Polyphosphonate FRs fill the void

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The past two years have seen some of the most significant changes in flame retardant (FR) regulations ever. Actions have continued against individual chemicals such as TBPA, TCEP and melamine, which have become substances of very high concern (SVHCs) in the EU. More significantly, a legal finding in March 2022 confirmed actions to restrict the whole family of halogenated FRs in the enclosures and stands of TVs as valid.

This followed an essentially identical ban being signed into law in New York State on 31 December 2021. Then in June 2023, Washington State confirmed legislation that bans all halogenated FRs from the enclosures of essentially all electrical equipment in the home, and a requirement to notify the state of the presence of such FRs in outside equipment.

Additionally, the last 12 months have seen increasingly rapid action against per- and poly-fluoro chemical substances (PFAS). The common polycarbonate (PC) FR potassium perfluorobutanesulfonate (KPFBS), known as Rimar Salt, was issued with a Final Health Advisory in June 2022 and is already designated an SVHC in the EU. This was followed by Maine requiring notification of any intentionally added PFAS chemical in goods sold in the state from 1 January 2023.

Typical Properties	HM1100	HM7000	CO6000	CO6010-EX
Descriptions	Homopolymer	Homopolymer	Copolymer, miscible with PC	Copolymer, miscible with PC
Phosphorus, %	10.60%	10.60%	6.60%	6.60%
Tg, °C	105	104	121	121
MVR 260°C/1.2 kg, cm^3/10min"	20	40	8	8
YI	40	35	100	45

Figure 1 - Properties of Nofia polyphosphonate & poly(phosphonate-co-carbonate) grades

In the meantime, there have been multi-billion dollar settlements between PFAS producers and different bodies affected by pollution, with 3M announcing its exit from fluorine products by the end of 2025. OEMs and brand owners are moving more quickly and some are also requesting the removal of polytetrafluoroethylene (PTFE), which many NGOs and some regulatory authorities also consider to be a PFAS.

Polyphosphonate FRs

Driven by regulatory pressure and demand from OEMs and brand owners, many resin producers and compounders are looking for alternative FRs. In the last few months, FRX Polymers has received a steady flow of inquiries seeking FR solutions for PC and PC blends that are non-halogenated, KPFBS-free and PFAS free.

Nofia* is a family of halogen-free, phosphorus-containing, inherently FR polymers with outstanding safety profiles. Their polymeric nature means they are non-migrating and thus pose low concern to human health and the environment. They have received Green Screen's Benchmark 3 accreditation, have been recognised by the ChemForward 'SAFER' programme, are TCO-certified and have been named to the Oeko-Tex 100 list.

The technology is based on a chemistry that allows the polymerisation of a phosphonate monomer into oligomeric and polymeric FRs. By using different co-monomers, the properties of the polyphosphonates can be tailored to specific needs. For example, by replacing some of the phosphonate monomer with diphenyl carbonate, various phosphorus-containing

	230316-1	230309-2	230309-3	230316-3	230316-4	230802-7*	230613-8	230629-2*	230802-3*	230629-3*
PC, PC60 (MFI 6)	68%	67%	66%	65%	74%	81.5%				
PC, Lexan 141R (MFI 10)							66%	66%	70.0%	63%
Nofia CO6010-EX	32%	32%	32%	32%	24%	8%	32%	32%	24.5%	32%
Phosphazene, SPB-100						3%			3%	
Fyrolflex RDP						5%				
Metablen S 2130		1%	2%	3%	2%	2%	2%	2%	2%	
Lotader AX8900										5%
Joncryl ADR 4400						0.5%			0.5%	
Total	100%	100%	100%	100%	100%	100.0%	100%	100%	100%	100%
P content	2.10%	2.10%	2.10%	2.10%	1.60%	1.45%	2.10%	2.10%	1.98%	2.10%
"Compounding temp., °C, feed to die"	200/225/225/225/220/220/215/215					200/265/265/265/260/260/260/260				
NI at 3.2mm, J/m	90	360	860	830	800	700	800	790	760	730
UL-94 at 1.6mm	V-0	V-0	V-0	V-0	V-1	V-0	V-0	V-0	V-0	V-2
t max, sec	6	4	3	6	13	6	7	5	7	15
t total, sec	28	21	14	29	49	38	27	24	33	48
# Drips/flaming drips	0/0	0/0	0/0	0/0	1/0	0/0	2/0	2/0	1/0	3/1

* PC and Nofia were dried before compounding. In all other formulations, they were in open bag and used as is.

Figure 2 - Application of Nofia CO6010-EX in PFAS-free FR PC for V-0 at 1.6mm

analogues of PC can be made with phosphorus content from very low levels to >10 wt%.

These poly(phosphonate-co-carbonate) copolymers can be made to be fully miscible with PC, thus making transparent blends. In addition, by varying the reaction conditions (time, temperature, pressure and catalyst), polymers of different molecular weight can also be produced. Figure 1 shows a few Nofia grades currently being produced commercially.

Nofia FRs' main application has been in PET resin-related systems. They are spun directly into PET fibre for flame retarded technical textiles, carpets, wire and cable braiding, wigs and hair extensions. They are also blended into PET to make very thin (as low as 13 microns) and transparent FR BOPET films. In addition, they are used to make FR-TPU and TPEE engineering compounds.

As stated earlier, some Nofia FRs are compatible with PCs and are thus a natural choice for FR-PC, PC blends, and glass-filled PC. FR PC-ABS blends based on Nofia can have an heat deflection temperature (HDT) up to 30ºC higher than the typical small molecule FR systems. However, their use in PC resin-related systems is not as widespread as might be expected for their safety profile and mechanical and thermal properties.

One reason for this is the high YI of the Nofia copolymers, such as CO6000, which prevented its adoption where colour matching, especially white, is important. Another reason is the moisture-sensitivity of Nofia homopolymer, which proved to be difficult to handle for compounders without drying capability.

FRX has developed a new copolymer grade, Nofia CO6010-EX, with much lower YI than the traditional CO6000. All the grades, including the homopolymers and copolymers, are now pre-dried in the manufacturing facility and packed in moisture-proof packages. The low moisture content (400-600 ppm when an uncompromised package is opened) means they can be used without further drying as long as there is minimal exposure to ambient air before use.

FRX has focused on the application development of Nofia FR in PC and PC blends that are either KPFBS- or PFAS-free (the former still have PTFE present) as there is a need for both. Below, we present examples of the performance of Nofia FR in both cases. A 27-mm twin-screw extruder was used for compounding. Notched Izod (NI) impact strength was measured according to ASTM standard D256, and an FR test was performed according to UL-94.

In FR PC – PFAS-free

Figure 2 shows various PFAS-free formulations for PC based on Nofia CO6010-EX compounded at different temperatures and moisture content. With about 2% phosphorus content, the Nofia-only formulations with Metablen* S-2130 as impact modifier achieved the target FR (i.e. V-0 at 1.6mm) and excellent impact properties, despite variations in moisture content and processing temperatures. It also further reduced the after-burn time. The formulation with Lotader* AX8900 as impact modifier at 5%, however, negatively impacted flame retardancy. Phosphorus content lower than 2% could also achieve V-0 at1.6mm when Nofia FR is used together with phosphazene and/or resorcinol bis(diphenyl phosphate (RDP), as shown in Figure 2.

As well as CO6010-EX, Nofia homopolymer HM1100 can also be used for PFAS-free FR PC with V-0 at 1.6 mm (Figure 3a). As indicated, Joncryl* ADR 4400, a polymeric chain extender with a medium epoxy equivalent weight that reacts with the chain ends of polycondensation polymers, significantly improved the NI and FR.

The epoxy group on the Joncryl can react with the chain ends of both HM1100 and PC to compatibilise the blend and increase its melt viscosity, which could help with dripping. Attention should be paid during compounding to minimise the exposure of pre-dried HM1100 to ambient air to avoid moisture reabsorption.

PFAS-free FR PC with V-0 at 0.8mm or below can also be made with Nofia polyphosphonate with excellent impact properties (Figure 3b). The addition of impact modifiers restored the NI to PC level, while the use of phosphazene reduced the total loading of FR in the formulation.

The ultimate optimised formulation could include other FRs acting as synergists, such as RDP and BDP, impact modifiers, chain extenders and stabilisers, which could further reduce the total FR loading and thus cost. Although in these examples the HDT has not been measured, the high glass transition temperature (Tg) of polyphosphonate will ensure an HDT much higher than other traditional small molecule FRs, as shown in commercial formulations based on Nofia.

In FR PC-PBT & PC-PET blends - PFAS-free

In addition to FR PC, Nofia FR can also be used to make PFAS-free formulations for PC blends (Figure 4a). All three impact modifiers evaluated not only improved NI to 100% ductile break, but also reduced overall dripping and flaming drips. Two eliminated the dripping entirely and increased the FR to V-0 at 1.6 mm; Lotader AX8900 even helped achieve V-0 at 0.8mm.

Another advantage is that the torque for PTFE-free formulations was relatively low compared to the PC-PBT blend with PTFE. Although data are not presented here, both FRX and its customers have noted improved chemical resistance because of the addition of Nofia FR. Customers have reported a comparative tracking index for FR PC-PBT blend based on Nofia FR as high as 600V.

A similar phenomenon was observed for FR PC-PET blends based on Nofia FR (Figure 4b). The addition of the two impact modifiers improved both NI and FR. V-0 at 1.6mm and 0.8mm was achieved without PTFE while achieving 100% ductile NI for a Paraloid* EXL-2690 based formula.

PC, PBT, PET and polyphosphonate are incompatible polymers. The interactions between them, especially the transesterification reaction, are important for compatibilisation, which in turn directly affects processing and properties. The addition of impact modifiers, some of them carrying reactive groups, adds another level of interaction.

The selection of impact modifiers is therefore crucial to making PFAS-free FR PC or its blends based on Nofia. For example, for PC-PET based on Nofia, Paraloid EXL-2690 appears to be a better option than Lotader AX8900, contrary to the case of FR PC-PBT blend (Figure 5). For PFAS-free FR PC using Nofia copolymer CO6010-EX, Metablen S-2130 is a better choice than Lotader AX8900 (Figure 2).

Work on PFAS-free PC-ABS blends based on Nofia FR is currently under

Figure 3 - Application of Nofia HM1100 in PFAS-free FR PC for V-0 at 1.6mm (a) & 0.8 mm (b)

Dried materials used	230629-2	23629-5	230629-6	220725-6
PC, Lexan 141R	66%	78%	77.5%	84.5%
Nofia CO6010-EX	32%			
Nofia HM1100		20%	20%	10%
Phosphazene, SPB-100				3%
Metablen S-2130	2%	2%	2%	
Lotader AX8900				2%
Joncryl ADR 4400			0.5%	0.5%
Total	100%	100%	100%	100%
P content	2.10%	2.10%	2.10%	1.45%
Compounding temp. setting, °C, feed to die	200/265/265/260/260/260/260/260			
NI at 3.2mm, J/m	790	690	820	855
UL-94 at 1.6mm	V-0	V-2	V-0	V-0
t max, sec	5	3	3	6
t total, sec	24	17	16	24
# Drip/flaming drips	2/0	6/4	0/0	0/0

Dried materials used	161110-3	230629-7	220725-4	220725-5
PC, Lexan 101 (MFI 6)	76.45%			
PC, Lexan 141R (MFI 10)		60%	74.5%	79.5%
Nofia HM1100	20%	35%	20%	15%
Phosphazene, SPB-100	3%		3%	3%
Lotader AX8900		5%	2%	2%
Joncryl ADR 4400	0.5%		0.5%	0.5%
Irganox 168	0.05%			
P content, %	2.51%	3.71%	2.51%	1.98%
Compounding Temp. setting, °C, feed to die	200/250/250/250/250/245/240/240C	200/275/275/270/265/260/260/260		
NI at 1.6mm, J/m	960			
NI at 3.2mm, J/m		765	810	835
UL94 at 0.8 mm	V0	V-0	V-0	V-0
tmax, sec	5	3	5	6
t1+t2, sec	18	15	16	31
# Drip/flaming drips	2/0	0/0	0/0	0/0

Dried materials used	230420-1	230420-2	230420-4
PC, Lexan 141R	50%	40%	40%
PET, Auriga 7800	30%	30%	30%
Nofia HM7000	20%	20%	20%
Lotader AX8900		10%	
Paraloid EXL-2690			10%
Total	100%	100%	100%
Compounding temp. C, from feed to die	200/275/275/270/265/260/260/260		
NI at 3.2mm, J/m	60	870	760
UL-94 at 1.6mm	V-2	V-1	V-0
t max, sec	2	19	8
t total, sec	19	48	32
# Drip/flaming drips	1/1	0/0	0/0
UL-94 at 0.8mm	V-2	V-1	V-0
t max, sec	2	12	9
t total, sec	13	41	48
# Drip/flaming drips	13/6	0/0	1/0

Dried materials used	180731-7	230327-1	230327-3	230327-4	230327-5
PC, Lexan 141R	66.70%	45%	35%	35%	35%
PBT, Ultradur B 4520, BASF	33%	30%	30%	30%	30%
Nofia HM7000		25%	25%	25%	25%
Metablen S 2130			10%		
Lotader AX8900				10%	
Paraloid EXL-2690					10%
PTFE, Teflon 6C	0.30%				
Compounding temp. C, from feed to die	200/235/235/235/230/230/225/225				
Torque at 100 rpm, 10 kg/hr	79%	58%	57%	46%	58%
Notched Izod at 3.2mm, J/m	NA	60	730	685	635
UL-94 at 1.6mm	Not Rated	V-2	V-1	V-0	V-0
t max, sec	burnt up to clamp	1	20	5	9
t total, sec		10	100	18	26
# Drip/flaming drips		16/3	2/0	0/0	0/0
UL-94 at 0.8mm				V-0	V-1
t max, sec				7	15
t total, sec				30	73
# Drip/flaming drips				0/0	0/0

Figure 4 - Application of HM70HM00 in PFAS-free FR PC-PBT blend (a) & PFAS-free FR PC-ET blend (b) for V-0 at 1.6mm & 0.8mm

way. Similar considerations are being applied. We are examining both impact modifiers and other additives, such as stabilisers or chain extenders. They would be most beneficial to FR performance and mechanical properties if they also promote the compatibility between the ingredients in the blend.

PTFE has been a very efficient anti-dripping agent for FR PC and its blends. As low as 0.1-0.3% loading could prevent dripping and improve the FR performance dramatically by its fibrillary formation. A one-for-one replacement for PTFE would be quite challenging, however.

Some researchers are looking into replacement materials that can be exfoliated at nano-scale in polymer melts, such as nanoclay and carbon nanotubes. Although the nanostructure when formed could prevent dripping, it does not necessarily provide other FR mechanisms provided by PTFE, such as effective char formation. More FRs would therefore need to be added to achieve the same FR performance.

The fatal flaws of adding increasingly higher loadings of small molecule FRs are increased migration of FR to the surface, worse mechanical properties and continued reduction in melt strength and thermal properties. Polymeric FRs like polyphosphonates allow a much bigger formulation space to optimise for FR and mechanical properties without such negative effects.

The examples showcased so far in this article are for demonstration purposes and are in no way optimised. For example, FR synergists can be further introduced into Nofia FR only formulations to reduce the total FR loading and cost.

In PC & PC blends – KPFBS-free

In KPFBS-free formulations, PTFE is still allowed. This makes the use of polyphosphonates much more efficient in FR PC and PC blends. In pigmented FR PC with PTFE, 2% Nofia CO6010-EX can provide robust V-0 at 1.6mm. When used together with phosphazene, about 10% CO6010-EX and 1% phosphazene with PTFE can achieve V-0 at 0.8mm.

In 40% glass-filled PC with PTFE, 1% phosphorus from the combination of Nofia HM1100 and bisphenol-A bis(diphenyl phosphate) (BDP) could achieve V-0 at 0.8mm (about 5% Nofia HM1100/5% BDP). In FR PC/ABS, for a formulation where about 7% of BDP is needed to achieve V-0 at 1.6mm, 8% Nofia CO6010-EX was reportedly found to achieve the same FR, but with much higher impact properties and HDT. This has been universally observed when polyphosphonate FRs are used in comparison to the traditional small molecular FRs. ●

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