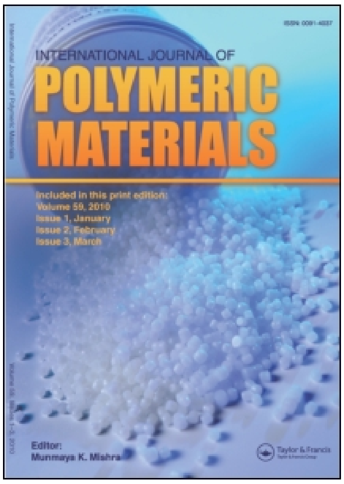

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New Types of Ecologically Safe Flame Retardant Systems for Polymethylmethacrylate

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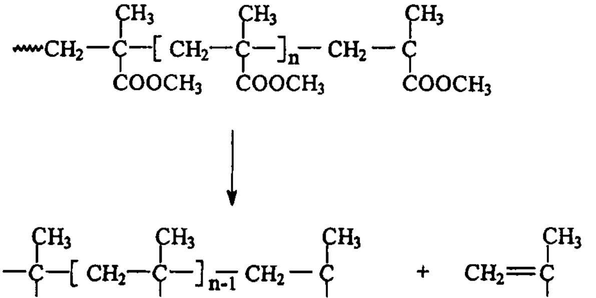
The addition of silica gels is explored to develop an environmental friendly flame retardant polymethylmethacrylate system.

KEY WORDS Flame retardancy, polymethyl-methacrylate, silica gel.

INTRODUCTION

Thermal degradation of PMMA is the only source of fuel to sustain burning. It may also be the source of volatile decomposition products that quench flame, and it may lead to the formation of a char which impedes heat transfer back to polymer.

PMMA provides one of the simplest degradation routes. Following chain homolysis, the macroradical simply depropagates to monomer, a process sometimes described as "unzipping." The average zip length for the process is about 200 repeat units:



$$\sim CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-[\,CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-]_n-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}$$

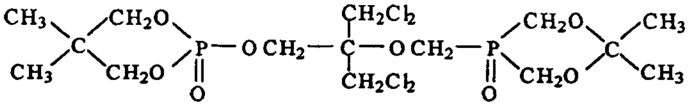
$$\downarrow$$

$$\sim CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-[\,CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-]_{n-1}-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}} \;+\; CH_2=\underset{COOCH_3}{\overset{CH_3}{C}}$$

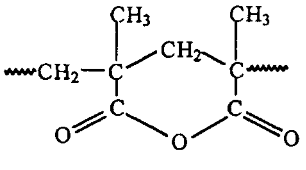
By this process, the polymer can provide an abundant supply of fuel for burning. PMMA doesn't produce any char (if it's pure).

Fire retardants incorporated into polymers can prevent or reduce the formation of fuel, they can quench flame, or they can make it more difficult for heat to be transferred back to the bulk of the polymer (e.g. causing a char form).

Ammonium polyphosphate is well known flame retardant for PMMA. On heating this loses ammonia, water to form first an ultraphosphate and then polyphosphoric acid, which at still higher temperatures fragments to give smaller phosphoric acid type fragments.[1] These species effect in the condensed phase, modifying the degradation route of the polymer. When ammonium polyphosphate is used as a fire retardant in PMMA, the effect is to greatly reduce the zip length and give in addition some char.[1]



The action of Sandoflam 5085 fire retardant is similar, although the effectiveness is improved by the good compatibility. This compound breaks down thermally to give some traces of HCl and phosphoric acid type residue as the flame depressants. This acid may interact with the PMMA chain to convert some of esters' units to the cyclic anhydride structures.[2]



When the polymer chain begins to unzip following scission, the unzipping process stops at the first ring structure instead of continuing for 200 units. Further chain scission is needed more monomer, so the temperature of breakdown is raised significantly and furthermore, the anhydride rings result in some char residue. The halogen-containing degradation product may have a role in the gas phase in flame quenching. The other "types" of Sandoflams—Sandoflam 5086 and Sandoflam 5087 also have a halogens (Br and Cl) as the active components. Another way of increasing the PMMA combustion characteristics is to alloy it with PVC.[3]

Wilkie *et al.*, have demonstrated that certain transition metal compounds can induce char formation in PMMA.[4–8] There were founded some factors which are important in stabilization/destabilization of PMMA: (1) the acidity of metal ion; the strength of the bond between the transition metal and its counter-ion. An ion which is unable to coordinate to the polymer will not effect the degradation process. Ions which may coordinate and which also have relatively weak M—X bonds lead to destabilizing effects on the degradation, whereas ions which coordinate but have stronger M—X bonds have a stabilizing effect. However, this research still doesn't indicate a clear dependence of PMMA combustibility vs. transition metal compounds' incorporation.

The subject of ecological safeness of polymer flame retardants has become a major problem in the modern polymer industry. The different types of polymer flame retardants based on halogens (Cl, Br), heavy and transition metals (Zn, V, Pb, Sb) or phosphorus-organic compounds may redue risk during polymer combustion and pyrolysis, yet may present ecological issues.

That is why, our study has been focused on the way to find out new types of ecologically safe flame retardant systems for PMMA. This goal might be achieving by means of the strong "char" barrier on the PMMA surface to heat and mass transfer process. This barrier needs to be coherent, fast-forming, but the barrier material need not be entirely carbonaceous.

Another our approach to preventing the burning away of the char was to produce a ceramic layer containing (Si—C) bonds. In the work of I. Janigova and I. Chodak it was studied the crosslinking process of polyethylene by Silica Gel initiated by thermal decomposition of high temperature peroxide.[9]

From all above the facts we proposed an ecologically safe flame retardant system for PMMA:

Silica Gel-(3% wt.) + Luperox 2,5-2,5(2,5-Dimethylhexane-2,5-dihydroperoxide)-(0.5% wt.)

Half-life of "Luperox" at selected temperatures

Temperature, C°	Half-life, hours
145	19.0
160	6.1

EXPERIMENTAL

Materials

The PMMA used in this work was supplied by Scientific Polymer Products, Inc., USA, Silica Gel—28-200 mesh (Fisher Sci. Co.), High temperature peroxide—LUPEROX 2,5-2,5 (Luisidol Div., USA).

Preparation of Samples, Incorporation of Additive

The samples for combustion measurements (PMMA, blend of PMMA, Silica Gel and Luperox 2,5-2,5—96.5%:3%:0.5% by wt.) were prepared in a laboratory blender at room temperature (10 min), the mixed samples were compression molded at temperature 80°C for 10 min. The weight of samples was 55 ± 0.3 g.

Cone calorimeter tests on the polymer samples, as discs (radius 35 mm), were carried out at 35 kW/m^2. Each specimen was wrapped in aluminum foil and only the upper face was exposed to the radiant heater.

RESULTS AND DISCUSSION

Cone results (Figures 1 – 6) suggest an improvement of fire resistance of the PMMA-SG composition in comparison with pure PMMA. Char yield of PMMA-SG composition exceeds the amount of initial additives in twice (Figure 2). This is an evidence of carbonization process in this systemm during combustion. Rate of Heat release suggest improvement of fire resistance characteristics for PMMA-SG composition in comparison with PMMA (Figures 1 and 3), and Total Heat Release (Figure 4), Mass Loss Rate (Figure 5) and Heat of Combusion (Figure 6). However, a

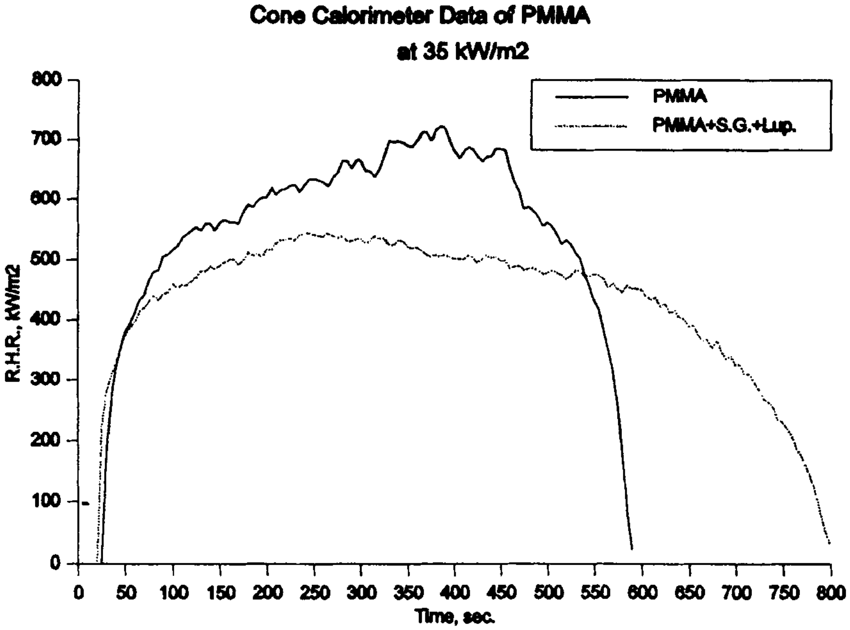


FIGURE 1 Cone calorimeter data of PMMA and PMMA + Silica Gel. Rate of Heat Release at 35 kW/m^2 as function of time.

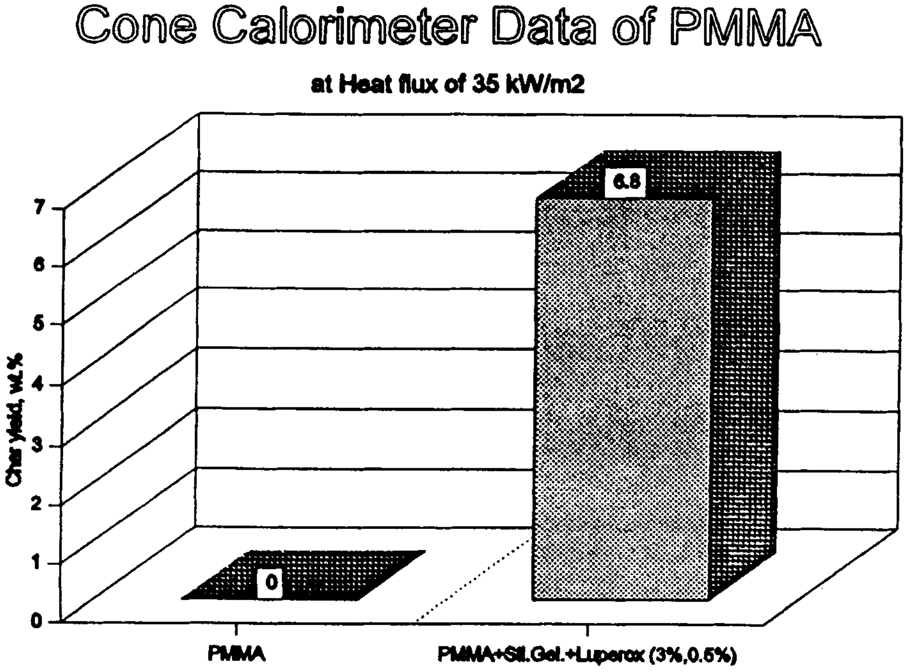


FIGURE 2 Cone calorimeter data of PMMA and PMMA + Silica Gel. Char Yield at 35 kW/m^2.

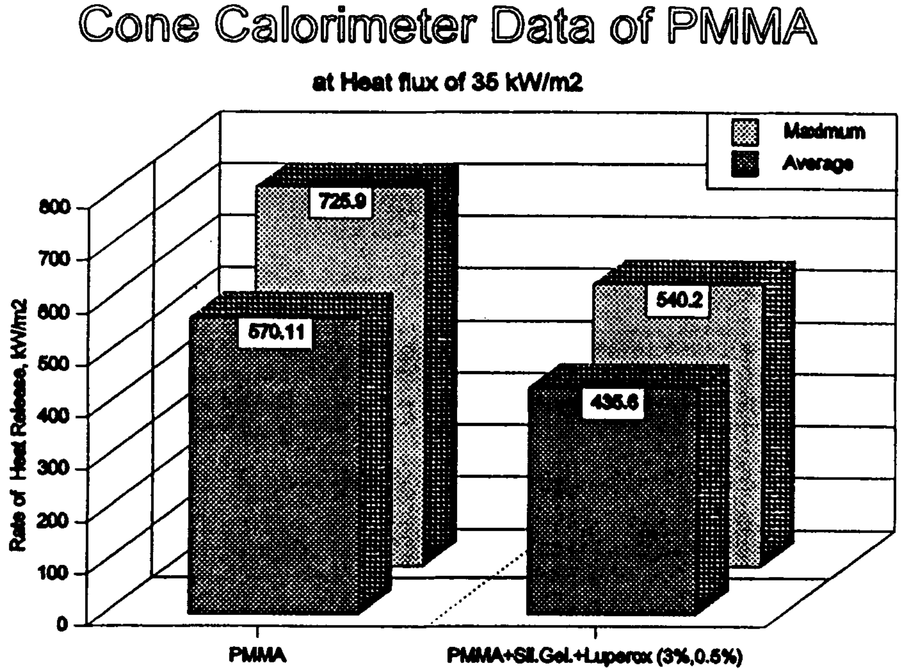


FIGURE 3 Cone calorimeter data of PMMA and PMMA + Silica Gel, Rate of Heat Release at 35 kW/m^2.

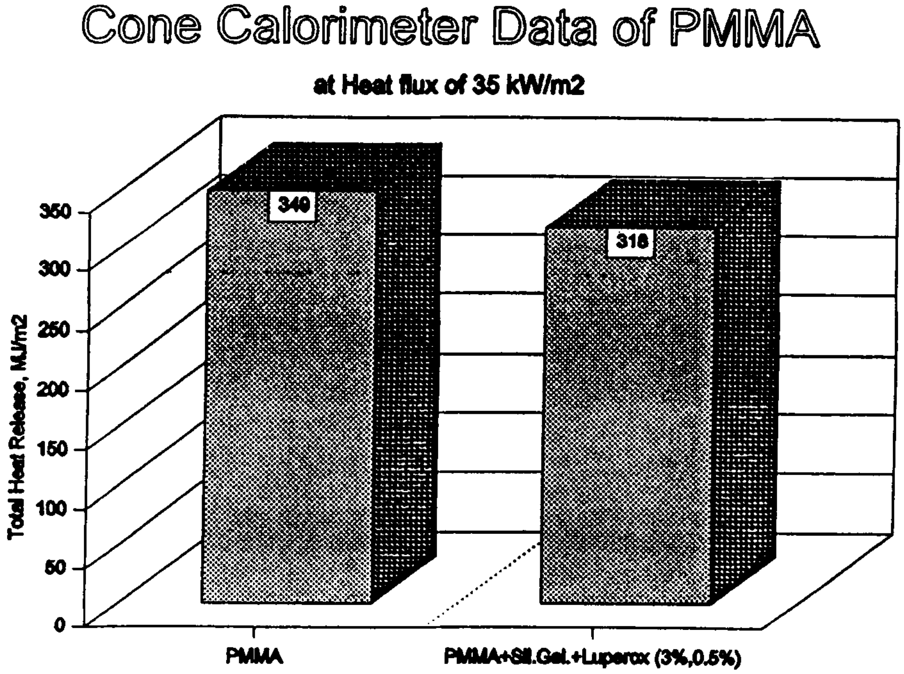


FIGURE 4 Cone calorimeter data of PMMA and PMMA + Silica Gel. Total heat release at 35 kW/m^2.

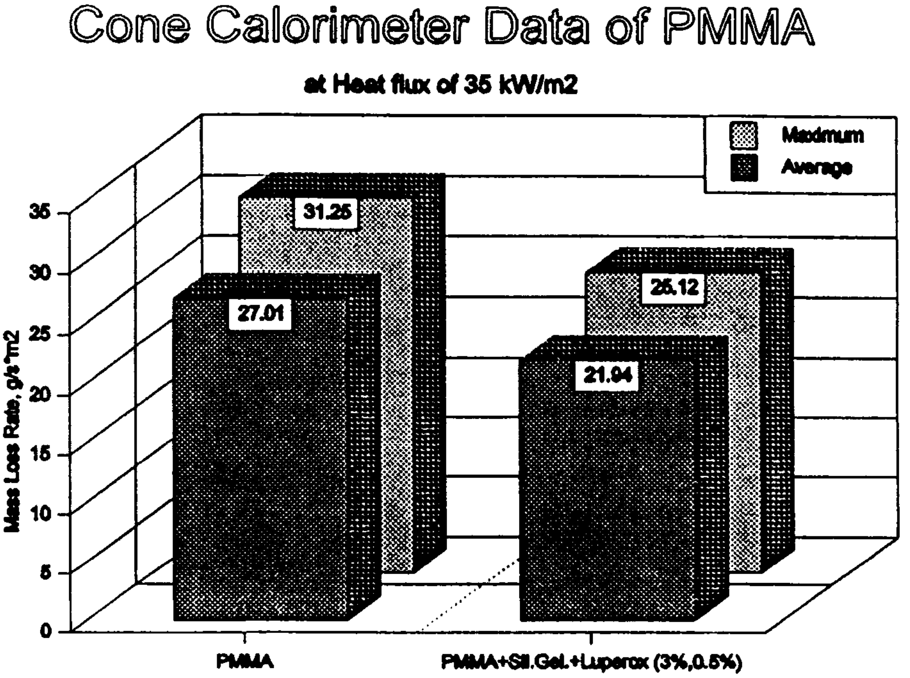


FIGURE 5 Cone calorimeter data of PMMA and PMMA + Silica Gel. Mass loss at 35 kW/m^2.

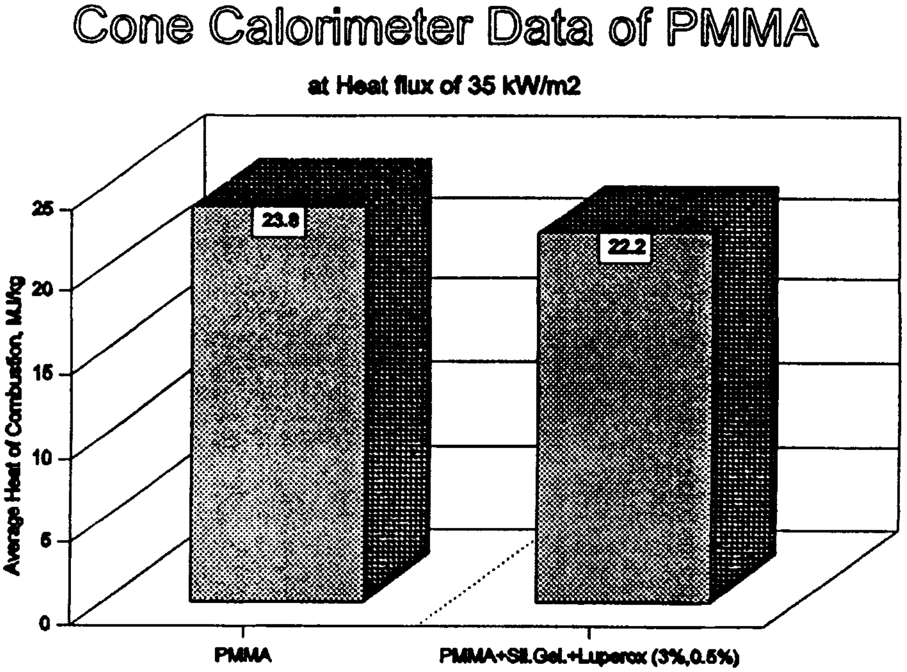


FIGURE 6 Cone calorimeter data of PMMA and PMMA + Silica Gel. Average heat of combustion at 35 kW/m^2.

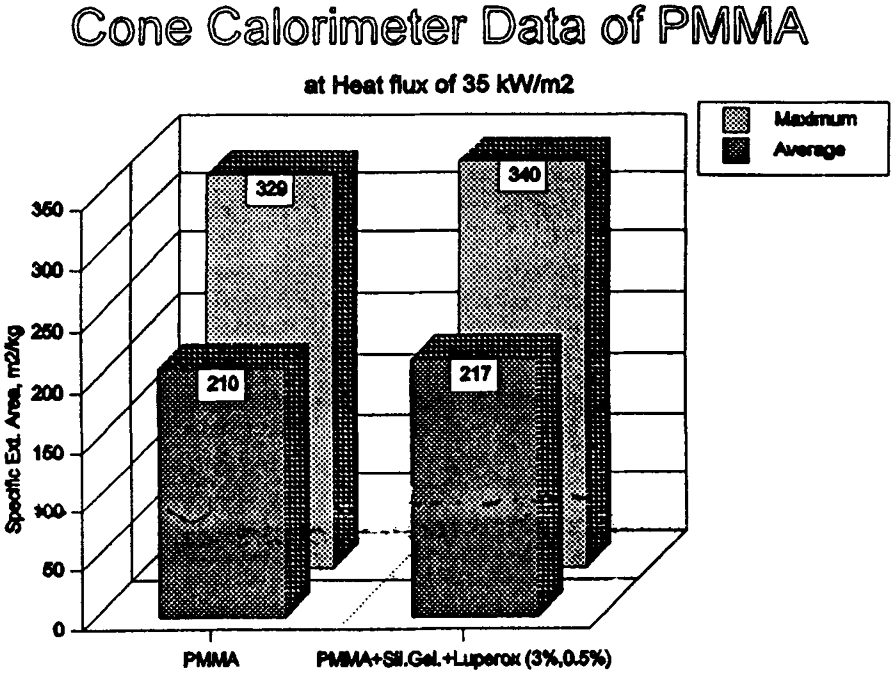


FIGURE 7 Cone calorimeter data of PMMA and PMMA + Silica Gel. Maximum and average smoke area at 35 kW/m^2.

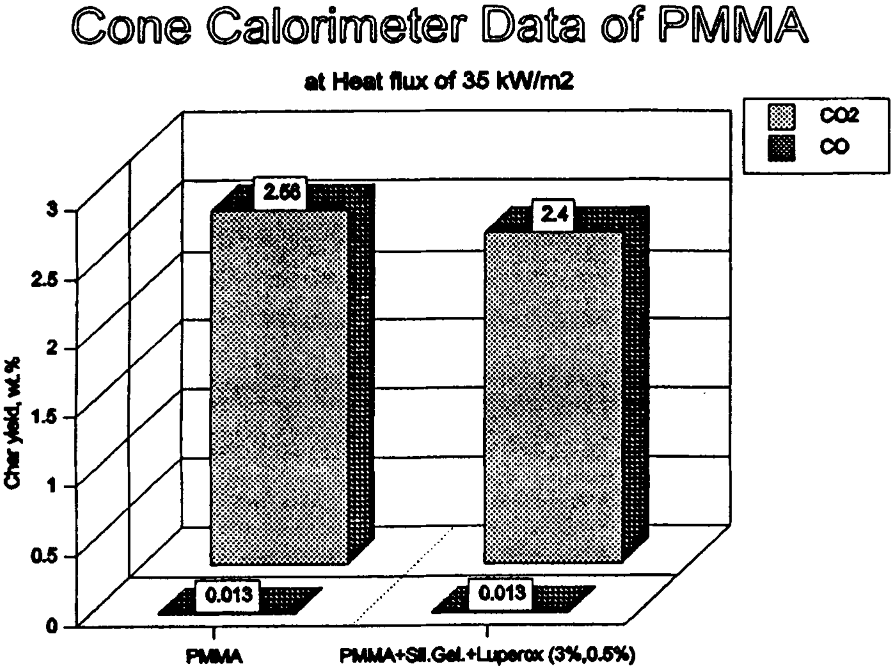


FIGURE 8 Cone calorimeter data of PMMA and PMMA + Silica Gel. CO_2 and CO generation at 35 kW/m^2.

less satisfactory correlation is given in the determination of Ext. Smoke Area (Figure 7). Also the Cone measurements do not show an increase of Carbon monoxide (Figure 8).

CONCLUSIONS

Proposed PMMA-SG composition represents one of the "transition" flame retardant system. Our final goal is to design an ecologically safe char/ceramic "former." It would be desirable to investigate more closely an influence of Silica Gel (in different compositions) on the polymer combustion.

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