Polymer Flame Retardant Chemistry

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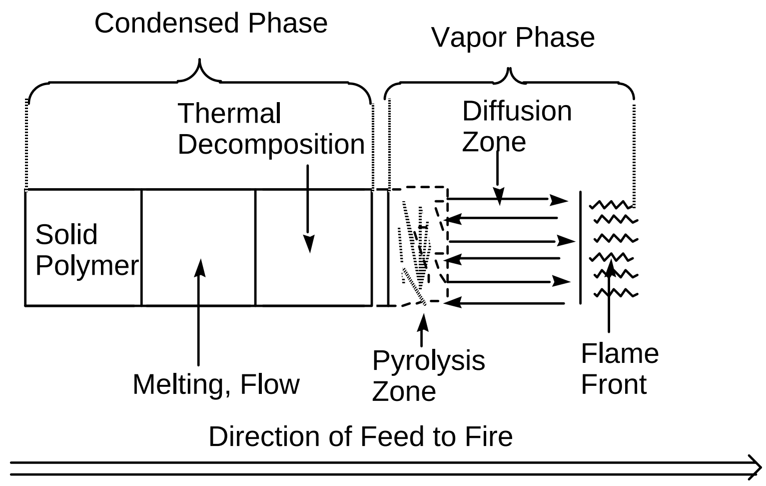
Outline

- Polymer Flammability and Flame Retardancy
  - Polymer Flammability Basics
  - What is a Flame Retardant?
  - Flame Retardant Design/Use in Relation to Tests
- Specific Classes of Flame Retardants
  - Halogen, Phosphorus, Mineral Fillers, Intumescents, Inorganics, Nanocomposites
- Future Technology and Trends
  - Additives vs. Reactive Flame Retardants
  - The Unexplored Elements
  - The Future of Polymeric Fire Safety

Flame Retardancy Fundamentals

Matching the Flame Retardant Chemical Mechanism To The Polymer Burning Behavior

Polymer Flammability

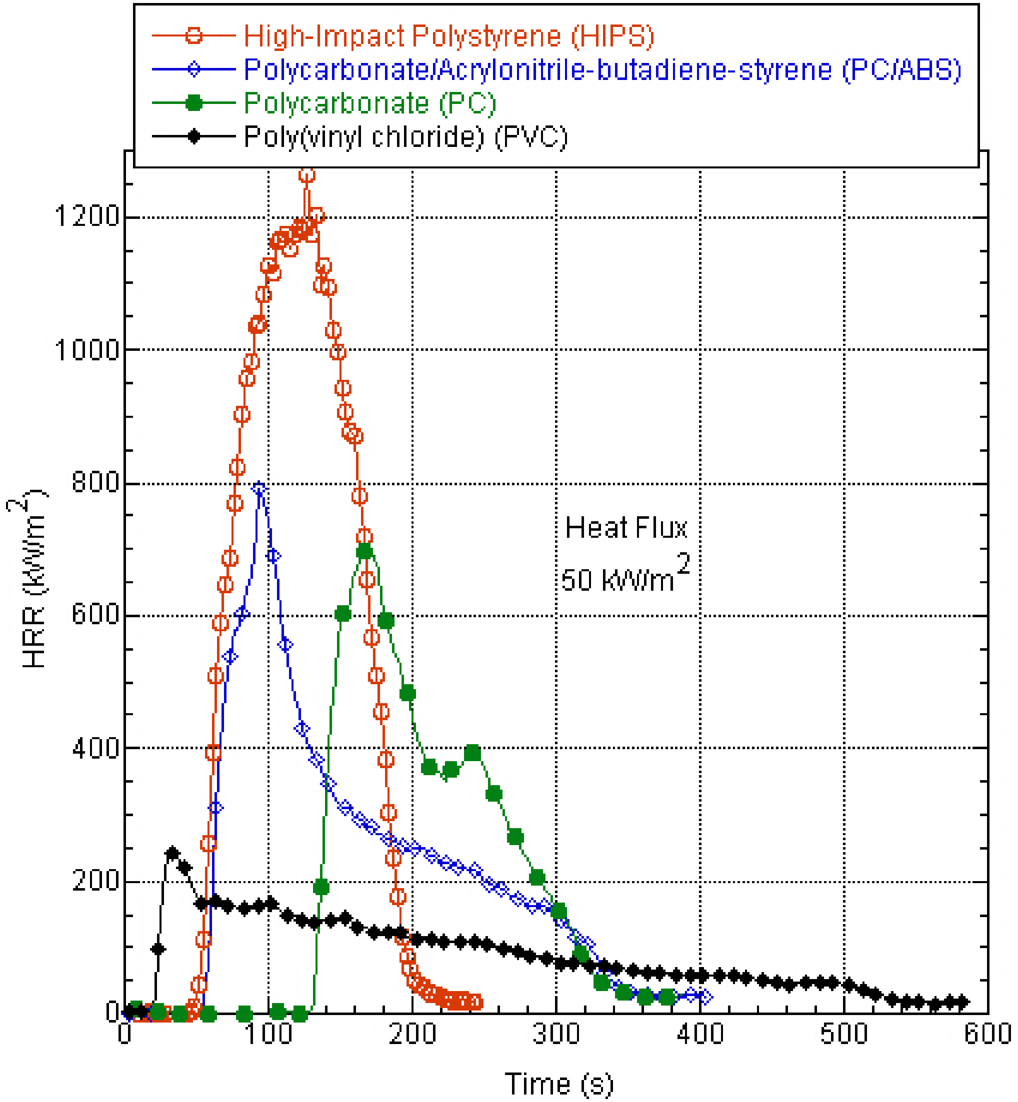


(Stevens, M.P.; Polymer Chemistry: An Introduction, 2nd ed. Oxford, NY; Oxford University Press 1990. p 126)

- Solid polymer melts, flows, and then decomposes to flammable gases.
  - Some thermosets or crosslinked materials do not melt, and decomposition products may be directly pyrolyzed.
- Gases with oxygen and combust generating heat and radiant energy.
- Radiant energy goes back to condensed phase continuing the burning of the polymer.
  - Polymer structure dictates flammability.

Flammability of Commodity Polymers

- The cone calorimeter measures the flammability of a material under constant external heat flux.
- The flammability is measured by the heat release rate (HRR). As HRR increases, flame spread and flashover increase.
- PVC has the lowest HRR, due to release of HCl during burning.
- PC has the next lowest HRR due to its polymer structure (release of CO_2)
- HIPS highest HRR due to chemical structure (hydrocarbon burning).



HRR Data courtesy M. Bundy, NIST-BFRL

What is a Flame Retardant?

- A Flame Retardant (FR) is a molecule (inorganic or organic) found to be useful for inhibiting flame growth by one of three mechanisms.

- A Flame retardant is a molecule used for a specific application, much like a drug is a molecule used to treat disease, a pigment is a molecule used to give paint a color, or a surfactant is a molecule to use as a soap.
  - FR is used to put out a fire either passively (guard against fire) or actively (extinguishing agent).
  - Some FR additives have multiple chemical applications – again application based upon chemical structure and how it interacts with fire.
    - Ex: $Mg(OH)_2$. In powder form can be used in antacids or can be used as flame retardant filler in wire and cable jackets.
      - But the product used for wire and cable is not the same product you eat nor can the two be used interchangeably.

Flame Retardant Molecule Design / Use Criteria

- Current flame retardant polymer solutions are tailored to the regulatory test the polymer must pass to be sold. So the molecules are designed and applied to solve the following problems:
  - Ignition Resistance
  - Flame Spread
  - Heat Output
  - Structural Integrity Under Fire and Heat
  - Smoke/Toxic Gas Output
  - Combinations of one or more of the above
- What works for one test may not (and often does not) work for another test!!!!
- The Flame Retardant Chemist will design to the test, not universal flame retardancy.
  - The Chemist can only design to the criteria given (fire, cost, performance, lifetime, etc.). It is impossible to design for the unforeseen criteria that may occur 10-20 years later.
- "If we knew what we were doing, it wouldn't be called research, would it?" - Albert Einstein

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Fire Safety Engineering and Chemistry

- By knowing the chemistry of a polymeric material, one can assess the level of fire risk with that polymer.
  - Polymer chemical structure dictates flame retardant chemistry and approach.
  - Polymer chemical structure => fuel value of decomposition products => fire risk.
- Ideal route for design of a material to meet a fire risk scenario:
  - 1. Pick a polymer with a low heat release - provided it meets other product requirements.
  - 2. Consider what FR approaches can work with the chosen polymer from a chemical standpoint.
  - 3. Use FR agents that provide a solution to the fire safety shortcoming of the chosen material.
- The selection and use of a particular flame retardant for a particular polymer is not arbitrary, but sometimes there is no perfect solution and so a compromise additive is selected.

Specific Classes of Flame Retardants

Polymer Flame Retardants

- Plastic combustion can be stopped by:

  (1) Inhibit combustion at flame front.

  (2) Remove heat from polymer.

  (3) Prevent polymer decomposition / fuel release.

- Each of these approaches can be used alone, or combined to generate flame retardancy in a polymeric material.

- Each type of flame retardant falls into a category that fits one or more of the above approaches.

General Flame Retardant Classes

I- Gas Phase Flame Retardants (ex. Halogen, Phosphorus)
- Reduce heat in gas phase from combustion by scavenging reactive free radicals, thus inhibiting combustion.

II- Endothermic Flame Retardants (ex. Metal Hydroxides, Carbonates)
- Function in Gas Phase and Condensed Phase by releasing non-flammable gases (H_2O, CO_2) which dilutes the fuel and cools the polymer.

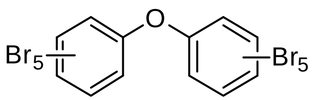
III- Char Forming Flame Retardants (ex. Intumescents, Nanocomposites)
- Operates in Condensed Phase by preventing fuel release and providing thermal insulation for underlying polymer.

Halogenated Flame Retardants

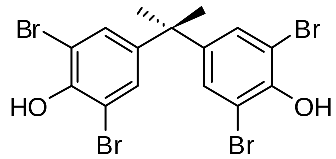
- Halogenated FR additives cover a wide range of chemical structures.
  - Aromatic additives often used for higher release temperature, higher % loading of halogen per molecule.
  - Aliphatic additives used for lower release temperatures, or to induce polymer depolymerization. Not used as often.
  - Brominated FR is the most common. Chlorinated FR is used, but not as often.
  - Fluorine and Iodine tend not to be as effective for FR polymer additive use.
    - Fluorinated compounds inherently non-flammable (Teflon, Halon)

- Halogenated FR additives often include synergists so that they can be more effective at lower loadings.
  - Antimony oxide the most common synergist.
  - Sometimes the synergist will be incorporated directly into the FR structure (ex – phosphorus – halogen)

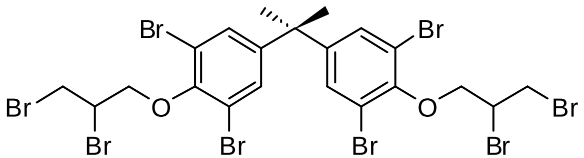
Uses of Common Brominated FR Additives



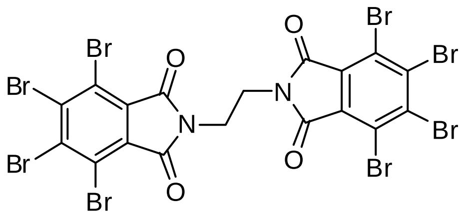
Decabromodiphenyl ether



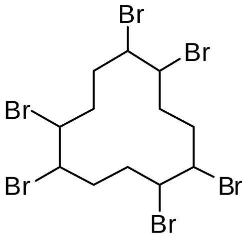
Tetrabromo bisphenol A



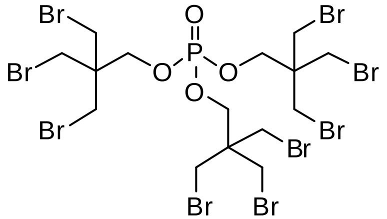
Bis(2,3-dibromopropyl ether) of Tetrabromo bisphenol A



1,2-ethylene bis(tetrabromophthalimide)



Hexabromocyclododecane



Tris(tribromoneopentyl) phosphate

- Decabromodiphenyl ether, 1,2-ethylene bis(tetrabromophthalimide):
  - Electronic cases, wire and cable jackets.
- Tetrabromobisphenol A:
  - Epoxy Circuit Boards (copolymerized – reactive FR)
- Hexabromocyclododecane:
  - Thermoplastic foams, textiles
- Bis(2,3-dibromopropyl ether)… / Tris(tribromo…)phosphate:
  - Polyethylene/polypropylene
- Many other additive systems available, including polymeric and oligomeric species for more specific applications.

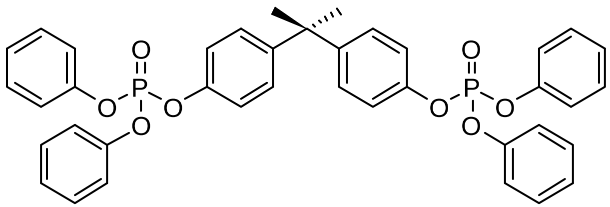
Halogenated Flame Retardants

- Halogenated FR additive benefits:
  - Very effective at lowering flammability in a wide range of polymers.
  - Provide good fire performance even after repeated recycling of polymer + FR resin.
- Halogenated FR additive drawbacks:
  - Always generate more smoke and carbon monoxide during burning.
  - Can be overwhelmed in high heat flux fires (little to no FR effectiveness).
  - Under regulatory scrutiny due to perceived environmental problems.
- Overall an old technology (since 1930s) but proven to work.

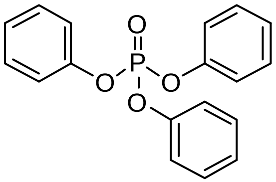
Phosphorus Flame Retardants

- Phosphorus FR additives cover a wide range of chemical structures and can be both gas and condensed phase FR additives.
  - Aromatic/aliphatic structures are used for polymer compatibility purposes.
  - Oligomers are used for cost effectiveness or ease of manufacture.
  - Inorganic phosphorus FR is used when more condensed phase effects are desired.
  - Elemental phosphorus (red) can be a very effective flame retardant for some systems.
- Phosphorus FR additives do not typically need synergists, but sometimes they are more effective when combined with other types of flame retardants or elements.
  - Halogenated FR (Phosphorus-halogen vapor phase synergy)
  - Nitrogen compounds (Phosphorus-nitrogen condensed phase synergy)

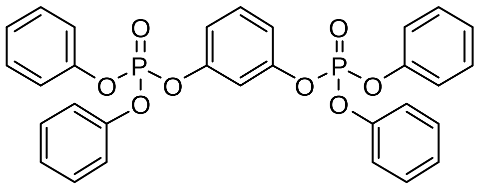
Common Phosphorus FR Structures and Chemistry



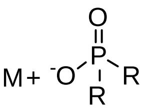
Bisphenol A Diphosphate



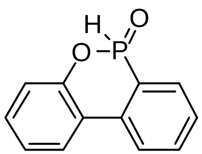
Triphenylphosphate



Resorcinol Diphosphate



Phosphinate Salts
M = Al, Zn
R = Alkyl



9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)

$[NH_4PO_4]_n$

Ammonium Polyphosphate

- Some Phosphorus FR Uses
  - Phosphates/phosphinates
    - Electronic plastics
  - DOPO
    - reactive material for circuit boards
  - Ammonium polyphosphate
    - Fire wall barriers / paints

Phosphorus Flame Retardants

- Phosphorus FR additive benefits:
  - Can be both vapor phase and condensed phase flame retardants.
  - Can be very effective at lowering heat release rate at low loadings of additive.
- Phosphorus FR additive drawbacks:
  - Tend to generate more smoke and carbon monoxide during burning.
  - Not effective in all polymers.
  - Starting to be under regulatory scrutiny.
- Newer technology (1950s). A mature technology but lots of other possible chemical structures to explore and use for flame retardancy.

Mineral Filler Flame Retardants

- Mineral filler flame retardants cover hydroxides and carbonates.
  - Hydroxides (Al, Mg)
    - $Al(OH)_3$ releases water at a low release temperature (180-200 °C)
    - $Mg(OH)_2$ releases water at a higher release temperature (320-340 °C)
  - Carbonates (Ca, Mg)
    - Calcium carbonate often used as a bulk filler, and since it is non-flammable it dilutes the total amount of fuel to be consumed.
    - Magnesium carbonates used in a form called "hydromagnesite" which releases a combination of water and CO_2 at 350 °C.

- Mineral fillers do not typically use synergists, but sometimes they will be combined with other FR additives to provide a beneficial effect on polymer flammability.
  - Al, Mg hydroxides sometimes used to lower smoke output while providing FR performance.

Mineral Filler Flame Retardants

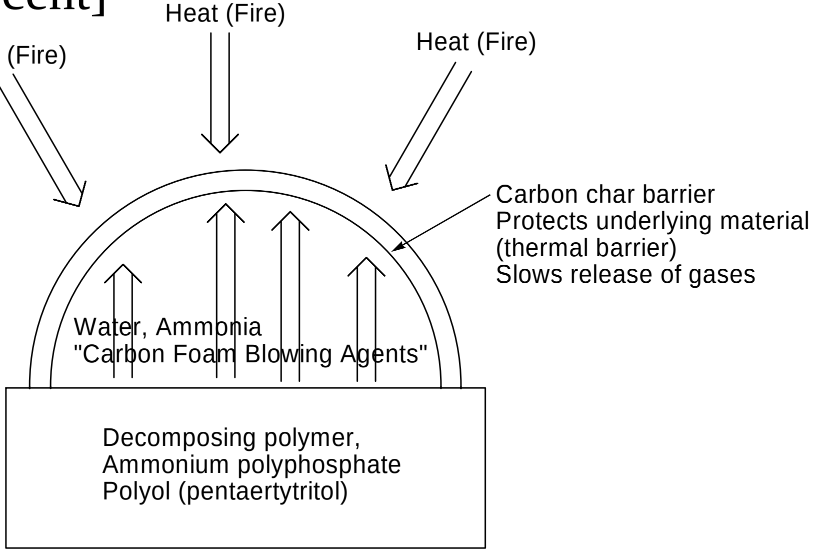
- Mineral Filler FR additive benefits:
  - Effective at lowering heat release rate and smoke release.
  - No environmental scrutiny – considered to be very “green” FR additives.

- Mineral Filler FR additive drawbacks:
  - Not as effective per wt% basis as other FR additives. Large loadings of material (50-80wt%) can be required to obtain FR performance in polyolefins.
  - High loadings often cause mechanical property problems which can lead to the use of polymer compatibilizers that offset some of the cost benefits of using a mineral filler in the first place.

- Depending upon what sources you believe, could be very old technology (1600s) or 20th century (1920s).

Intumescent Flame Retardants

- Intumescent FR additives are often mixtures of different additives that work together under fire conditions to form a protective barrier (carbon foam) at that "rises up in response to heat" [Intumescent]
  - Intumescent FR packages include:
    - Carbon source
      - Polymer or Polyol
    - Acid source
      - Ammonium Polyphosphate
    - Gas-blowing additive.
      - Melamine



  - There are FR systems where more than one aspect of the intumescent package can be incorporated into the additive structure (additive is carbon/acid source and gas-blowing additive) .
  - Sometimes the polymer actively participates in the charring process by serving as the carbon source.

Intumescent Flame Retardants

- Intumescent FR additive benefits:
  - Very robust fire safety and flame resistance performance.
  - One of the few systems that can use select polymer structures to actively participate in flammability reduction.

- Intumescent FR additive drawbacks:
  - Can have water pickup issues.
  - Can be expensive.
  - Can have low temperature limits that limit processing ranges.

- Intumescents are often used for applications requiring high levels of flame retardancy.
  - Building and construction, firewall/firedoor barriers, aerospace, military, wire & cable, mass transport, etc.

Inorganic Flame Retardants

- Inorganic Flame Retardants are a broad class of materials that mostly affect condensed phase phenomena.
  - Zinc Borate ($2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$)
    - Can release water, but mostly helps as a FR synergist for many systems, and helps to lessen afterglow (smolder) conditions in mineral filled FR systems.
  - Stannates ($ZnSnO_3$, $ZnSnO_3 \cdot 3H_2O$)
    - Smoke reducing additives for halogenated FR systems.
  - Silicon compounds
    - Can form protective silicon oxide barrier against fire.

- Inorganic FR additives are typically synergists for other FR additives, or they offset an undesirable property brought by the main FR.

Inorganic Flame Retardants

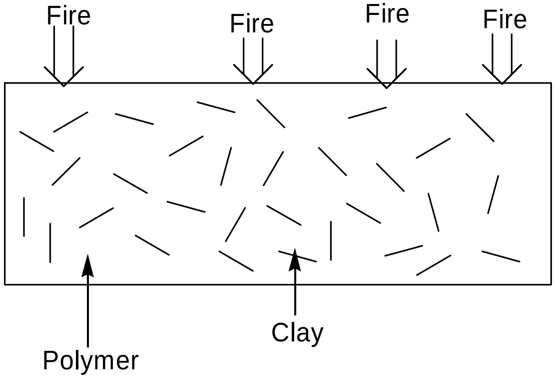
- Inorganic FR additive benefits:
  - Typically used in small amounts to offset an undesirable FR property.
- Inorganic FR additive drawbacks:
  - Not effective by themselves except in very specific systems – not a universal class of FR additives.
  - Tend to be expensive.
- Newer technology
  - Still a niche class of materials – tend to be best used with others, not by themselves.

Polymer Nanocomposite Flame Retardant Materials

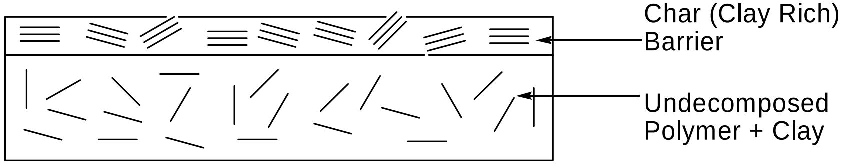
- Polymer nanocomposites are a new class of FR additives that work only in the condensed phase.
  - Use organically treated layered silicates (clays), carbon nanotubes/nanofibers, or other submicron particles at low loadings (1-10wt%).
- By themselves, polymer nanocomposites greatly lower the base flammability of a material, making it easier to flame retard the polymer containing a nanocomposite structure.
  - Are effective when combined with just about all types of FR additives.
  - Work best when combined with other FR additives.
  - In effect, nanocomposites are a class of *nearly* universal FR synergists.
    - Exceptions do exist of course.
- As polymer nanocomposites become commercial materials – they will also be flame retardant materials at the same time due to their inherent properties.

Polymer Clay Nanocomposite FR Chemistry

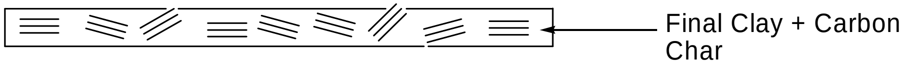
- Polymer nanocomposite exposed to heat, polymeric material burned at slower rate (reduced mass loss rate)



- As polymer burned away, clay rich carbon barrier forms.



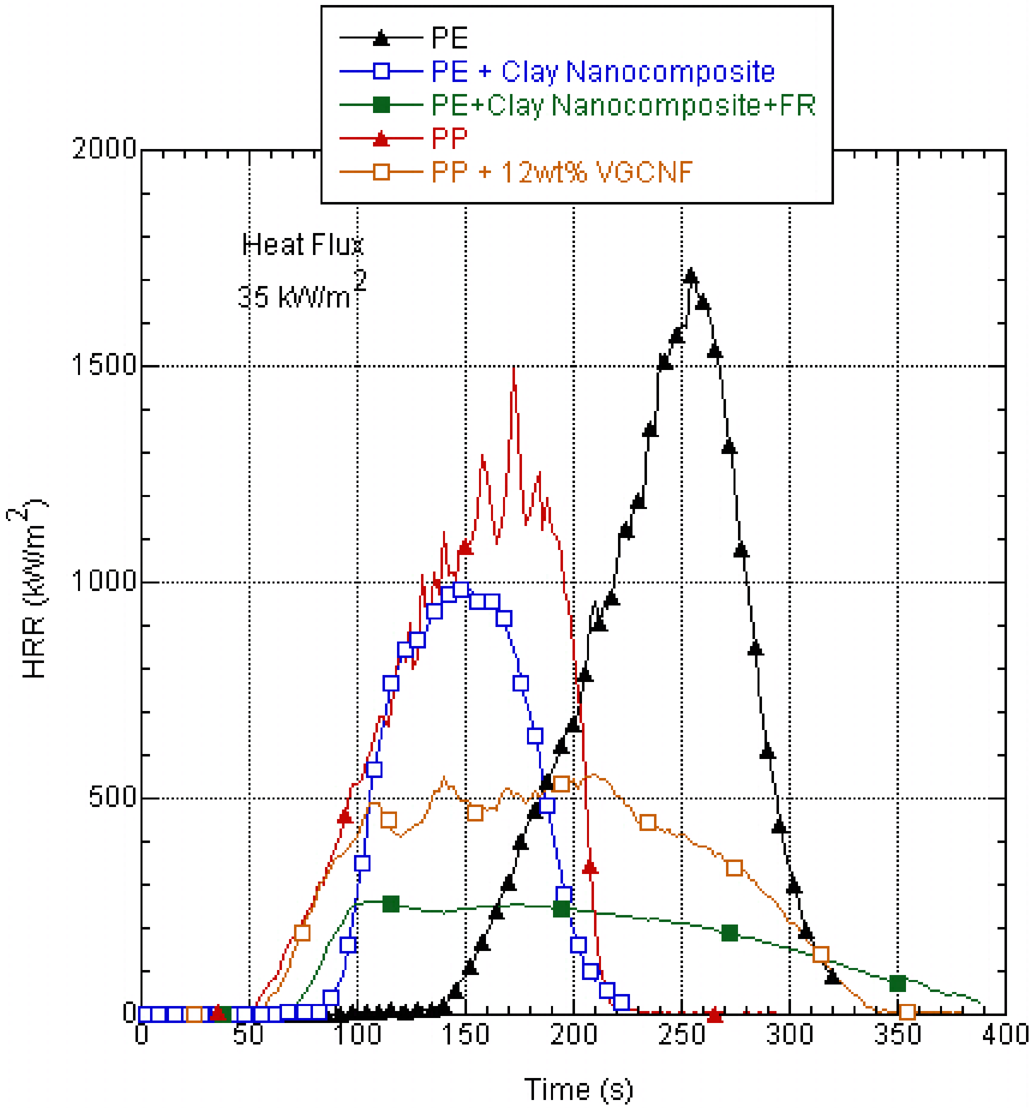
- Final char formed at end of burning very rich in clay content. Clay slows down mass loss rate and reduces heat release rate, but it does not stop burning.



- Nanotubes and nanofibers have similar mechanism (reduced mass loss rate) but instead create a network "web" of fibers which keep polymer mass from pyrolyzing.

Polymer Nanocomposite Cone Calorimeter Data

- For PE + clay nanocomposite (5wt% inorganic), peak HRR is reduced, but Total HR remains unchanged.
- Polymer clay nanocomposites lower the mass loss rate, which in turn reduces the base flammability, but additional FR is needed to lower HRR further.
- PE + Clay + FR even better fire performance.
- Similar behavior seen for nanocomposites made with nanofibers and nanotubes



Flame Retardant Polymer Nanocomposites

- Polymer nanocomposite benefits:
  - Brings balance of mechanical and flammability properties to a system.
  - Very little additive needed (no great cost increase).
  - Tend to inhibit polymer dripping / flow under fire conditions.
  - Multifunctional performance (ex: electrical conductivity from carbon nanotubes)

- Polymer nanocomposite drawbacks:
  - Difficult to set up a polymer nanocomposite structure.
  - Design of the nanocomposite requires careful design and analysis, which can bring additional R&D cost to a product.
  - Lots of unknowns with nanocomposite technology (long-term aging, EH&S, etc.)
  - New technology (1990s – maybe not proven enough for conservative fire safety principles)

Future Technology and Trends

Additives Vs. Reactive Flame Retardants

- Additives widely used because they are cheap and easy to use.
  - Can leach out or lead to other polymer property drawbacks.

- Reactive Flame Retardants are newer materials with react directly into the polymer.
  - Eliminate all of the issues with additives, but can lead to significant changes in the polymer properties (both positive *and* negative).

- New additives and reactives take time to discover, scale-up, register, and make economically viable.

- **<u>No matter how good the new FR compounds are, if they cannot be made cost effective no one will use them.</u>**

The Unexplored Elements

- Known chemical compounds useful for flame retardancy only use a very small amount of the periodic table.
  - New chemistries may be yet undiscovered which are far more effective and useful than halogen, phosphorus, or any existing technology.
  - The same new chemistries may not be any better from environmental impact than existing solutions.

- Possible new technologies:
  - Catalysts – Metal compounds which convert the flammable polymer to graphite under fire conditions.
  - Low-melting glasses and ceramics – materials which set up an inorganic (cannot be oxidized or burned further) protective layer.
  - New vapor phase combustion inhibitors – oxygen scavengers or even more potent free-radical inhibitors.

The Future of Polymeric Fire Safety

- Future polymeric materials will most likely require all of the following:
  - Passes New Flammability Test (based upon fire risk scenarios AND fire safety principles).
  - Environmental Friendly, Recyclable and Sustainable.
    - Recyclable could mean energy recovery until we can truly separate out the additives and recycle them as well.
  - Inexpensive.

- Ideal future material to meet all of the above may be:
  - Derived from inorganic feedstocks.
  - Inherently flame retarded polymer.
  - Bio-renewable.
  - Designed with fire safety / fire risk scenarios considered.

- Expect more, not less, polymeric materials to require fire safety / flame retardancy performance.

Burning Questions?