New High-Performance Organophosphorus Flame Retardant

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Abstract

A new non-halogen flame retardant has been developed and is useful for a variety of high performance applications. This non-reactive phosphorus-based material satisfies fire safety needs for a broad range of resins including epoxy, polyolefin, and polyamide. The combination of excellent flame retardant efficiency, high thermal stability and exceptional electrical properties is unique to this organophosphorus flame retardant and makes it a breakthrough technology for high speed, high frequency use in fast growing wireless and wired infrastructures. Resin performance data, including formulations with synergists, are presented in this paper.

Introduction

Current flame retardant research is focused on developing new flame retardants which not only meet the higher performance requirements required by today's polymer producers, formulators, and original equipment manufacturers but which also have superior toxicological and environmental profiles.¹⁻³ The company developed flame retardant (PFR-1) is a new organophosphorus flame retardant that satisfies both high performance and environmental responsibility needs for a variety of polymeric systems.

The printed circuit board market was the initial target for developing a new high performance phosphorus flame retardant. Over 100 compounds were synthesized. High thermal stability is critical for success in high performance circuit boards. TGA 5 wt% loss greater than 350°C was met by one third of candidates. Four additional areas of importance are shown in Figure 1 and listed below.

- 1) Flame retardant efficiency (UL-94 V-0 at 3 wt%P)
- 2) Technical performance (defined as laminate $T_g \ge 180^{\circ}C$)
- 3) Sustainability: environmental, health and regulatory outlook (not P-B-T)
- 4) Cost-in-use

Though all factors are essential, considerable emphasis was placed on flame retardant efficiency, where a UL-94 V-0 rating was targeted at 3wt% phosphorus loadings. Lower efficiency compounds would likely have to be used at higher loadings and could lead to poor physical and mechanical performance characteristics. This high flame retardant efficiency requirement was met with six of the candidates. Half of these compounds allowed retention of a high epoxy laminate glass transition temperature ($\geq 180^{\circ}$ C). Two of the remaining three candidates were predicted by modeling to have a favorable environmental,

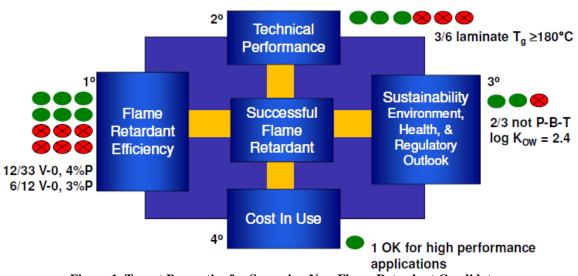


Figure 1. Target Properties for Screening New Flame Retardant Candidates.

health and regulatory outlook. They were predicted to be non-toxic and non-bio-accumulative and therefore would not be classified as Persistent-Bio-accumulative-Toxic (P-B-T). The log of the octanol-water partition coefficient, log K_{ow} , was 2.4 for PFR-1 and also indicates that it is not expected to bio-accumulate. Another characteristic, solubility in prepreg processing solvents, is desirable, but not essential for high performance applications. Examples of insoluble flame retardants, also with good P-B-T profiles, used in high performance circuit boards include 1,2-bis(pentabromophenyl)ethane (BrFR-1) and N,N-ethylenebis(tetrabromophthalimide) (BrFR-2) shown in Figure 2.⁴

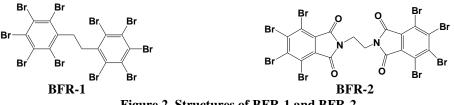


Figure 2. Structures of BFR-1 and BFR-2.

Many phosphorus-based flame retardants are suitable for only one or two application areas. Some of these flame retardants fall short of meeting broad requirements including flame retardant efficiency, thermal stability, physical and mechanical properties, and electrical properties of the polymers to which they are added. The company's new organophosphorus flame retardant is melt blendable in some resin systems, has excellent flame retardant efficiency, thermal stability and UV color stability. It can be used in both thermoplastic and thermoset polymers. A variety of applications have been explored, including:

- Circuit boards (epoxy, hydrocarbon, others...)
- Aerospace (epoxy, phenolics, others...)
- Films and fibers (polyolefin, polyamide, polyester)
- Connectors and light emitting diode (LED) parts (high temperature polyamide)
- Wire and Cable (polyolefin, others...)

We anticipate identifying additional areas of promise for this broadly applicable new flame retardant. This paper summarizes some of the performance attributes of this new developmental organophosphorus flame retardant in a few selected polymer systems.

Experimental

Epoxy Laminate Preparation and Testing

A variety of 4-ply laminates were prepared by blending flame retardants with a multifunctional epoxy novolac resin solution in methyl ethyl ketone (MEK) and using a phenolic curing agent and 2-phenylimidazole promoter. In general, stock solutions of resin, curative and promoter were all prepared and stored separately to facilitate experimentation. An 85wt% phenol epoxy novolac resin solution, containing 15 wt% 2-butanone (MEK) was used along with a novolac curing agent. A novolac resin solution was prepared by dissolving 50 wt% of the novolac curing agent in 50 wt% MEK solvent. FR-1 was ground using a coffee bean grinder to reduce the particle size of the compound to a d50 of about 6 µm prior to combining with the resin. A flame retardant resin mixture containing about 3 weight% phosphorus was prepared. The novolac to promoter ratio was about 525 with a gel time of about 4 minutes. The viscosity of the resin mixture was adjusted by adding additional MEK, and the formulation was thoroughly blended using a high shear mixer stirred at 6,000 rpm for 15-30 minutes. The resulting varnish was applied to 7628 woven glass fabric with 643 finish and B-staged at 170°C in a forced air oven for about 3.5 minutes. The edges were removed, and 4 layers of prepreg were stacked between two layers of Pacothane release film and two steel plates (1/8 inch thick, 12 inch by 12 inch square dimensions). The laminate was formed in a hot press at 5,000 psig for 1-2.5 hours.

The glass transition temperature, T_g , for the laminate was measured using a differential scanning calorimeter (DSC) similarly to IPC method IPC-TM-650 (method 2.4.25c), using a 20°C/min heating rate (nitrogen atmosphere) with the following differences: isothermal hold temperatures were 200°C for laminates based on the phenol epoxy novalac resin, 220°C for laminates based on a higher functional phenol epoxy novolac resin and 250°C for laminates based on a higher functional phenol epoxy novolac resin with no flame retardant. In some cases, a third scan was performed to determine the delta T_g between the first, second, and third scans. Laminate decomposition temperature (T_d) was measured as the 5% weight loss temperature using a 10°C/min heating rate (nitrogen atmosphere) using a thermogravimetric analyzer (TGA). The UL-94 flammability test was performed using ASTM D3801-06 in a UL-94 burn chamber to obtain flammability ratings for sets of five coupons. T1 + T2 burn times were added to give a total burn time for 5 coupons. Compounding, Molding, and Testing

PFR-1 was evaluated with a thermally stable melamine-based synergist, N-syn-2. Other additives included a primary antioxidant, a phosphite secondary antioxidant, synthetic hydrotalcites (DHT-4A, DHT-4C); an anti-drip agent, partial sodium salt of ethylene/methacrylic acid copolymer (Na ionomer anti-drip), and polytetrafluroethylene (PTFE) anti-drip agent.

Glass fiber was fed downstream in the extrusion process to maintain good physical properties of the parent resin. Compounded resin was dried rigorously (16h, 120°C) before performing melt flow and rheology measurements. Powder mixing using a timed bi-directional tumble mixer was also employed. Various resins and flame-retardants were hand mixed in a plastic bag and/or tumble-mixed prior to extrusion. The compounding was conducted on a twin-screw extruder. Extrusion temperatures for high temperature polyamide were in the range of 265-330°C and for polyethylene in the range of 180-240°C. Extruded strands were pelletized on-line. Test parts were formed in an injection-molding machine. Molding temperatures and pressures for the 0.4mm polyamide molds were as follows: injection pressure (1000/1350 psi), nozzle (288°C), zone 1 (296°C, 1100 psi), zone 2 (291°C, 1050 psi), zone 3 (285°C, 1000 psi), zone 4 (800 psi), zone 5 (700 psi), hold time of 8 sec, and cooling time of 30 sec.

Testing was performed on samples according to the following ASTM test standards: Tensile Strength and Elongation at Break (ASTM D638) specimen type 1; Heat Distortion Temperature (ASTM D648) 1/8" at 264 psi and 120°C/h; Notched-Izod Impact Strength (ASTM D256) method A; Melt Flow Rate (ASTM D1238) procedure A, conditions as noted; and Volume resistivity and surface resistivity (ASTM D257). The UL-94 flammability test (ASTM D3801-06) was performed on 3.2 mm (1/8 inch), 1.6 mm (1/16 inch), 0.8 mm (1/32 inch), and 0.4 mm (1/64 inch) bars as noted. Initial color measurements (ASTM D1925) were made using Hunter Lab scale, D65 illuminant, 10° observer, and integrated-sphere geometry. Initial YI* and Initial L* were recorded. For Xenon-Arc UV weathering (ASTM D4459-99), the following conditions were used: continuous light cycle, 0.3W/m² at 340nm, black panel temperature of 55°C, chamber relative humidity of 55%, 100 hour, 200 hour, and 300 hour exposure, CIE L*a*b*, 10° observer, and D65 Illuminant. YI* and Delta E* (ASTM D1925) values were recorded. Un-notched charpy impact strength measurements were performed at the company's Bergheim, Germany site according to ISO179/1eU. Data were recorded for samples oriented edgewise with 3.3 mm height and 12.8 mm width. Capillary rheology measurements were performed at constant 1,000 sec⁻¹shear.

Electrical property measurements were performed at Pennsylvania State University. The frequency range of interest for the polypropylene samples was between 1 GHz and 20 GHz. Resonant cavity techniques were employed because of the low dielectric loss for the samples. The microwave dielectric properties of linear low density polyethylene samples with flame retardant were investigated with a split cavity technique. ⁵⁻⁶ Disk samples (2" diameter x 1/8" thick) were individually placed within a split cavity for microwave testing. Three samples of each material were tested to ensure reproducibility of the measurement. In a second characterization technique, R-band and X-band cavities were completely filled with powder, and the dielectric properties were obtained by the resonant cavity frequencies. Two cavity sizes were used for 2 GHz (R-band) and 10 GHz (X-band). All of the loss (D_f) values were low and approached the lower threshold value of the measurement technique. The dielectric constant (D_k) values for the powders could not be accurately measured by this technique.

Results and Discussion

Epoxy Laminates

As global data transmission speeds increase, so does the need for higher performance materials in circuit boards. This new organophosphorus flame retardant PFR-1 exhibits a unique combination of excellent flame retardant efficiency, high thermal stability, and exceptional electrical properties useful for fast growing wireless and wired infrastructures. Typical properties of PFR-1 are shown in Table 1.

Table 1. Properties of PFR-1 Flame Retardant.					
Property	Value				
Form	Solid, white powder				
Specific Gravity (g/cm ³)	1.4				
Melting Point, °C (by DSC)	300				
TGA (10°C/min, nitrogen)					
1% weight loss, °C	330				
5% weight loss, °C	365				
10% weight loss, °C	380				

Tetrabromobisphenol-A (TBBPA) is the leading flame retardant used in the FR-4 printed circuit board industry.⁷⁻⁹ DOPO, 6H-Dibenz[c,e][1,2]oxaphosphorin, 6-oxide (dihydrooxaphosphaphenanthrene), is the leading organophosphorus flame

retardant used in standard FR-4 markets (Figure 3).⁹⁻¹¹ Some alternate reactive phosphorus flame retardant technologies have been proposed.¹²⁻¹³

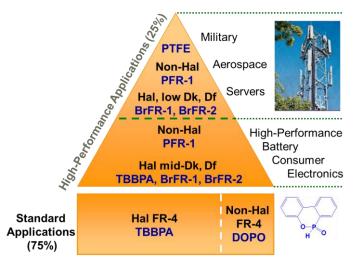


Figure 3. Flame Retardants Used in Circuit Board Markets

Several 4-ply laminates were prepared by blending PFR-1 by itself or in combination with a melamine-based nitrogen synergist (N-syn-1) in a multifunctional epoxy novolac resin solution in MEK and using a phenolic curing agent (Figure 4). A V-1 (borderline V-0) rating was obtained using only PFR-1 to make a laminate containing 3wt% phosphorus. Combining PFR-1 with a nitrogen synergist resulted in a solid V-0 rating at 3wt% phosphorus in the laminate. The phosphorus content could be further decreased to 2.4wt% phosphorus using PFR-1 in combination with a nitrogen synergist.

With addition of silica filler, a UL-94 V-0 rating was obtained for a formulation containing as low as 1.8wt% phosphorus. In the case of silica addition, the effect is not synergistic, rather a simple replacement of resin with an inert filler. Laminate producers utilize fillers to lower the cost of the formulation and to improve laminate dimensional stability, stiffness, thermal conductivity, compressive strength and hardness.¹⁴

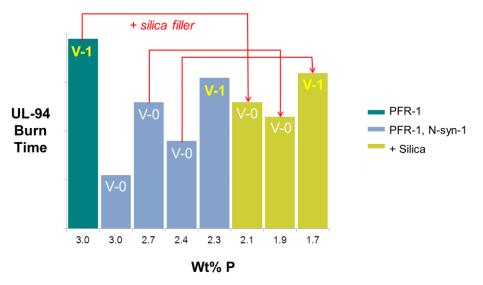


Figure 4. Flame Retardant Efficiency of PFR-1 in Epoxy Novolac Laminates.

Glass transition temperature and thermal stability of laminates containing PFR-1 are shown in Figure 5. A higher glass transition temperature (170-180°C) was obtained upon formulating with a nitrogen synergist. Though the laminate decomposition temperature was decreased by inclusion of a nitrogen synergist, a high TGA 5 weight% loss temperature, $T_d > 370^{\circ}$ C, for the laminate was still maintained.

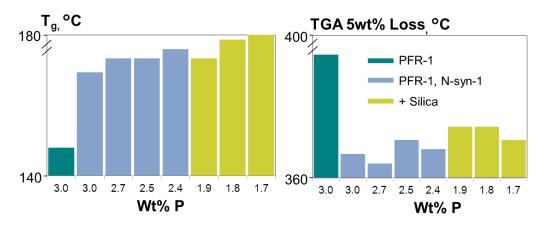


Figure 5. Glass Transition Temperature and Decomposition Temperature for Laminates Containing PFR-1.

Electrical properties (Df, dissipation factor) of neat flame retardant powder were measured at 2 GHz (Table 2). The values obtained for PFR-1 (0.001) were comparable to those values obtained for BrFR-1 (0.001) and BrFR-2 (0.002), brominated flame retardants used in high performance circuit board applications. At 10 GHZ, values for all three flame retardants were identical. The influence of air in these measurements can be an issue, so the samples were compacted under pressure. R-band and X-band cavities were completely filled with powder.

Table 2. Neat Flame Retardant Dissipation Factors.								
Electrical Properties (neat powder)	PFR-1	BrFR-1	BrFR-2					
D _f , Dissipation Factor (2 GHz)	0.001	0.001	0.002					
D _f , Dissipation Factor (10 GHz)	0.001	0.001	0.001					

Polyolefins

The performance of PFR-1 in linear low-density polyethylene (LLDPE) was compared at different loadings and with use of a nitrogen synergist (Table 3). Use of antimony trioxide (ATO) with brominated flame retardants is preferred in polyolefins, for example 21% BrFR-1, 7% ATO, and 15% talc. In this case, loadings of BrFRs similar to that of PFR-1 were used to compare electrical properties and UV stability. Electrical properties (D_f , dissipation factor and D_k , dielectric constant) of flame retardant-containing LLDPE resin were measured at 18 GHz.

Ingredient		1	Neat Resin	PFR-1	PFR-1	PFR-1	BrFR-1	BrFR-2
LLDPE Resin			100	60	70	70	70	70
FR Loading (wt%)				40	30	20	30	30
N-syn-1						10		
Flame Retardant Proper	rties							
UL-94 Flammability (3.2	2 mm, 1/8")			V-0	V-2	V-0		
T1 + T2 (sec)				8	19	8		
Electrical Properties								
D _f , Dissipation factor (18 GHz)			0.0002		0.0003	0.0007	0.0003	0.0003
D _k , Dielectric Constant (18 GHz)		2.29		2.51	2.55	2.37	2.39
Volume Resistivity		$cm(x10^{17})$			4.0	0.5	2.7	1.7
Surface Resistivity	Ohm/sq (x10 ¹⁷)				3.5	1.8	4.5	5.1
UV Stability, CIE L*a*b*, 10° observer, D65 Illuminant								
Initial Color	Initial YI ³	k	3.4		3.7	2.3	12.6	15.3
		Initial L*	94.8		94.5	95.1	91.5	95.2
After 100 h Xenon	YI*		11.2		10.4	6.5	27.1	25.6
		Delta E*	4.7		4.1	2.6	8.4	7.2
After 200 h Xenon	YI*		13.1		12.8	8.8	34.3	26.5
		Delta E*	5.7		5.4	3.9	12.6	8.8
After 300 h Xenon	YI*		14.5		14.8	10.7	41.6	26.9
		Delta E*	6.5		6.6	5.0	16.9	9.5

The D_f values (0.0003) were low and identical for all evaluated flame retardant systems (slightly higher vs. the neat resin, 0.0002). The D_k values were lowest for neat resin (2.29), followed by resin with flame retardant: BRFR-1 (2.37) and BRFR-2 (2.39) and PFR-1 (2.51) and PFR-1 with N-syn-1 (2.55). Retention of good resin electrical properties points towards potential use in polyolefins and related resin systems where electrical properties are important, such as those used in printed circuit boards and wire and cable applications.

PFR-1 (40 wt%) was used to obtain a V-0 rating. With 30 w% PFR-1, a V-2 rating (flaming drip) was obtained. By decreasing the PFR-1 loading to 20 wt% and adding 10 wt% nitrogen synergist, a V-0 rating was obtained, allowing lower loadings of PFR-1, while maintaining good flame retardant performance.

Excellent UV color stability was observed with XP-7866 formulations in polyethylene (with and without nitrogen synergist), where delta E* was less than ten after 300 hours of xenon-arc weathering (Table 3). The UV stability of PFR-1 in LLDPE is even better than the polyethylene containing BrFR-2, which is considered to have good UV performance. UV absorbers/stabilizers can be used to further improve performance; No UV stabilizers have been added to these formulations.

Additional physical properties were also improved by formulating with a nitrogen synergist (Figure 6). Properties evaluated include melt flow index (MFI), Izod impact strength, elongation at yield and elongation at break.

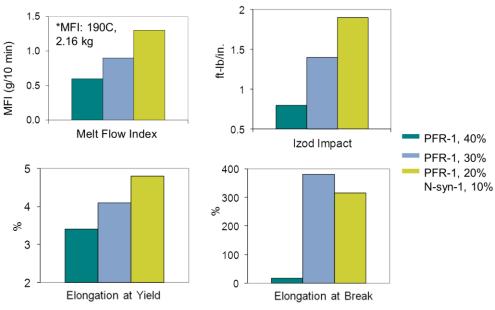


Figure 6. Physical Properties of PFR-1 in LLDPE Resin.

High Temperature Polyamide 6T

Both brominated flame retardants, including a commercial brominated polystyrene, BrFR-3 from the company, and phosphorus flame retardants, including a commercial phosphorus flame retardant, PFR-2, have been used extensively in engineering thermoplastic resins, including a variety of polyamides for connectors.¹⁵⁻¹⁶ Table 4 summarizes comparisons of PFR-1 with PFR-2 and BrFR-3 in glass-filled high temperature nylon (HTN).

Use of PFR-1 in combination with a nitrogen synergist, N-syn-2, allowed for attainment of good flame retardancy without sacrificing thermal properties such as heat distortion temperature (HDT) and physical properties, such as tensile strength. Without nitrogen synergist, high loadings of PFR-1 are required to achieve a UL-94 V-0 rating. For a formulation containing 20% PFR-1 and no synergist, lower values were obtained for several properties, including HDT (252°C), tensile strength (16x10³ psi), elongation at break (1.2%) and charpy impact strength (27 kJ/m²) compared with a formulation containing 10% PFR-1 and 10% N-syn-2, where HDT (271°C), tensile strength (22x10³ psi), elongation at break (1.7%) and charpy impact strength (39 kJ/m²) values were improved by inclusion of a nitrogen synergist. Such a formulation would also be more cost advantageous. Additional synergists will be explored for use with PFR-1.

Use of DHT-4C in place of DHT-4A gave lower burn times for the 0.8mm thick molds. With increased DHT-4C loading (from 0.1 to 0.25%), a UL-94 V-0 rating was obtained for 0.4 mm thick parts. More data will be collected using this new 0.4

mm mold. When the partial sodium salt of ethylene/methacrylic acid copolymer anti-drip agent was omitted from the formulation, a V-2 rating (flaming drips) was obtained.

Ingredient	GF Resin	BrFR-3	PFR-1	PFR-1	PFR-1	PFR-1	PFR-1	PFR-1	PFR-2
FR Loading (wt%)		18.6	20	11	11	10	10	10	10
Antimony trioxide		6.0							
N-syn-2				11	11	10	10	10	10
PTFE		0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Na ionomer anti-drip		2	2	2		2	2	2	2
Phosphite		0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
DHT-4A		0.1	0.1	0.1	0.1	0.1			0.1
DHT-4C							0.1	0.25	
330		0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
1° Antioxidant		0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Flammability Units									
UL-94 (3.2mm)	Burn	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0
T1+T2 Sec	346	8	7	7	7	8	7	7	12
UL-94 (1.6mm)	Burn	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0
T1+T2 Sec	138	8	12	11	20	12	14	8	33
UL-94 (0.8mm)	Burn	V-0	V-0	V-0	V-2	V-0	V-0	V-0	V-1
T1+T2 Sec	328	9	14	16	16	28	16	17	83
UL-94 (0.4mm)								V-0	
T1+T2 Sec								19	
Properties, Units									
MFI, g/10 min	16	17	0	10	41	10	14	10	4
(325°C, 1.2 kg)	16	17	9	19	41	19	14	18	4
Rheology, Pa-s	121	66	69	68	64	69	74	74	118
HDT, °C	290	283	252	265	268	271	271	272	279
Moisture, %	0.02	0.03	0.05	0.08	0.05	0.05	0.05	0.04	0.07
Tensile strength, psi*10 ³	24.4	23.8	16.2	20.3	23.8	22.2	22.4	23.6	20.2
Tensile Modulus, psi*10 ³	14.5	16.9	17.8	17.9	20.2	16.5	16.5	17.1	15.4
Elongation @ break, %	2.02	1.97	1.18	1.44	1.54	1.71	1.68	1.87	2.06
IZOD impact, ft-lb/in	1.62	1.70	1.42	1.31	1.58	1.42	1.44	1.43	1.23
Charpy impact, kJ/m ²	56	75	27	39	46	39	54	50	46

	Table 4. Evaluation Data for PFR-1 in High Temperature Polyamide with 30 weight % Glass Fibe	er.
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Molded articles of this resin are shown in Figure 7. Molds of formulations containing PFR-1 and BrFR-3 were light in color. Both of these flame retardants are melt blendable, and melt flow characteristics were similar for these two systems (MFI and rheology values). The PFR-2 molded articles were brown in color with some off-gassing observed during processing, demonstrating that under equivalent processing conditions, PFR-1 is more thermally stable than PFR-2. Significant color differences between PFR-1 and PFR-2 molds are shown in Figure 7. Formulating and processing with better stabilization of PFR-2 is planned to allow better property comparison with PFR-1 and BrFR-3.

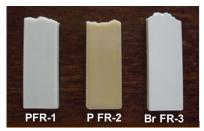


Figure 7. Flame Retardant High Temperature Polyamide Molds (3.2 mm, 1/8").

Capillary rheology data is shown in Figure 8. Only one data point at 69 Pa-s was collected in the automated test for 20% PFR-1 indicating viscosity was not stable throughout the one minute duration test. A continuous decrease in viscosity was observed for PFR-2 with N-syn-2. Improved stabilization should eliminate such a trend. Viscosity was reasonably stable for other flame retardant samples, including BrFR-3/ATO and PFR-1/N-syn-2 in high temperature polyamide. Viscosity was

significantly lower for these samples compared with glass-filled resin and PFR-2/N-syn-2 samples. BrFR-3 is commercially used in high temperature polyamide, is melt blendable, higher flow, and allows for rapid processing of molded parts.

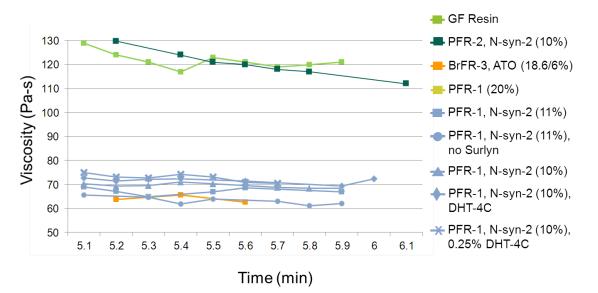


Figure 8. Capillary Rheology for Flame Retardant High Temperature Polyamide (at 1000⁻¹ sec Shear).

Rheology data for PFR-1 similarly exhibits this potential. PFR-2 is not melt blendable, so there may be limitations to achieving a high flow system, as reflected in MFI and rheology values. Use of PFR-1 as a flow enhancer for non-halogen flame retardant high temperature polyamides will be explored.

Conclusions

As technology progresses, so does the need for advanced materials. Anticipating this need, this material was developed as a high performance non-halogenated flame retardant technology. This new flame retardant can be processed at high temperatures and has a unique combination of high flame retardant efficiency, high thermal stability and superior electrical properties. It can be applied in many different resin systems such as those used in printed circuit boards, aerospace, films and fibers, wire and cable, and connector applications. With a high melting point, it is melt blendable in applications where resins are processed at high temperature. The performance characteristics of this flame retardant make it attractive for a broad range of applications.

References

¹ Corbridge, Derek E. C. "Phosphorus: Chemistry, Biochemistry and Technology", 6th ed.; CRC Press, **2013**.

² Rakotomalala, M., Wagner, S., and Doering, M. *Materials* **2010**, *3*, 4300.

³ Levchik, S. V. and Weil, E. D., J. Fire Sci. 2006, 24(5), 345.

⁴ Maxwell, K. A. and Ranken, P. F. "Halogen-Free Flame Retardants for PWBs: Challenges and Opportunities", *Proceedings* of *IPC EXPO* 2007.

⁵ Janezic, M. D. and Baker-Jarvis, J. "Full-wave analysis of a split-cylinder resonator for nondestructive permittivity measurements", *Microwave Theory and Techniques, IEEE Transactions* **1999**, 47(10), 2014.

⁶ Kent, G. "Nondestructive permittivity measurement of substrates", *Instrumentation and Measurement, IEEE Transactions* **1996**, 45(1), 102.

⁷ Landry, S. D. "Tetrabromobisphenol A – The Flame Retardant of Choice for Printed Wiring Boards", *Proceedings of IPC APEX EXPO* **2009**.

⁸ Hardy, M. "Regulatory Status of the Flame Retardant Tetrabromobisphenol A", *Proceedings of IPC EXPO* 2000.

⁹ Thompson, S. G., Hardy, M. L., Maxwell, K. A., Ranken, P. F. OnBoard Technology 2005, 8.

¹⁰ Levchik, S. V. and Wang, C. S. "Comparative Study of Phosphorus-based Flame Retardants in Halogen-Free Laminates", *Proceedings of IPC EXPO* **2007**.

¹¹Lin, C. H.; Wang, C. S. Polymer **2001**, 42 1869.

¹² Timberlake, L. D., Hanson, M. V., Bol, K., Narayan, S. "A Combination Flame Retardant Curing Agent Material for Non-Halogen PCB Laminates", *Proceedings of IPC APEX EXPO* **2011**.

¹³ Levchik, S. V.; Weil, E. D. "Developments in Phosphorus Flame Retardants", Advances in Fire Retardant Materials", Horrocks, A. R. and Price, D., Eds.; Woodhead Publishing: Cambridge, UK, **2008**, 49-66.

¹⁴ Lau, D. Y. H. "Evaluation of Halogen-Free Laminates Used in Handheld Electronics", University of Waterloo, Waterloo, Ontario, Canada, **2009**.
¹⁵ Weil, E. D. and Levchik, S. V. "Flame Retardants for Plastics and Textiles: Practical Applications", Hanser Gardner

¹⁵ Weil, E. D. and Levchik, S. V. "Flame Retardants for Plastics and Textiles: Practical Applications", Hanser Gardner Publications, **2009**.

¹⁶ Troitzsch, J. "Plastics Flammability Handbook", Hanser Gardner Publications, **2004**.