

Halogen vs Non-halogen Flame Retardants: Some inconvenient truths!

(with apologies to Al Gore)

Prof Dick Horrocks University of Bolton Bolton BL3 5AB

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(Broad brush) Costs:

<

Inorganics (& Ncontaining)

Halogen (plus synergist)

< Organophosphorus

Eg.

Alumina trihydrate (ATH) (< magnesium hydroxide (MDH)) Zinc borate APP Melamine + salts Intumescents Zinc stannates

Eg.

Chloro- and bromo- phosphates Decabromodiphenyl ether (Deca) Hexabromocyclododecane (Hexa) Tetrabromobisphenol A (TBBPA) Bromine-containing polymerics eg Brominated polystyrene Poly(pentabromobenzyl acrylate)

Eg.

Triaryl phosphates Resorcinol bis(diphenyl phosphate) (RDP) Aluminium diethyl phosphinates THP-derivatives eg Proban Cellulose reactive phosphonamides eg Pyrovatex

Potential ecotoxicity?

65 ppm in seawater 5000 ppm in the Dead Sea Sea salt ~2000ppm?

Bromine under the spotlight:

- Persistent organic pollutants (POPs)
- Currently banned BrFRs include polybromobiphenyls and octa- and penta-bromodiphenyl ethers (2003-2005)
- Withdrawn: "hexa" (2015)
- Partially withdrawn/under threat: "deca"
- Under scrutiny: Tetrabromo-bisphenol A (TBBPA)

• Phosphorus?

- Essential to life
- Organophosphate agrochemicals have known H&S issues
- Nerve agents are based on organophosphorus!

Nitrogen?

- Basis of protein chemistry
- Melamine: 2008 Chinese baby's milk adulteration!
- Nox (NO₂) and air pollution (Guardian, 2 April, 2015: 29000 deaths in UK per annum)

Carbon??

- Carbon monoxide is the main killer in fires!

- For acceptable (ie pass "standard" test requirements) FR levels:
 - 5-15 wt% Bromine (requires synergist eg antimony III oxide)
 - 1-2 wt% Nitrogen (usually in combination with phosphorus)
 - 1-3 wt% Phosphorus
 - >55 wt% Aluminium/magnesium hydroxides!

Relative effective

requirements)

For acceptal

Most BrFRs contain 40-80% Br but require ATO with Sb/Br=1/3 Typical "Deca"/ATO combination present at 2:1 mass ratio Total [BrFR+ATO] levels 10-25 wt% in final polymer.

- 5-15 wt% Bromine (arres synergist eg antimony III oxide)
- 1-2 wt% Nitrogen (usually in combination with phosphorus)
- 1-3 wt% Phosphorus
- >55 wt% Aluminium/magnesium hydroxides!

- For accer
 requirem
 Melamine salts rich in nitrogen: Melamine cyanurate (MC): 49% N Melamine polyphosphate (MPP); 37.5%N (and ~14%P)
 Urea: 47%N
 - 5-15 wt%
 - 1-2 wt% Nitrogen (usually in combination with phosphorus)
 - 1-3 wt% Phosphorus
 - >55 wt% Aluminium/magnesium hydroxides!

- For acceptable (ie pass "standard" test requirements) FR low
 - 5-15 wt% Bro antimony III d

Most PFRs contain 8-15%P and so 1-3% wt P ~ 5 - >30 wt% in the formulation; additional N-containing species may also be required (eg melamine salt)

- 1-2 wt% Nitroge, melam phosphorus)
- 1-3 wt% Phosphorus
- >55 wt% Aluminium/magnesium hydroxides!

- For acceptable (ie pass "standard" test requirements) FR levels:
 - 5-15 wt% Bromine (requires synergist eg antimony III oxide)
 - 1-2 wt% Nitr
 phosphorus
 Most hydrated inorganics at >55
 wt% significantly reduce properties
 of the polymer matrix
 - 1-3 wt% Phosphoru
 - >55 wt% Aluminium/magnesium hydroxides!

Polymer spectrum

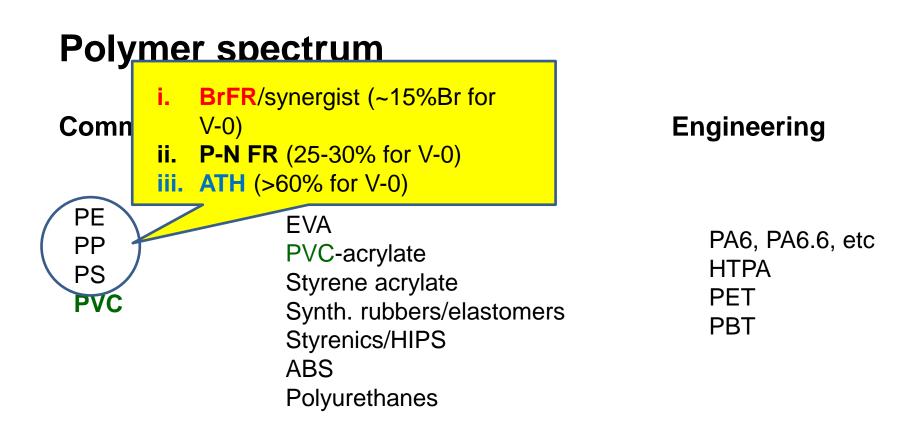
Commodity	Copolymerics	Engineering
PE PP PS PVC	EVA PVC-acrylate Styrene acrylate Synth. rubbers/elastomers Styrenics/HIPS ABS Polyurethanes	PA6, PA6.6, etc HTPA PET PBT

Thermosets:

Vinyl & Unsat. polyester

Ероху

Phenolics

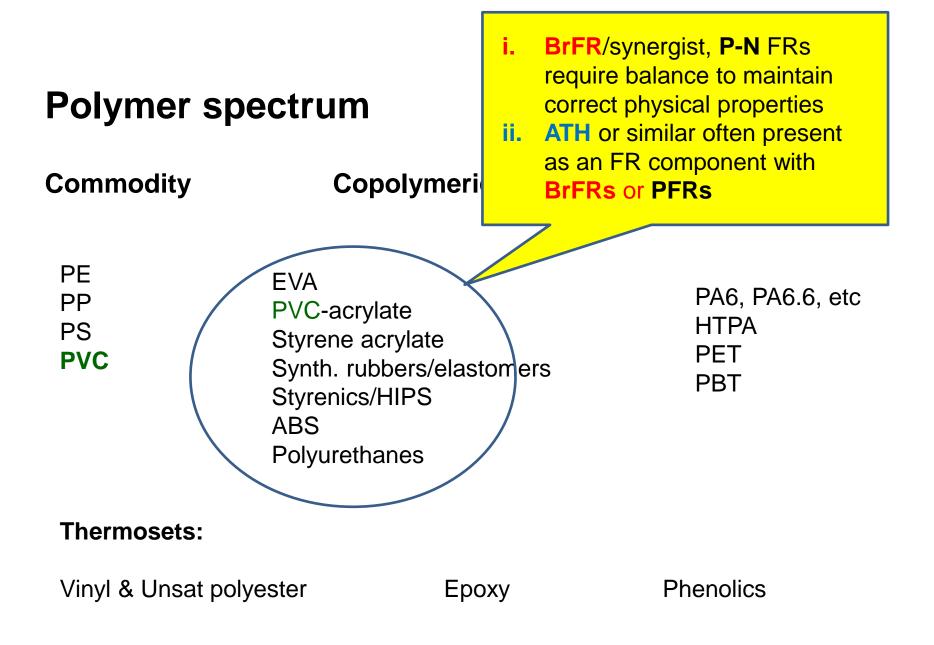


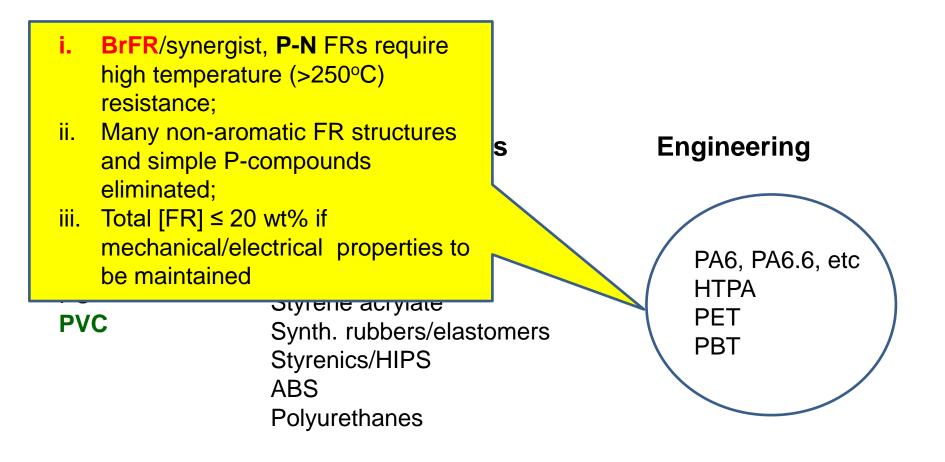
Thermosets:

Vinyl & Unsat. polyester

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Phenolics





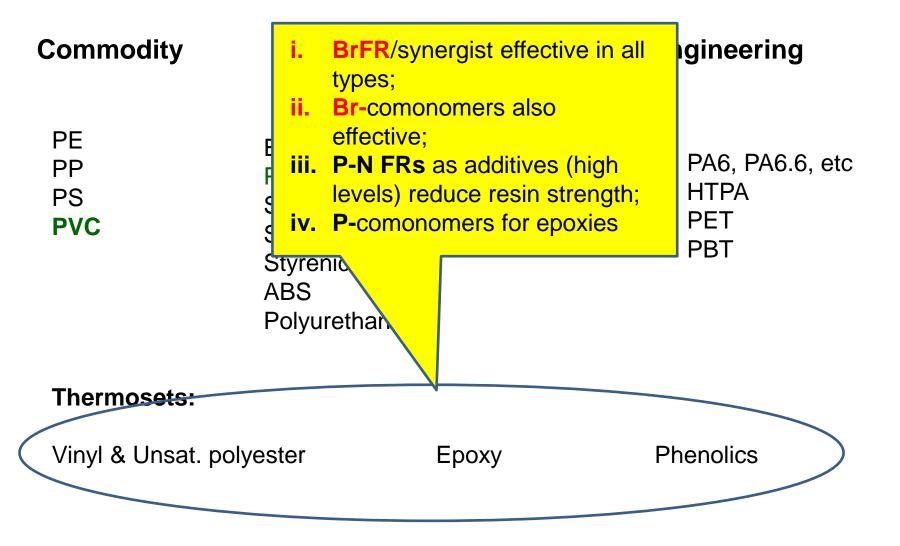
Thermosets:

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Ероху

Phenolics

Polymer spectrum



"New/recent" Technologies

Nanotechnology

- Nanoparticles alone reduce ignition times, slow down overall burning rate
- Nanoparticles + FR can reduce total [FR] required;
- eg EVA/65%ATH ~
 EVA/45%ATH/5%nanoclay (Kabelwerk, Belgium)
- Nanoparticles on surface can create fire protective ceramic layer

Surface treatments

- Thermally thin (<4mm): Must still generate high levels of FR required for normal bulk polymer (eg 1-3%P, 5-15%Br, 1-3%N, etc)
- Plasma
- Sol gel
- Layer-by-layer
- Thermally thick (>4mm), then surface layers can form fire barriers (eg The "fire resistant paint" effect).

Volatile Phosphorus?

- Hastie & Bonnell (1980): Volatile P via HPO[•] And similar radicals are as effective as Br[•] radicals at terminating flame chemistry radical reactions
- Horrocks et al, (2008): Volatile P (as tributyl phosphate or Fyrol 51(oligomeric phosphate-phosphonate)) essential in a textile coating as a potential BrFR replacement.
- **DOPO** (dihydro-oxa-phosphaphenanthrene oxide): polyesters, epoxies?
- Al dialkyl phosphinate: PA6, PA66, HTPA, PET, PBT

Three Case studies

- Textile back coatings
- Polyolefins
- Engineering polymers

1. Textile backcoatings

- Work at Bolton 1999-2007
 - [BrFR] may be reduced significantly if other FRs (eg, P-NFRs, ATH) present
 - P-NFRs function ONLY on 100% cotton if mobilised (ie fluid or volatile) <300°C (T_{ig} ~ 350°C); APP best of examples tried
 - Addition of heavy metal salts may reduce melting/liquefaction temperature of APP
 - Best results obtained in a condensed + vapour phase active formulation (*specific to 100% cotton*):

Pentaerythritol phosphate + Fyrol 51 + Melamine (Char former) (Volatile P) (Volatile nitrogen)

2. Polyolefins (HDPE)

• **BrFR** vs **P-NFR** for V-2 in HDPE

- >30-35 wt% of proprietary P-N intumescent
- 10 wt% (~8 wt% Br) DecaBDE + 3.5 wt% ATO
- BrFR vs synergist (antimony III oxide vs zinc hydroxy stannate)
 - 17 wt% (~12 wt% Br) BrFR + 2wt% ATO
 - 14 wt% (~10 wt%Br) BrFR + 4 wt% ZHS

3. Engineering polymers

- Ideally total [FR] $\leq 20 \text{ wt}\%$
- Often contain glass fibre (~30 wt%)
- Work at Bolton 2008-2014 for PA6, PA6.6 and HTPA suggests:
 - With BrFRs (especially polymeric BrFRs), zinc stannate (ZS) often more effective than ATO and so total [BrFR] may be reduced;
 - Some evidence that Sn-P synergies exist; at present time in PA6 only V-2 achieved with ZS + PFR
 - In HTPA 15wt% PFR may be reduced to ~11wt% if ~4wt% ZS present AND smoke reduced by ~20%

Conclusions

- Current climate demands that ALL flame retardant presence is reduced in consumer products.
- To attack bromine and promote a total ban on BrFRs will divert the attention to the next "easy target", P-NFRs
- FR development should be based on interactive combinations of individual components such that:
 - [total FR] is minimised in any given substrate;
 - Flame retardancy and hence fire safety are maximised
- There is no "silver bullet" based on a single flame retardant!