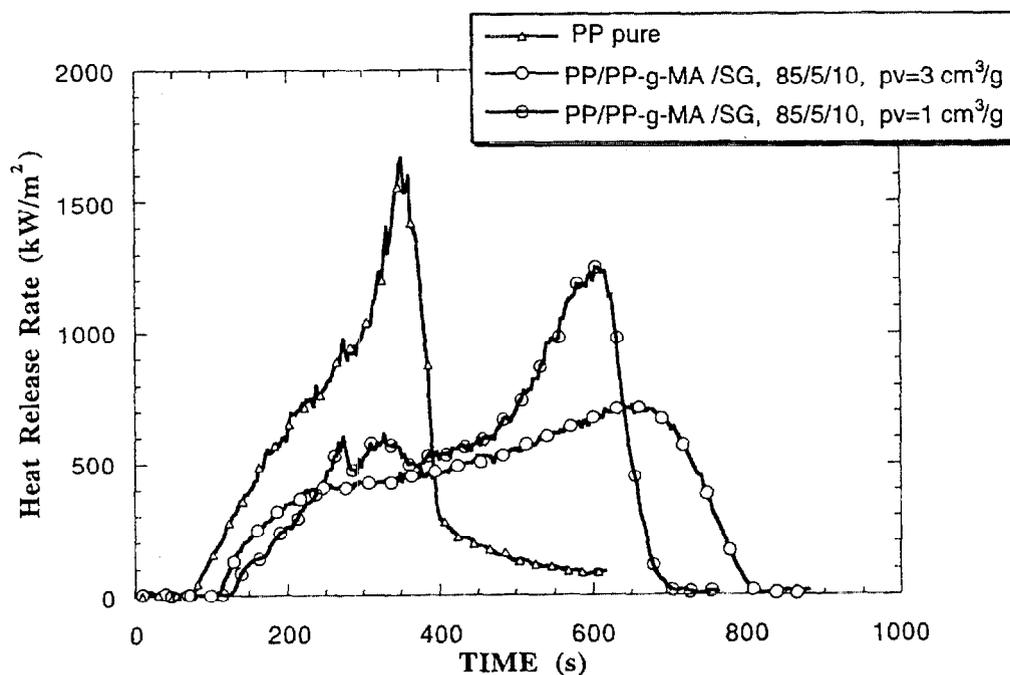


Fig. 8.3 Heat release rate vs. time plot for PP, PP/PP-g-MA (5%), PP/PP-g-MA (5%) with 3.0 cm³/g pore volume silica gel (10%) and PP/PP-g-MA (5%) with 0.8 cm³/g pore volume silica gel (10%).

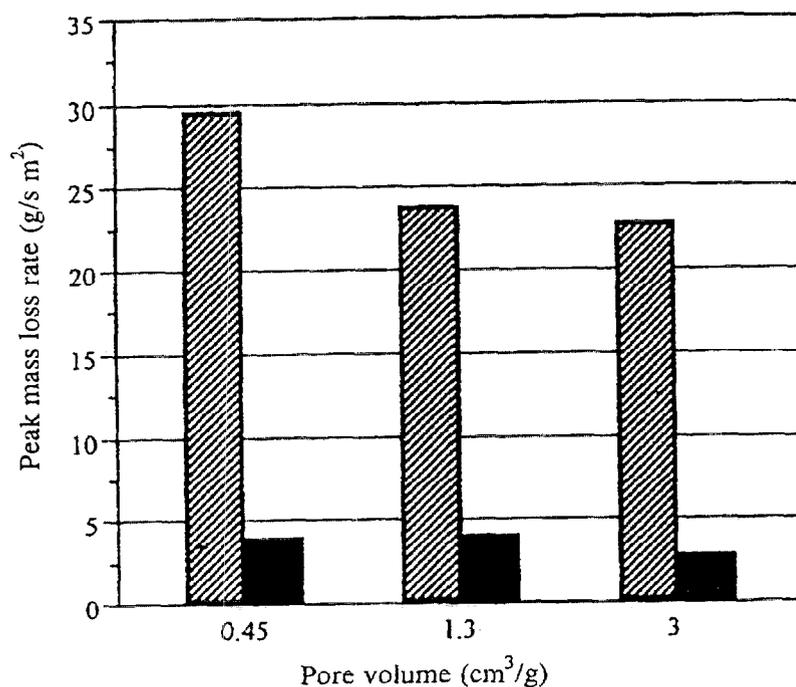


Fig. 8.4 Mass loss rate vs. pore volume plot for PP/PP-g-MA with silica gels with pore volumes of 0.45 cm³/g, 1.3 cm³/g and 3.0 cm³/g. ▨ Mean (peak mass loss, g/s m²); ■ standard deviation (peak mass loss, g/s m²).

and smoke yield, *SEA*, are not significantly different from those of the pure PP. There was no effect of the particle size on the flammability properties. However, a small but statistically significant effect of silanol content or heat treatment temperature was observed. One possible explanation for the reduced PP flammability at higher silica gel pore volumes is that the larger pores may be able to accommodate the PP macromolecule within the pore. The radius of gyration of PP in this molecular weight range ($M_w \sim 300,000$ g/mol, $M_n \sim 90,000$ g/mol) is ~ 70 nm, when measured in solution [13], and may be somewhat smaller in the melt. The nominal average pore diameter of the high pore volume material is ~ 28 nm. Since there is a broad distribution of pore diameters it seems likely that a significant fraction of the pores may be able to fit a PP macromolecule and trap or delay the loss of decomposition products from the condensed phase. Another possible explanation is that the silica gel is acting as a thickening agent [14], increasing the melt viscosity of the PP during the pyrolysis. A more viscous melt may trap or slow the evolution of decomposition products, thereby reducing the mass loss rate.

If we assume that the silica gel flame retardant mechanism is dominated by the above pore effect, and that the pore effect holds for the other polymers studied, then the following conclusions may be made. The polymer-pore effect seems to have a different result depending on the polymer. The *carbonaceous* char yields for PP, PMMA, nylon 6, SAN and PS, are only 2–10%, so it is most likely that the interaction of the pores of the silica gel and these polymers results primarily in a delay of the loss of decomposition products from the condensed phase. It appears that for PVA (and possibly for cellulose) the interaction results in a permanent retention of carbon in the condensed phase, since the *carbonaceous* char yield for PVA is substantially increased from 4% to $\sim 30\%$ in the presence of silica gel.

With this substantial improvement in performance of silica gel in reducing PP flammability, we will continue both our investigation of the fire retardant mechanism, and our study of the general effectiveness of silica gel as a flame retardant for epoxies, vinyl esters, polyimides and other resins.

8.3 Zirconium oxide – borate flame retardant studies

A second metal oxide system under investigation involves combining zirconium oxide, ZrO_2 , with either ammonium pentaborate (APB) $[(NH_2)_2B_{10}O_{16} \cdot 8H_2O]$ or boric acid and K_2CO_3 [6]. We became interested in these additives because of the known catalytic properties of ZrO_2 for isosynthesis [15], and the low melting glass properties of borate salts [16, 17]. Our initial investigations involved preparing samples by mixing the polymer and the additives in powder form, followed by compression moulding. Typically the zirconia-borate additives were combined with a commodity polymer such as polyethylene (PE), PP, or high temperature engineering polymers such as phenolic-triazine (PT) (PT-30TM), and polyetherimide (UltemTM) at mass fractions of 5% to 20%.

The resulting reduction of the peak heat release rate is from 35% to 80%! The cone calorimeter data for PE, PP, PT and polyetherimide, are shown in Table 8.2. In

Table 8.2 Cone calorimeter data for ZrO₂-borate system.

Polymer sample	Char* yield (%)	Peak HRR ($\Delta\%$) (kW/m ²)	Mean HRR ($\Delta\%$) (kW/m ²)	Mean <i>H_c</i> (MJ/kg)	Total heat released (MJ/m ²)	Smoke: ext. area (m ² /kg)	Mean CO yield (kg/kg)
PE ³⁵	0	1820	1110	40	240	443	0.03
PE ³⁵ 10% additives‡	~ 1	829 (54%)	579 (48%)	37	246	641	0.03
Vinyl ester ³⁵ brominated	6	314	185	6.6	27	2300	0.13
Vinyl ester ³⁵ brominated 10% additives‡	15	185 (35%)	137 (26%)	7.8	22	1960	0.14
PP ⁵⁰	0	2074	920	40	262	650	0.04
PP ⁵⁰ 10% additives§	~ 3	800 (61%)	544 (41%)	37	206	665	0.04
PT ⁷⁰	58	973	336	15	59	430	0.03
PT ⁷⁰ 20% additives§	72	186 (81%)	96 (71%)	12	49	470	0.02
Polyetherimide ⁷⁰	52	173	88	12	45	465	0.07
Polyetherimide ⁷⁰ 20% additives‡	70	114 (34%)	76 (14%)	12	23	292	0.06

H_c = Heat of combustion; 35 = 35 kW/m² flux; 50 = 50 kW/m² flux; 70 = 70 kW/m² flux.

‡ = (1:1, ZrO₂:APB), § = (1:1:1.25, ZrO₂:boric acid:K₂CO₃), * indicates carbonaceous char yields.

addition, a special advantage of this system is that the effectiveness of this FR is maintained even at very high heat fluxes (70 kW/m^2). This is not the case for some fire retardants, which may lose their effectiveness at these heat fluxes. Although these additives do not greatly increase the char yield in the case of PP or PE they do significantly increase the *carbonaceous* char yield for the phenolic-triazine and polyetherimide.

In recent studies evaluating the fire retardant effect of these additives on various crosslinked vinyl ester resins, we have observed the combined effect of using these char enhancing additives with a *brominated* bisphenol-A vinyl ester resin (DerakaneTM 510A, Dow). The HRR plot, shown in Fig. 8.5, reveals that addition of a mass fraction of 10% total additives (1:1 ratio of ZrO_2 to APB) to the brominated resin, results in a 35% reduction in the peak HRR. The data in Table 8.2 show this is accomplished with a reduction in the smoke yield and an increase in the *carbonaceous* char yield.

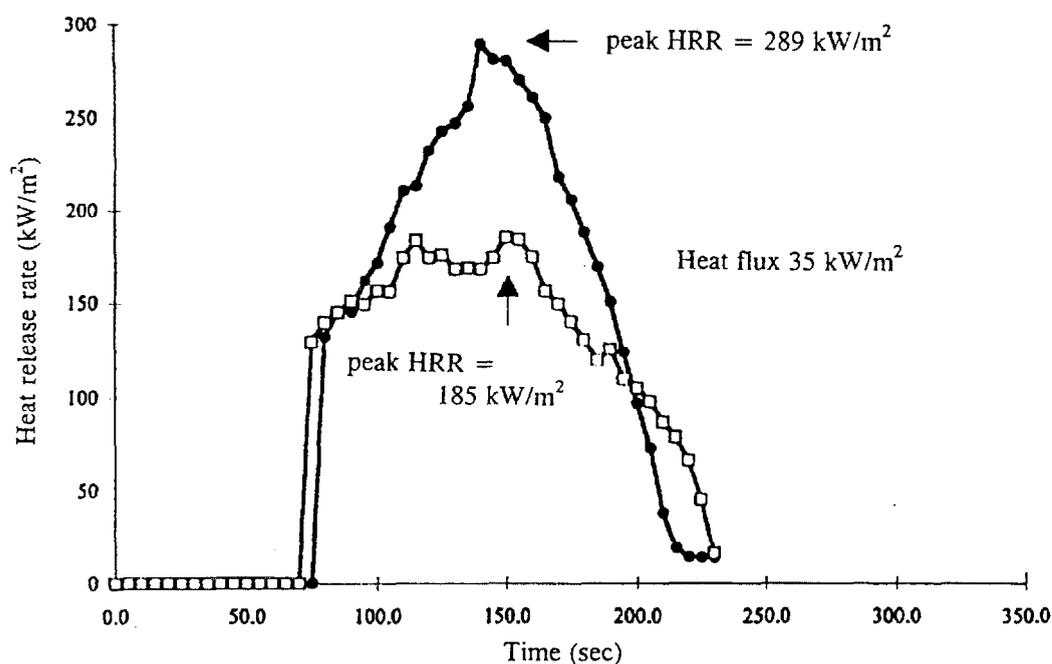


Fig. 8.5 Heat release rate vs. time plot for *brominated* bisphenol-A vinyl ester resin (●), and *brominated* bisphenol-A-vinyl ester resin with ZrO_2 /APB additives (□) (mass fraction of 10% total additives, 1:1 ratio).

The mechanism responsible for this enhanced charring may be related to the catalytic properties of ZrO_2 , mentioned above. It is reported that, with the appropriate surface treatment, ZrO_2 causes the isomerization and oligomerization of straight chain alkenes to highly branched alkanes of higher molecular weight [18]. This is observed even at atmospheric pressure at 250°C . Lewin [19] has found that, in the presence of hexavalent oxygenated sulphur compounds, ZrO_2 improves the oxygen index when compounded with polyamides. Furthermore, recently ZrO_2 has been reported to affect the ceramic yield from pyrolysis of polydimethylsiloxane [20]. These

effects on the flammability may also be due to the formation of molten borate glass, in which ZrO_2 is soluble [21]. As mentioned above, borate glasses have been shown to have good fire retardant properties [17].

8.4 Preceramic polymer blends

Polymer blending is a common method of achieving new properties in polymer systems. Blending of organic-inorganic polymers such as siloxanes with organic systems has been used to enhance the low temperature flexibility, processing and flame retardancy of plastics [9]. However, polymer-polymer blends involving other inorganic polymer systems (such as preceramic polymers, phosphazines, etc.) are less common.

In order to design materials which possess both an enhanced char forming ability and yet still maintain desirable engineering properties, we prepared a series of polymer-polymer blends. Preceramic polymers such as PCS, polycarbosilane (Dow Corning) and PSS, polysilastyrene (Huls America) were blended with two thermoplastic-elastomers, SBS (polystyrene-polybutadiene-polystyrene, Shell Chemical Co., KratonTM) and PTME-PA (polytetramethylenylether-glycol-b-polyamide-12, block copolymer, 1% polyamide-12, Elf Atochem, PebaxTM 2533). Polysilsesquioxanes (Impact International, $-[R-SiO_{1.5}]_n-$, R = Me, Phenyl, 1:1) were also combined with SBS, PTME-PA and polypropylene. The structures of the preceramics are shown in Fig. 8.6.

Compositions for the PTME-PA/PCS and PTME-PA/PSS blends, ranging from 20/80 to 80/20 (mass ratio) were prepared via solution blending in tetrahydrofuran (THF). Blends of SBS/silsesquioxane, SBS/PCS and PTME-PA/silsesquioxane were also prepared via solution blending in THF. The mechanical and thermal properties were investigated. Table 8.3 contains a partial listing of the thermal and mechanical properties for PCS, PSS, silsesquioxane and the PTME-PA/PCS, PTME-PA/PSS blends [22].

Several overall trends are apparent from the data shown in Table 8.3. For example, as the amount of preceramic polymer in these compositions increases so does the modulus of the resulting blend. In all cases the modulus of the blend is higher than that for pure PTME-PA. This is roughly consistent with that expected for the mixing of a high modulus material with one of low modulus. In addition, as the relative amount of preceramic in these blends increases, the amount of ceramic produced (char yield) upon pyrolysis is also observed to increase (Fig. 8.7).

The char yields for the PTME-PA/PCS blends do not appear to be significantly increased by any interactions between the decomposition of the preceramic and PTME-PA; that is, no significant additional carbon from the PTME-PA is retained in the ceramic char. This is also the case for the PTME-PA/PSS blends. However, the PTME-PA/PSS blends, containing mass fractions of 70% and 80% PSS, actually show a *lower* char yield than the theoretical or calculated yield (see Fig. 8.7). These results may be due to the fact that the PCS is slightly crosslinked and the PSS is linear. Crosslinking has been shown to be a very effective method for increasing the ceramic yield from any preceramic material [23].

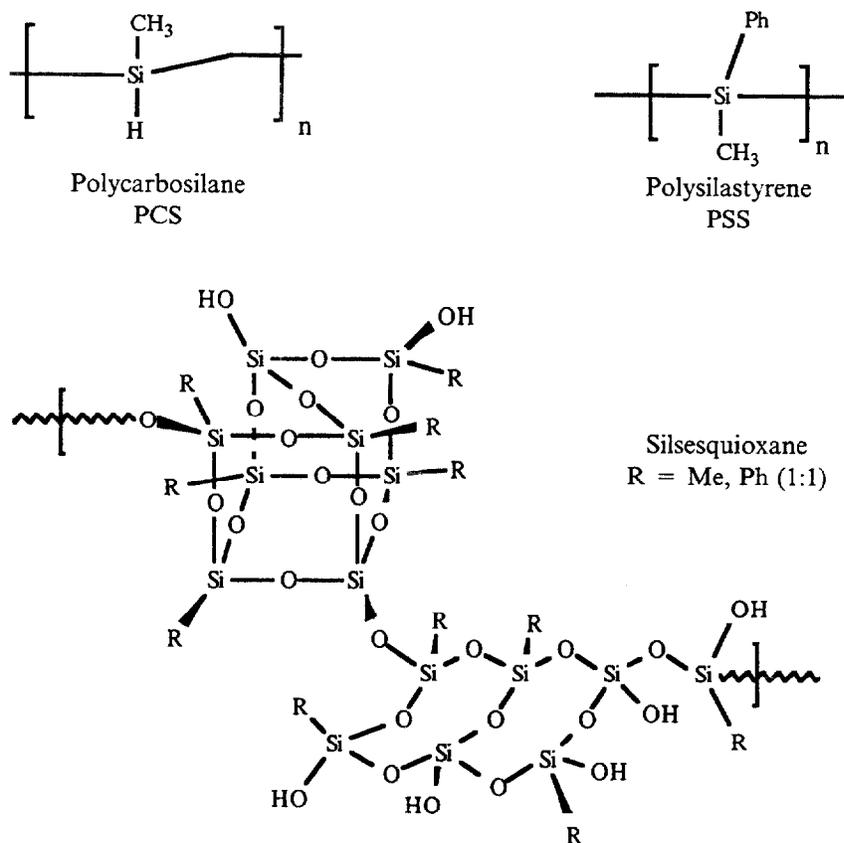


Fig. 8.6 PCS, PSS and silsesquioxane structures.

Table 8.3 Properties for PCS, PSS, silsesquioxane and PTME-PA/PCS, PTME-PA/PSS blends.

Material	T_m (°C)	Char yield (%)*	Young's modulus (psi)
PTME-PA/PCS 80/20	118	18 (17)	1894
50/50	125	44 (38)	8333
30/70	216	56 (53)	47 850
20/80	200	69 (59)	—
PTME-PA/PSS 80/20	118	15 (18)	745
50/50	110	43 (41)	2253
30/70	73	43 (56)	5021
20/80	52	50 (63)	15 530
PTME-PA	119	2	581
PCS	199	74	—
PSS	148	79	—
Silsesquioxane (Me, Ph)	125	82	—

* Numbers in *italics* represent calculated values (fraction of preceramic \times observed char yield for pure preceramic).

Uncertainties: $\pm 5\%$ for T_m and char yields; $\pm 15\%$ for Young's modulus.

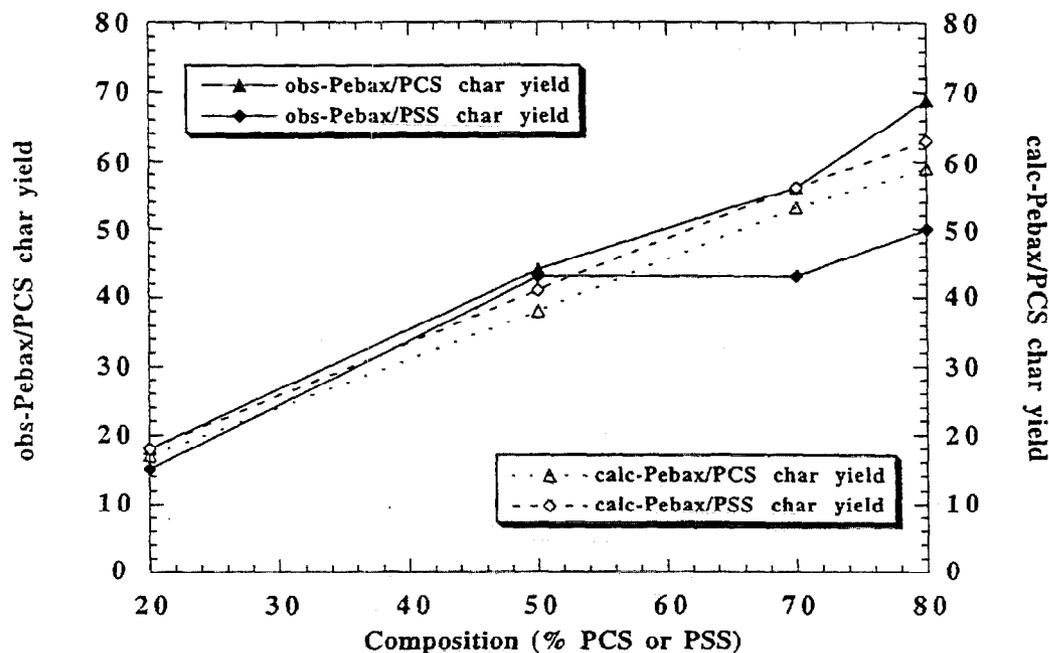


Fig. 8.7 Plot of observed (obs) and calculated (calc) char yields for PTME-PA/PCS and PTME-PA/PSS blends at various blend compositions. Observed char yields were done via TGA (10°C/minute, to 1000°C, N₂). Uncertainty: ± 5% for char yields.

Differences between the two blend systems in Table 8.3 are also apparent in the observed melt transitions. The blending of PSS with PTME-PA results in depression of the melt transition of the blends relative to pure PTME-PA. Since PTME-PA is a thermoplastic elastomer with amorphous rubbery PTME domains reinforced by crystalline PA domains, this suggests that the PSS is plasticizing or disrupting the crystalline domains present in the PTME-PA. Investigation of the effect on T_g are under way. In contrast to the above, the blending of PCS to PTME-PA did not produce depressed melt transitions in the resulting materials. Instead a discontinuous change in melt transition versus blend composition was observed. Scanning electron microscopy (SEM) was used to examine the morphology of the blends. The PTME-PA/PCS compositions in Table 8.3 were found to be phase separated with 5 μ m to 10 μ m domain dimensions (Fig. 8.8).

The inhomogeneous character of these materials may result from insufficient mixing. However, it is most likely that the non-linear, partially crosslinked structure of PCS and the insolubility of PTME-PA in the blending solvent (THF) also may have contributed to the inhomogeneous character. Phase separation however, was not observed by SEM, for any of the PTME-PA/PSS compositions discussed above. In addition, while the chemical compositions of PCS and PSS are somewhat different, the linear polymeric structure of the PSS may have facilitated the blending of this preceramic polymer with the THF-swollen PTME-PA.

Owing to the limitations of the PTME-PA/PSS blends (lower pyrolysis char yields at high preceramic fractions) we have focused our initial flammability studies on the PTME-PA/PCS, PTME-PA/silsesquioxane PTME-PA/PCS and PTME-PA/silsesquioxane blends.



Fig. 8.8 SEM of PTME-PA/PCS blend (mass fraction 50/50).

We evaluated the flammability properties of these novel blends using the cone calorimeter. Samples (63 mm × 75 mm × 9 mm, 50 g) were run at 35 kW/m² heat flux. The results, shown in Figs 8.9 and 8.10, and Table 8.4, reveal that both PCS and silsesquioxane are effective at reducing the HRR of not only PTME-PA and SBS, but also PP. This is accomplished at relatively low levels of incorporation of preceramic.

Although the preceramic polymers reduce the peak HRR and average HRR in both of these blend systems, the char yields following combustion in the cone calorimeter are about the same as the calculated yields (see Table 8.4 calculated yields in brackets). The addition of the preceramic polymers in these blends does not significantly increase the yield of carbonaceous char. This is the same result as that obtained in the TGA for PTME-PA/PCS blends, shown in Fig. 8.7. The mass loss rate data from the cone calorimeter, shown in Table 8.4, reveal that the primary reason for the lower HRR for the blends is the reduced mass loss rate, that is, the rate at which fuel is released into the gas phase for combustion. Furthermore, the cone data also show that the preceramics are not affecting the gas phase combustion processes, since the heat of combustion, H_c , carbon monoxide yield and smoke yield, SEA , are not significantly different from those of the pure polymers. This means that the reduction in flammability is due to the protecting effect of the ceramic residue formed during the burning process, not from retention of carbon (fuel) in the condensed phase.

In the PTME-PA blends the silsesquioxane preceramic is more effective than the PCS preceramic at reducing the HRR. Only half as much is needed to give a greater reduction in peak HRR, and a comparable reduction in average HRR. This is not the case for the blends with SBS. In the SBS blends the PCS appears to function as well as it does in the PTME-PA blends. The silsesquioxane, however, performs less effec-

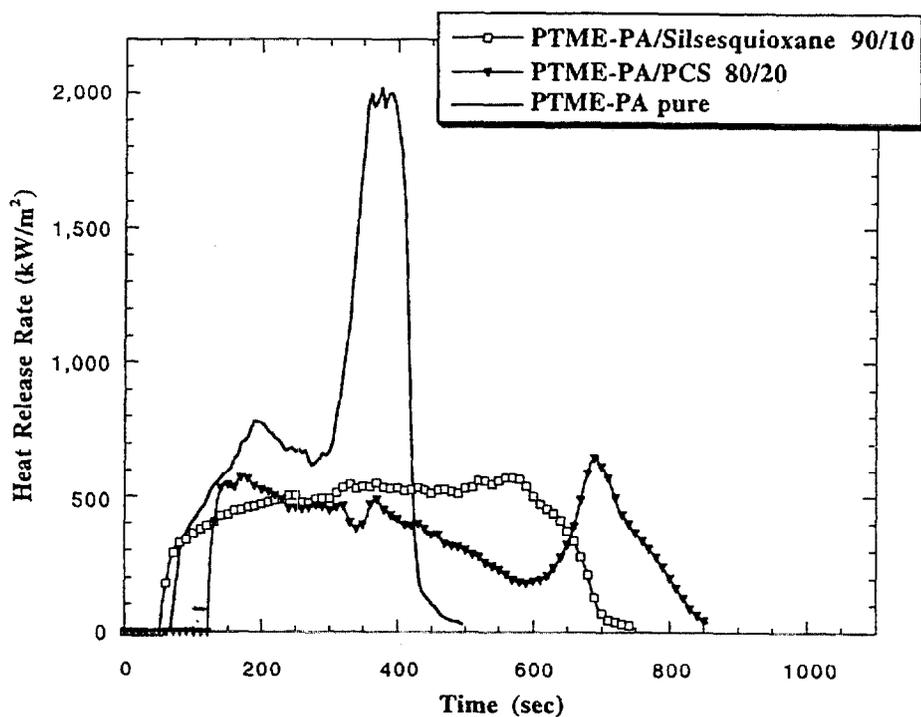


Fig. 8.9 Heat release rate (HRR) data for PTME-PA, PTME-PA/silsesquioxane 90/10 and PTME-PA/PCS 80/20. These data show a 60% to 70% reduction in the peak HRR, and a 45% reduction in the average HRR for the blends.

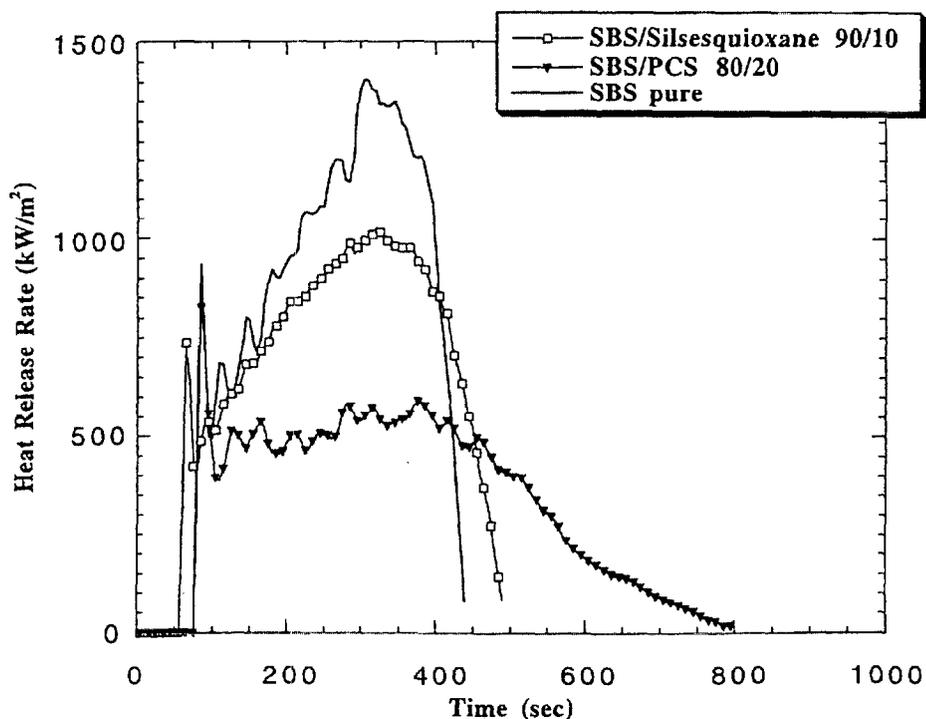


Fig. 8.10 Heat release rate (HRR) data for SBS, SBS/PCS 80/20 and SBS/silsesquioxane 90/10 blends. The data show a 30% and 40% reduction in the peak HRR, a 20% and 60% reduction in average HRR, respectively, for the blends.

Table 8.4 Cone data for PP, SBS and PTME-PA combined with silsesquioxane and PCS preceramics.

Sample	Char yield (%)	Mean mass loss rate (g/s m ²)	Peak HRR ($\Delta\%$) (kW/m ²)	Mean HRR ($\Delta\%$) (kW/m ²)	H_c (MJ/kg)	SEA (m ² /kg)	Mean CO yield (kg/kg)
PP	0	25.4	1466	741	34.7	650	0.03
PP/silsesquioxane 80/20	17 (16)	19.1	892 (40%)	432 (42%)	29.8	820	0.03
PTME-PA	0	34.2	2020	780	29.0	190	0.02
PTME-PA/PCS 80/20	15 (15)	14.8	699 (65%)	419 (46%)	28.5	260	0.02
PTME-PA/silsesquioxane 90/10	6 (8)	19.8	578 (72%)	437 (44%)	25.2	370	0.02
SBS	1	36.2	1405	976	29.3	1750	0.08
SBS/PCS 80/20	20 (15)	18.5	825 (42%)	362 (63%)	26.4	1550	0.07
SBS/silsesquioxane 90/10	6 (8)	31.2	1027 (27%)	755 (23%)	26.9	1490	0.07

H_c = Mean heat of combustion; SEA = specific extinction area (smoke measurement).

Uncertainties: $\pm 5\%$ of reported value for char yields, HRR and H_c data; $\pm 10\%$ for the carbon monoxide and SEA data.

tively in the SBS blends, even if the lower loading levels are accounted for. The origin of the differences in performance for the two preceramics is under investigation.

8.5 Conclusions

In this overview of several new char enhancing approaches to reducing the flammability of polymers we have shown the effectiveness of certain inorganic additives. We have found that the effect that any of these additives have on the flammability of the polymers they are combined with, usually depends on the *inherent* char forming ability of the polymer. In some cases the additives increased *carbonaceous* char yields, and thus reduced the mass loss rate (or fuel feed rate) and the flammability. This was the case for polymers with inherent char forming properties. However, for non-charring polymers there was still a reduction in the mass loss rate, and a reduction in the HRR, even though the *carbonaceous* char yields were not improved substantially. These later cases may benefit from the addition of other additives which impart charring.

8.6 Future trends

Because of the current intense interest in the development of new low cost approaches to flame retarding polymers, one or more new FR systems may see wide application in the next several years. The most likely candidates for this are char enhancing systems, since these approaches have the intrinsic benefit that they usually reduce flammability without increasing soot or carbon monoxide yields.

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