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## New Flame Retardant Additives

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The fire safety of materials can be significantly enhanced by increased ignition resistance, reduced flame spread rates, reduced heat release rates, and reduced amounts of toxic and smoke products, preferably *simultaneously*. The use of more thermally stable polymers, of which many are available, might be a valid solution to these requirements but generally the cost of these materials is relatively high and, furthermore, their physical properties or processability may not be as desirable as those of less stable polymers. The most common approach to enhance fire safety performance is the use of flame retardant additives in large volume commodity polymers. The additives must have a minimum impact on physical properties and product cost. Although halogenated flame retardants are highly effective for reducing the heat release rate of commodity polymers, public perception of the environmental impact of recycling and incineration of certain halogenated flame retardants has become an issue in Europe [1,2]. Furthermore, concern over possible corrosion damage to metals by the combustion products from fire in which plastics containing halogenated groups or additives are involved, may impact the use of halogenated compounds. As our society becomes more dependent on high technology, the corrosion threat from fire in communication and electronic systems could become a problem.

Therefore, this study aims at developing other types of flame-retardant treatments. One possible alternative is the use of phosphorous based compounds whose effective flame retardant performance is well known [3,4]. However, it appears that the mechanism of flame retardancy depends on the polymer resin. It has been reported that the flame retardant operates in the condensed phase by forming char for rigid polyurethane [5] but, for polystyrene, phosphorous flame retardants act primarily in the gas phase [6]. To determine flame retardant effectiveness of phosphine oxides, various hydrolytically stable aromatic phosphine oxides were chemically incorporated into nylon 6,6, PET, and epoxy polymers. Their flammability properties were measured in the Cone Calorimeter. Another flame retardant approach used in this study is through the formation of char. There are several mechanisms whereby the formation of char reduces flammability: (1) part of the carbon (and hydrogen) stays in the condensed phase, thus reducing the amount of gaseous combustible degradation products evolved; (2) the low thermal conductivity of the char layer over the exposed surface acts as thermal insulation to protect the virgin polymer beneath [7]; and (3) a dense char acts as a physical barrier to gaseous combustible degradation products [8]. The majority of commodity polymers do not form char during their combustion and current research seeks to determine how to form char from these polymers. This char

forming approach is most successful when the polymer chars rapidly and early in the burning process. To be useful the charring process must be designed so that it occurs at a temperature greater than the processing temperature but before the polymer decomposition has proceeded very far. Our approach to char promotion is to investigate relatively inexpensive additives which form char from commodity polymers and to gain a fundamental understanding of the additive's char formation mechanism with the goal of optimizing the additive's performance. We have selected a combination of silica gel and potassium carbonate additives and determined their effects on flammability properties of commodity polymers [9].

All phosphine oxide copolymers were synthesized at Virginia Polytechnic Institute and State University and the synthetic methods used are described in refs. 10-12. The flammability properties of these samples were measured by the Cone Calorimeter (ASTM E1354) at external flux of either 35 kW/m<sup>2</sup> or 40 kW/m<sup>2</sup> in air. A significant decrease in heat release rate of nylon 6,6 is observed as the amount of the triphenylphosphine oxide, TPO, comonomers is increased. Piloted ignition delay time decreases slightly with increasing amount of the triphenylphosphine oxide. This is consistent with the slight decrease in the onset of thermal degradation temperature (from 410°C for nylon 6,6 to 402°C for the 30 mol% of the phosphine oxide sample [11]) seen in the TGA data (thermal gravimetric analysis) in air. The mass loss rate decreases with the amount of the triphenylphosphine oxide but this trend is much less than that of the heat release rate. The measured  $\Delta H_c$  show that the heat of combustion decreases with increase in triphenylphosphine oxide. A 40% reduction in the heat of combustion is about 40% from nylon 6,6 to the copolymer of triphenylphosphine oxide (30 mol%) and nylon 6,6. However, the yield of char after the test is from 2.3  $\pm$  0.2 % for nylon 6,6 to 8.7  $\pm$  0.8 % for the copolymer sample. These trends indicate that there is some flame retardant activity in the condensed phase but it appears the majority of the flame retardant activity is in the gas phase. This is confirmed by significant increases in CO yield and specific extinction area. Since the effect of the triphenylphosphine oxide on the mass loss rate is relatively small, the overall rate of CO and soot particles formation increased with an increase in the phosphine oxide content in the copolymer sample. Although the physical properties of the copolymer tends to be better than that of the blended sample, the cost of the copolymer sample might be higher than that of the blended sample. Another flammability study was carried out to compare the flame retardant effectiveness of the copolymer and a blend material. Triphenylphosphine oxide (10 mol %) was blended with nylon 6,6 and the flammability properties of this blend are compared with those of nylon 6,6 and of the nylon 6,6/TPO copolymer. The heat release rate of the blended sample does not differ significantly from that of the copolymer but the ignition delay time of the blended sample tends to be shorter than that for the copolymer sample. There are no significant difference in burning rate, heat of combustion, CO and specific extinction area. These results indicate that the flammability properties of nylon 6,6 with triphenylphosphine oxide as a blend or as a copolymer are not significantly different.

Other copolymers based on polycarbonate, PET, and epoxy (Epon 828) with triphenylphosphine oxide were synthesized to examine the effects of polymer chemical structure on flame retardant effectiveness of the phosphine oxide. The results are similar to those for nylon 6,6. The heat release rates of these polymers are reduced by the incorporation of triphenylphosphine oxide as a copolymer but an increase in the amount of CO and soot particulates was also observed.

The increase in the formation of soot particulates and CO, by the incorporation of triphenylphosphine oxide, could be caused by the combustion of pendant benzene groups from triphenylphosphine oxide. When benzene is a part of the polymer backbone, it tends to participate in formation of char [13]. However, pendant benzene groups do not always promote char formation. This is the case in polystyrene where the pendant benzene groups tend to generate soot particulates instead of char. In order to confirm this hypothesis, a new copolymer sample was synthesized with the pendant benzene replaced with methyl. The heat release rate of copolymer samples of diphenylphosphine oxide, DPO, with nylon 6,6 is not significantly different from that of copolymer samples of triphenylphosphine oxide with nylon 6,6. The mass loss rate, heat of combustion, CO yield, and specific extinction area of copolymer samples of diphenylphosphine oxide/nylon 6,6 are not significantly different from those of copolymer samples of triphenylphosphine oxide/nylon 6,6. These results indicate that the pendant benzenes do not enhance the formation of CO and soot particulates. To determine if benzene in the copolymer backbone was contributing to the increase in CO and soot particulates, we examined an aliphatic phosphine oxide blended with nylon 6,6. Trihydroxypropylphosphine oxide, THPPO, was used as the aliphatic phosphine oxide. The blended sample has 30 weight% of THPPO. The heat release rate of the blended sample with THPPO is compared with that of nylon 6,6 sample. The results, at an external flux of 35 kW/m<sup>2</sup>, show a significant reduction in heat release rate similar to the copolymer samples with TPO. In addition, the specific extinction area of the blended sample is much higher than that of nylon 6,6. The char yield of the blended sample was 4.2 %. These results are similar to those of the copolymer samples with TPO. The results suggest that phosphorous is the major factor in controlling the reduction of the heat release rate and the increase in CO and soot particulates. There is evidence to suggest the contention that, if phosphorous is released into the gas phase, it acts as a radical scavenger of H-atoms [14, 15]. On the other hand, the measurable char yield in the tested sample suggests that there is some activity in the condensed phase. If phosphorous stays in the condensed phase during combustion, phosphorous could be a significant char forming flame retardant.

The intention in using silica gel with K<sub>2</sub>CO<sub>3</sub> was to devise a method of in-situ formation of silicon based fire retardants during combustion. The reaction of silica gel and organic alcohols in the presence of metal hydroxides has been shown to give multicoordinate organosiliconate compounds [12]. If the reaction between the polymer and the additives occurs, it should crosslink the polymer and might assist in forming a silicon-

oxy-carbide, SiOC, type protective char during combustion. The flammability properties of these samples were measured in the Cone Calorimeter at an incident flux of 35 kW/m<sup>2</sup>. The results show that the additives enhance the formation of carbonaceous char even if the original polymer does not generate any char such as PP, PS and PMMA. The increases in carbonaceous char yield for PVA and cellulose is nearly a factor of 10. The reduction in peak heat release rate by the additives is quite significant, reaching about 50% for PP, PVA, cellulose, and nylon 6,6. However, the heat of combustion is not significantly affected by the additives and also the concentrations of particulates and CO in the combustion products do not increase with the additives. These trends are significantly different from those for halogenated flame retardant additives or even for above described copolymer samples of phosphine oxide. The results presented here clearly 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<sub>2</sub>CO<sub>3</sub>. The formation of carbonaceous char is also observed without K<sub>2</sub>CO<sub>3</sub>, which is water soluble, but the char yield is less than with K<sub>2</sub>CO<sub>3</sub>. It appears that K<sub>2</sub>CO<sub>3</sub> acts as a catalyst for the char forming reaction.

In order to understand the char formation reaction with silica gel, our unique molecular dynamics model, MD\_REACT, which accounts for the major reaction channels involved in the thermal degradation of polymers [16], was created by integrating a unique reactive dynamics code developed in this laboratory with a more generic commercial software package, Discover\_95, licensed by Molecular Simulations, Inc. [17]. Molecular dynamics consists of solving Hamilton's equations of motion for each of the 3N molecular degrees of freedom. The computer model accounts for many of the reaction pathways which are involved in the thermal degradation of polymers. Some of these reactions are: bond scission, depolymerization, intramolecular hydrogen transfer, chain stripping, intramolecular cyclization, intermolecular crosslinking and radical recombination reactions. Preliminary results of the interaction of silica gel with polypropylene will be presented.

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