

The Synthesis and Characterization of New Thermoplastic Fire Resistant Materials

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Abstract

Thermally stable high performance polyimides, poly(arylene ether)s, and poly(arylene sulfide) systems containing aryl phosphine oxide comonomers in controlled concentrations have been prepared and characterized. In general, tough thermoplastic materials have been produced that show significant char yield in air, which increase with the concentration of aryl phosphine oxide. Thus, they are considered candidates for fire safe thermoplastic materials. Preliminary cone calorimetry measurements have been conducted on lower performance aliphatic polyamides, which indicate that, indeed, the heat of combustion is reduced. Additional characterization studies are in progress and will be discussed at the meeting.

Introduction

Organic materials are widely utilized in aircraft interiors for various important functions, such as carpets, seats, bins, appliance housings, communication devices, etc. The relevance of the fire safety of these materials to airline transportation is well acknowledged, but poorly understood. There is an important need to further identify fundamental relationships between the molecular structure of the materials and their behavior in fires. This should assist in the rational design of fire resistant cabins for commercial aircraft. It is considered that basic research on synthesis, characterization, and processing of new materials will be necessary to improve the fire performance of material systems. A summary of these features has recently been provided (1).

Preliminary Results

Thermoplastic materials offer attractive advantages including rapid processability by methodologies such as injection molding, film extrusion and fiber spinning. In addition, the likelihood of generating recyclable materials is recognized to be more straightforward than for the other option, e.g. thermosetting network systems. The author and his colleagues have been involved in novel phosphorus containing polymers now for over five years (2-10). Emphasis has been placed upon

hydrolytically stable melt processable high performance polymeric materials that are capable of demonstrating either high glass transition temperatures and/or high semicrystalline melting points. The latter are of interest for applications requiring excellent chemical resistance, such as for textile fibers and many engineering thermoplastic applications. Amorphous high glass transition temperature materials are an alternate possibility, and such systems would be favored where transparency and exceptionally high impact strength are sought. Both morphologies are possible in the systems investigated thus far. The triphenyl phosphine oxide unit is inherently non-coplanar and leads, in general, to amorphous homopolymers which display high transition temperatures, good optical transparency, very high char yields when exposed to either nitrogen or air (TGA experiments), ductile mechanical behavior, and good adhesion characteristics (especially to metals). Many of these same characteristics can be applied to semicrystalline copolymers where the composition of the triaryl phosphine oxide structure is limited to about 50 mole percent or less (2). Examples of systems already demonstrated include the poly(arylene ether ketone)s, polyimides, polybenzoxazoles, as well as polycarbonates, polyesters, and polyamides. In addition, poly(thioarylene phosphine oxides) which are analogous to polyphenylene sulfides have also been synthesized.

Initial characterization of the homo- and copolymers was limited to thermogravimetric analysis (TGA) and rather crude laboratory Bunsen burner testing. However, these preliminary evaluations repeatedly demonstrated significant qualitative, but apparently fundamental, differences between the high performance aromatic polymers which contained hydrolytically stable phosphorus and their controls.

Some of the homo- and copolymers, as mentioned earlier, showed remarkably high weight retention in both inert atmospheres, such as nitrogen, as well as more aggressive air or oxygen systems. Representative data for poly(arylene ether)s including polyketone phosphine oxide copolymers and polyimides is provided in Figures 1, 2, and 3 (shown below).

The ability to retain semicrystalline morphological structures in poly(ether ketone) and polyether phosphine oxide copolymers is illustrated in Scheme 1 and Table 1. As expected, approximately 50 mole percent or more of the semicrystalline component is required to maintain an ordered structure.

All of the materials described in this section appear to be melt processable, if properly designed to the appropriate molecular weights.

These extensive laboratory experiments have recently been expanded to assess the fire resistance of the new material systems via cone calorimetry. This has been possible through the joint collaboration with the NIST Fire Research Laboratory, under the guidance of Dr. T. Kashiwagi (9,10). In the NIST program the primary interest has been placed on the improvement of high volume commodity materials, such as nylon 6,6, PET, polycarbonates, and epoxy networks. Progress has been made in this area and the heat release rate for a series of nylon 6,6 triphenylene oxide dicarboxylic acid copolymers is illustrated in Figure 4.

The data indicate that the heat release rate by these cone calorimetry measurements has been significantly reduced. There are certainly many additional unanswered questions concerning both the proper molecular design and the most appropriate fire test methodologies. For example, it is possible to replace one of the three phenyl groups with an alternate structure, such as a methyl group. This would increase the fraction of phosphorus in the repeat unit and might also reduce undesirable residual soot formation (9,10).

Conclusions

It was possible to synthesize high molecular weight performing aryl phosphine oxide copolymers based on poly(arylene ether)s and polyimides. Both materials can be designed to be melt processable to show good mechanical properties and each demonstrate a very significant char yield, suggesting improved fire resistance.

Current and Future Studies

Currently, a systematic series of copolymers based upon poly(arylene ether)s, poly(arylene sulfide)s, and poly(aryl ether imide)s, which vary in the concentration of aryl phosphine oxide comonomer are being prepared. These materials will be subjected to degradation studies, both by thermal analysis and cone calorimetry in selected cases and the results will be discussed at the meeting.

Acknowledgments

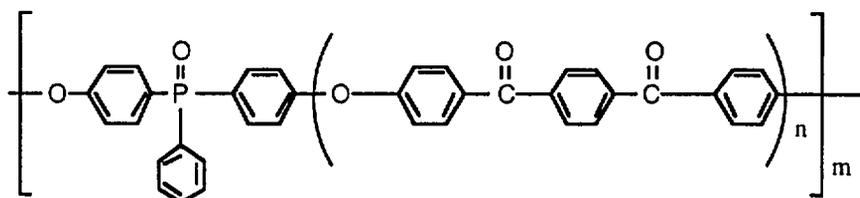
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References

1. R. E. Lyon and T. E. Lund, Advanced Aircraft Materials Research and Development Plan, p. 345-364, in Proceedings of the International Conference for the Promotion of Advanced Fire Resistant Aircraft Interior Materials, Atlantic City, New Jersey, February 1993; R. E. Lyon, Polymeric Materials: Science and Engineering, 71, 26 (1994)..
2. C. D. Smith, H. J. Grubbs, A. Gungor, J. Wescott, S.C. Liptak, P. A. Wood, and J. E. McGrath, "Fire-Resistant Hydrolytically Stable Poly(Arylene Phosphine Oxide) Material Systems," p. 259, in Proceedings of the International Conference for the Promotion of Advanced Fire Resistant Aircraft Interior Materials, Atlantic City, New Jersey, February 1993
3. Smith, C. D., Gungor, A., P. A. Wood, S. C. Liptak, H. Grubbs, T. H. Yoon, And J. E. McGrath, "Hydrolytically Stable Thermoplastic and Thermosetting Poly(Arylene Phosphine Oxide) Material Systems", *Makromol. Chem., Macromol. Symp.*, **74**, 185-188, (1993).
4. Y. Delaviz, A. Gungor, J. E. McGrath, and H. W. Gibson, "Soluble Phosphine Oxide Containing Aromatic Polyamides," *Polymer*, **34**(1), pp. 210-213, (1992).
5. C. D. Smith, H. F. Webster, J. P. Wightman, and J. E. McGrath, "Unique Features of Poly(Aryl Phosphorus Oxides)," *High Performance Polymers*, **4**(3), 211-229, (1991).
6. C. D. Smith, D. K. Mohanty, R. L. Holzberlein, S. D. Wu, D. H. Chen and J. E. McGrath, "Poly(Arylene Ether) Phosphine Oxide Thermoplastic Materials for Potential Electronic Applications," *SAMPE Electronic Materials and Processes Proceedings*, Los Angeles, CA, **3**, 141-147, June 20-22, 1989.

7. Wescott, J. M., Yoon, T. H., Rodrigues, D., Kiefer, L., Konas, M., Wilkes, G. L. and McGrath, J. E., "Synthesis and Characterization of Triphenyl Phosphine Oxide Containing Polyimide-Polydimethyl Siloxane Segmented Copolymers," *Polymer Preprints*, **34(1)**, 308-309, 1993; *J. Macromol. Sci., Pure Appl. Chem.*, **A31(8)**, pp. 1071-1085 (1994).
8. A. Gungor, C. D. Smith, J. Wescott, S. Srinivasan and J. E. McGrath, "Synthesis of Fully Imidized Phosphorous-Containing Soluble Polyimides," *Polymer Preprints*, **32(1)**, 172-173 (1991).
9. I. -Y. Wan, J. E. McGrath, and T. Kashiwagi, "Triarylphosphine Oxide Containing Nylon 6,6 Copolymers," *ACS Symposium Series 599, "Fire and Polymers II,"* ed. Gordon Nelson, Washington, D. C., 29-40, (1995)
10. D. M. Knauss, J. E. McGrath, and T. Kashiwagi, "Copolycarbonates and Poly(Arylates) Derived from Hydrolytically Stable Phosphine Oxide Comonomers," *ACS Symposium Series 599, "Fire and Polymers,"* ed. Gordon Nelson, Washington, D. C., 40-55, (1995)

Table 1
Solution and Thermal Characterization of PEPO/EEK Copolymers



EPO/EEK	IV ¹	T _g ² (°C)	T _m ² (°C)	TGA ³ (5%)	Char% 750°C(air)
50/50	0.41	201	no	550	56
40/60	0.42	200	*	548	63
30/70	-	198	346	542	23
20/80	-	198	377	534	22

* Shows a T_m peak after annealing

1. in NMP(25°C)
2. DSC 1st heat (10°C/min)
3. in air (10°C/min)

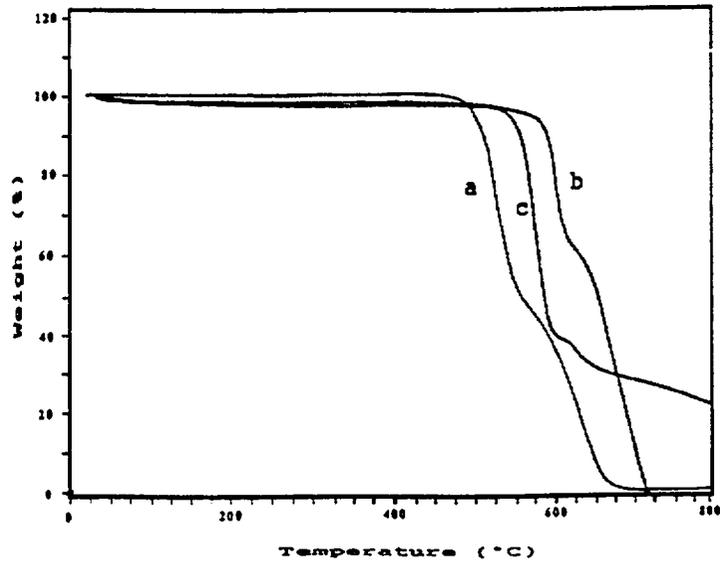


Figure 1
Dynamic TGA Scans in Air for (a) UDEL PSF, (b) PEEK and (c) BP PEPO

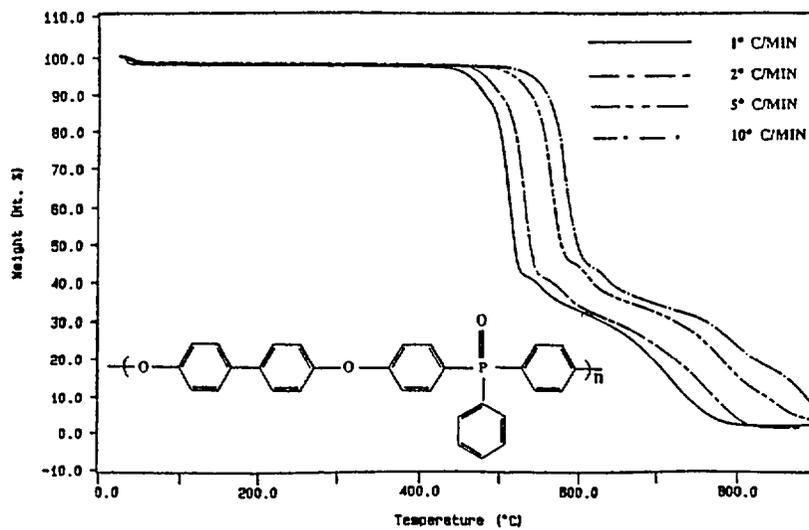


Figure 2
TGA Thermograms in Air of High Molecular Weight BP PEPO at Various Heating Rates

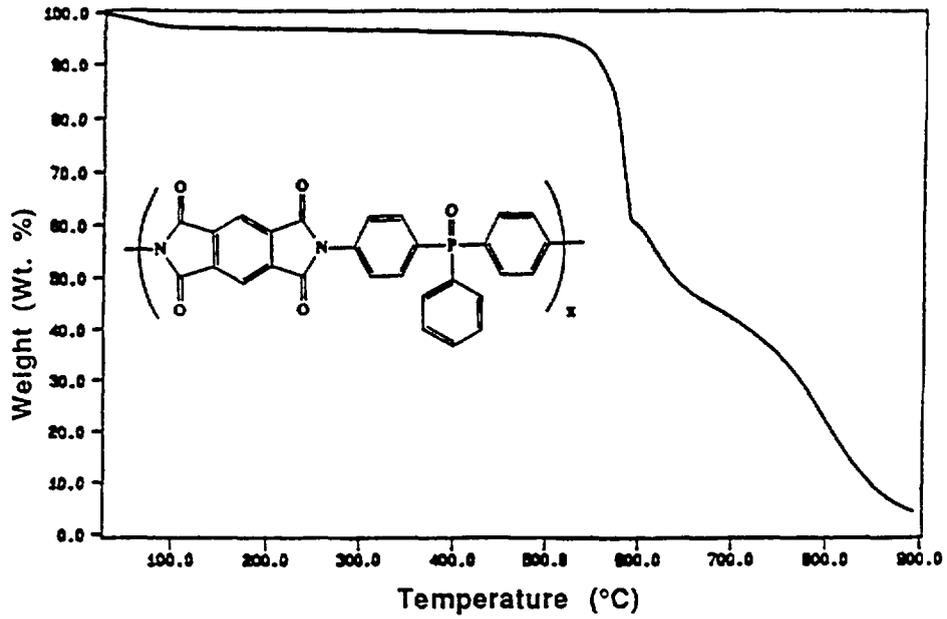


Figure 3
Dynamic TGA Thermogram PMDA-DDPPO (Air Atmosphere; Heating rate - 10°C/minute)

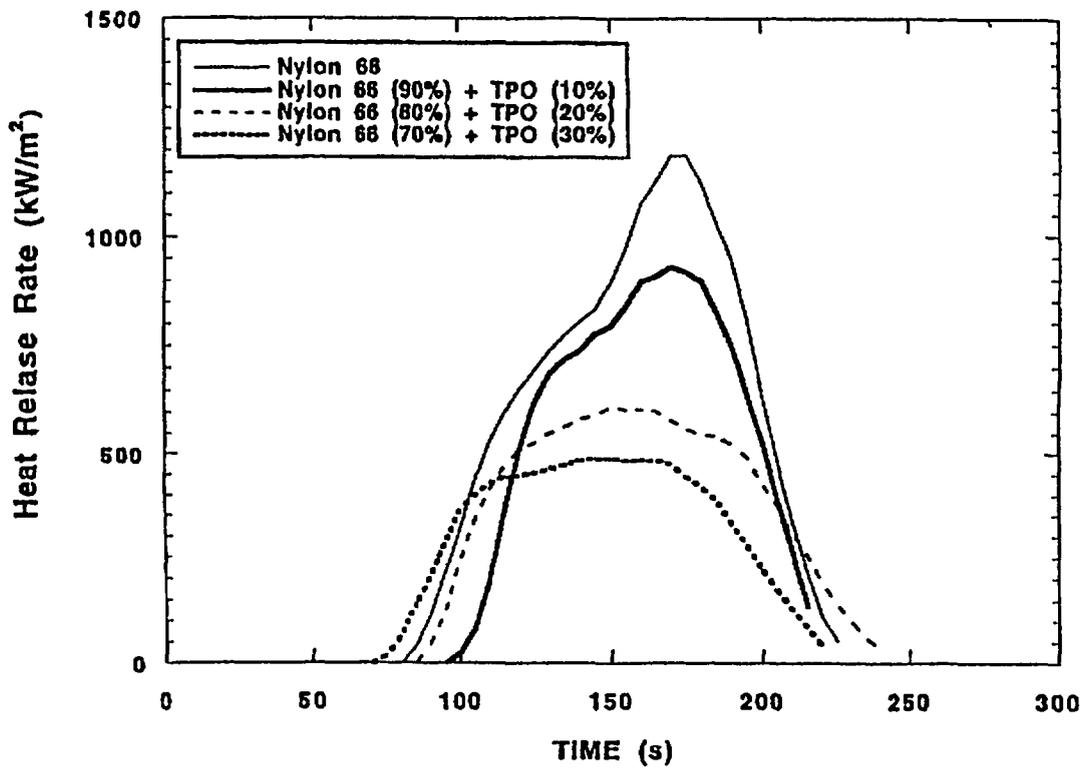
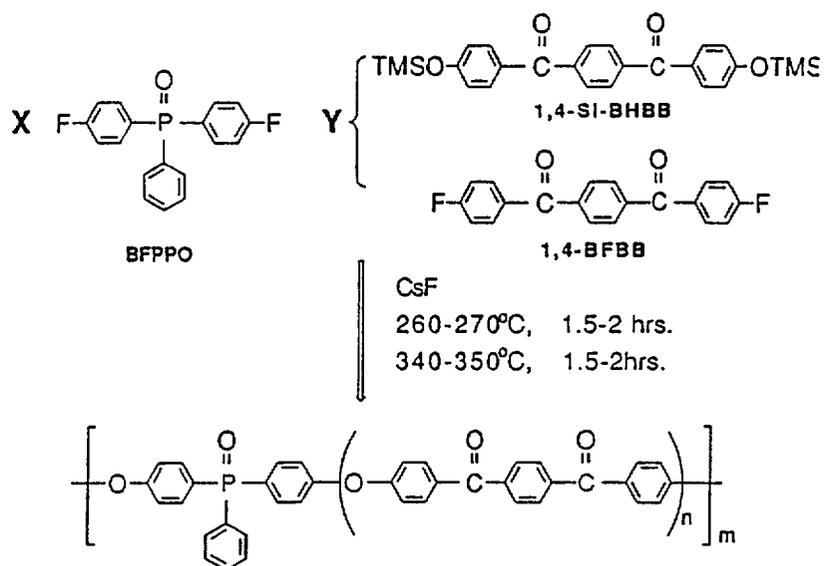


Figure 4
Heat Release Rate of Triarylphosphine Oxide Containing Nylon 6,6 Copolymers

Scheme 1
Synthesis of PEPO/EKK Copolymers Via Silylated Bisphenols



X / Y = 50/50, 40/60, 30/70, 20/80 mole ratios