Flame Retardant Materials - Overview

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TURI Workshop

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Acronyms

ABS	Acrylonitrile Butadiene Styrene
APP	Ammonium polyphosphate
BSEF	Bromine Science & Environmental Forum
BrFR	Brominated flame retardant
Deca-BDE	Decabromodiphenyl ether
EEE	Electrical and electronic equipment
EPS	Expandable polystyrene foam
FR	Flame retardant
GPPS	General purpose polystyrene
HBCD	Hexabromocyclododecane
HIPS	High-impact polystyrene
Melamine	Melamine cyanurate or polyphosphate
PA	Polyamide
PC	Polycarbonate
Penta-BDE	Pentabromodiphenyl ether
PFR	Phosphorus flame retardant
PO	Polyolefins
PPO	Polyphenylene oxide
PU	Polyurethane
PVC	Polyvinyl chloride
Sb_2O_3	Antimony trioxide
TBBPA	Tetrabromobisphenol A
XPS	Extruded polystyrene foam

Outline

- Why are flame retardants used?
- How do flame retardants work?
- Where are flame retardants used?

Why are flame retardants used?

- Save lives
- Reduce injury
- Reduce economic loss
- Reduce local environmental pollutants that are a result of fires

2002 & 2003 Fire Statistics

- Municipal fire departments went to 1,687,500 & 1,584,500 fires,
- Killed 3,380 & 3,925 civilians
- Injured 18,425 & 18,125 civilians
- Caused 10.3 & 12.3 billion $ in direct property loss

Source: *Fire Loss in the United States During 2002,* by Michael J. Karter, Jr. & *Fire Loss in the United States During 2003,* by Michael J. Karter, Jr.

2002 & 2003 Fire Statistics

- 519,000 & 519,500 Structural Fires – 2775 & 3,365 deaths
  - 77% & 80% occurred in residential properties
- 329,500 & 312,000 Vehicle Fires – 565 & 465 deaths
- 839,000 & 753,000 Outside Fires – 40 & 65 deaths

Source: *Fire Loss in the United States During 2002,* by Michael J. Karter, Jr. & *Fire Loss in the United States During 2003,* by Michael J. Karter, Jr.

Fire Testing Results

European TV (no FR) Low-level ignition source (fuel pill)	 0:08	 7:23	 8:00-9:00

Source – www.bsef.com

Fire Testing Results

European TV (no FR) Low-level ignition source (fuel pill)	 0:08	 7:23	 8:00-9:00
American TV (contains FR) Low-level ignition source (fuel pill)	 0:05	 1:40	 1:45

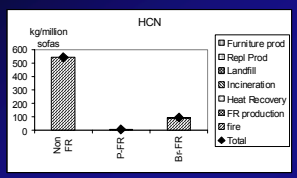
Source – www.bsef.com

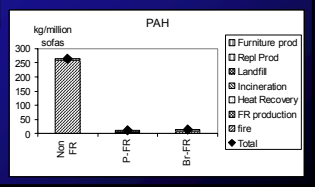
Fire Testing Results

Upholstered Sofa (no FR)	 0:00	 1:41	 4:48

Source – www.bsef.com

LCA of Upholstered Furniture Emissions to Air (10^6 Sofas, 10 years)





Source – EFRA API Paper Oct 19, 2004

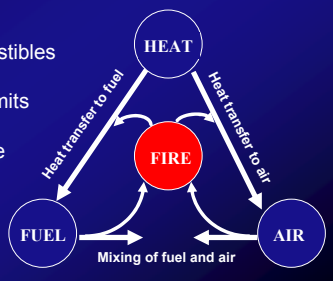
How Do Flame Retardants Work?

- Fire starts in 3 main ways
  - Accidents
  - Deliberate ignition or arson
  - Equipment failure (electrical malfunctions or overheating)
- How do you prevent fire?
  - The best solution is to prevent it from starting

How Do Flame Retardants Work?

- Combustion starts when

mixture of volatile combustibles
+
air within flammability limits
+
temperature above the ignition point



How Do Flame Retardants Work?

- Flame retardants reduce the heat supplied to the polymer
  - Modify the rate of chemical and physical processes
  - Perform their action in the initial stages of a fire
    - Vapor phase mechanism
    - Condensed phase mechanism
    - Combination of both

❖ FR action is not an instantaneous single event, but a combination of events over a wide range of temperature

Flame Poisoning

- Interrupt the physical and chemical processes of the combustion
  - Reduce the exothermic processes, cool down the system, reduce the supply of the flammable gases and eventually suppress the fire
- Halogenated flame retardants

Intumescence

- Condensed phase mechanism
- By formation of a foamed char on the surface of the polymer
  - Physical barrier to heat and mass transfer leading to reduced smoke production and dripping
- Compounds that are “carbonific” and “spumific”
  - Inorganic acids (formed in situ), carbon-rich compounds and organic amine or amides

Cooling Effect

- Creation of a heat-sink by a compound that decomposes in an endothermic process
  - Also gives off non-combustible volatile products
  - Lower effectiveness and hence high concentration of FR required
  - Metal hydroxides like $Al(OH)_3$ and $Mg(OH)_2$

Char Formation

- Combustible condensed phase shielded from gaseous phase with a solid or liquid protective layer
  - Condensed phase cooled, oxygen is excluded and heat transfer impeded
  - Phosphorus based compounds in cellulosic materials, certain P/N compounds and borates

Dilution

- By incorporating inert substances
- Evolve inert gases on decomposition, dilutes the fuel both in solid and gas phases and lowers the ignition point of the gas mixture
- Chalk, talc and other fillers

Melt-Dripping

- Polymer break down accelerated
- Increases the flow of the polymer and withdraws the flame away from the sphere of influence
- Radical initiators, aliphatic and alicyclic halides

Types of FR Additives

- Halogenated FRs
  - Mainly bromine containing, some chlorine
- Phosphorus containing FRs
  - Mainly phosphates
- Inorganic Materials
  - Primary FRs and synergists
- Other additives
  - Nitrogen, boron based & others

Brominated Flame Retardants

- Aromatic, aliphatic, and alicyclic brominated compounds
- Effective vapor phase agents
  - When used by themselves, they get into the vapor phase along with fuel and interfere with the physical/chemical aspects of the flame
  - When used with antimony trioxide, they get into the vapor phase as antimony tribromide and interfere with the physical/chemical aspects of the flame

Phosphorus FRs

- Red phosphorus
- Phosphates that work in condensed phase
  - Ammonium polyphosphate, melamine pyro and, polyphosphates etc…
- Organo phosphorus compounds that act in vapor/condensed phases
  - Resorcinol & bis-phenol-A phosphates, halo-phosphates
- Organo phosphorus compounds that act largely in vapor phase
  - Triphenylphosphate

Other FRs

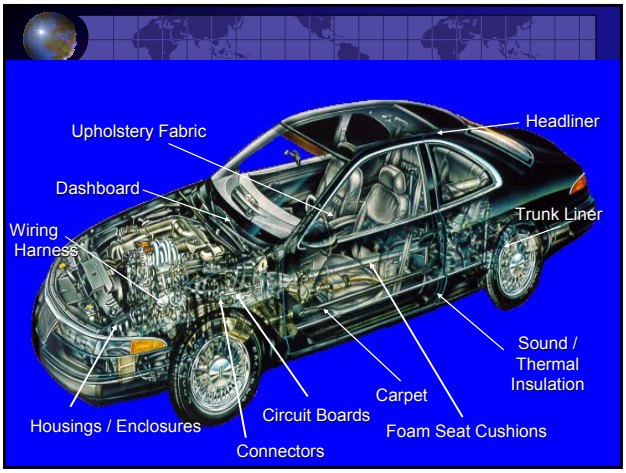
- Nitrogen containing FRs
  - Mechanism is not well understood
  - Used mainly in polyurethane and polyamides
  - Melamine, melamine cyanurate
- Boron containing FRs
  - Effective mostly in condensed phase thru the formation of boric acid
  - Works well with oxygen containing polymers
  - Very limited applications

Intumescent Flame Retardants

- Intumescent flame retardants
  - Specific to polymer and application
  - Combination of nitrogen and phosphorus
  - Single compound or multicomponent system
  - Acid, amine and carbon-rich compounds
- Phosphorus acid salts; melamine and other triazine derivatives; pentaerythritol derivatives

Where are Flame Retardants Used?

- Thermoplastic Resins
  - Styrenic resins
  - Engineering resins
  - Polyolefins
  - Others
- Thermoset Resins
  - Epoxy
  - Polyester
  - Polyurethane



Flame Retardant Selection Criteria

- Match up decomposition temp of FR with self-ignition temp of polymer
- Thermal stability for processing
- FR Efficiency
- Ability to meet particular fire safety standards
- Human Health & Environmental Profile
- Effect on physical properties
- Melt flow
- UV stability
- Non-blooming
- Cost in use
- Electrical properties
- Thermal aging
- Recyclability

Flame Retardant Styrenics

- GPPS - EPS and XPS foams
  - Uses additive BrFRs – HBCD is most common, very limited use of other aliphatic BrFRs
- High-Impact Polystyrene (HIPS) - EEE
  - Uses additive BrFRs – Deca-BDE is most common for TV backs, others used in this and other applications
- Acrylonitrile Butadiene Styrene (ABS) - EEE
  - Uses additive BrFRs
- Various Alloys - EEE
  - PPO/HIPS – Uses additive PFRs
  - PC/ABS – Uses additive PFRs

Flame Retardant PA & Thermoplastic Polyesters

- PA, PBT, PET, PTT, PCT – Electrical & Automotive
  - Electrical - Uses additive BrFRs, red P, melamine
    - Connectors
    - Switches
  - Automotive - Uses additive BrFRs, red P, melamine
    - Electrical connectors and switches
    - Small appliance housings
    - Conduit
    - Enclosures

Note -
Melamine cyanurate used in unfilled PA, melamine polyphosphate used in PBT

Flame Retardant Polyolefins

- Polypropylene
  - Wire nuts, slit film (raffia, carpet backing), some enclosures, electronic components (Christmas tree light strings), small appliance housings – Uses additive BrFRs, mineral FRs, melamine & APP (small volume, as synergist)
- Polyethylene, EEA and EVA
  - Wire and cable, film/sheeting (construction, outdoor tarps, geomembranes) – Uses additive BrFRs, Mineral FRs, APP
- Thermoplastic olefin
  - Single-ply roofing membrane – Uses Mineral FRs, additive BrFRs

Other Flame Retardant Resins

- PVC
  - Wire & cable, conveyor belts, flooring, foam, hoses, profiles, roofing, tubes & pipes – Uses Sb_2O_3 (only), mineral FRs, BrFRs (small volume, many as plasticizers)
- Textile Coatings
  - Building furniture and drapery backing, floor covering, auto fabric backing - Uses BrFRs, mineral FRs

Flame Retardant Epoxy

- Epoxy
  - Circuit boards, coatings (novolac encapsulation resins) – typically uses reactive BrFRs (especially TBBPA), mineral FRs (small volume), N-P-type products (very small volume)

Flame Retardant Thermoset Polyesters & Vinyl Esters

- Unsaturated Polyesters & Vinyl Esters
  - Building panels, electrical connection boxes, industrial containers, floor grating – Uses both reactive and additive BrFRs, melamine & APP (small volume)

Flame Retardant Polyurethanes

- Rigid PU Foam
  - Construction & building panels – Uses reactive BrFRs and both reactive & additive PFRs
- Flexible PU Foam
  - Auto, public furnishings, residential furnishings (CA residents), & industrial bedding – Historically used Penta-BDE in US and PFRs in EU; now looking at both additive and reactive BrFRs (that contain P), additive PFRs

Application	Polymer	Typical FRs Used
Cushioning & Insulation	PU Foam	BrFRs & PFRs
Building, Textile Coatings, and Wire & Cable	Textile	BrFRs, PFRs, Mineral FRs
	EPS, XPS	HBCD
	PO	BrFRs, PFRs, Mineral FRs
	PVC	Sb_2O_3, Mineral FRs, BrFRs
Electrical Components	PBT/PET/Nylon	BrFRs, PFRs, melamine
Business Equipment, TV's, & Appliances	HIPS	BrFRs
	PC/ABS, PPO/HIPS	PFRs
	ABS	BrFRs
Printed Wiring Boards	Epoxy	TBBPA

For More Information

www.bsef.com
Bromine Science &Environmental Forum

www.firesafety.org
Role of flame retardants in fire prevention

www.firemarshals.org
National Assoc of State Fire Marshals

www.acfse.org
European fire safety coalition

www.ebfrip.org
European brominated flame retardant industry