Polyurea & Fire Safety
Regulations, Fire testing and Flame Retardants

Jérôme De Boysère

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Outline

- Introduction
- Fire Safety notions
- Regulations
- Fire Testing
- Combustion of polymers and FR
  - Chemistries
  - Mechanisms
Why use FR?

- Polymers are increasingly used in our daily life
  - Consumer electronics
  - Household goods
  - Furniture
  - Decorative materials
  - Floorings
  - Transportation (cars, trains, planes etc)
  - Etc…

- Most polymers are flammable and represent a significant quantity of fuel (fire load)
  - Heat released by a burning TV or sofa is enough to lead to “flash-over” and to set fire to a room or even a whole building
Why use FR?

- Many building materials do not burn, but
  - steel loses its structural strength when temperatures exceed 470-500°C
  - “spalling” of concrete

- In Europe
  - One fire every two minutes

- Fire statistics in Germany
  - Approx. 600 dead victims every year
  - Main cause: poisoning through fire gases (CO…)
  - Approx. 6,000 burnt victims

- Economic costs (2000, Source: GDV):
  - Approx. 6 bn. € incl. 1,9 bn € insurance
  - Approx. 100,000 cases incl. 200+ > 500 000 €
Course of a Fire

Associated risks

- Ignition source
- Ignitability

Heat release capacity
- Flame propagation (vertical, lateral, dripping)
- Smoke: density, toxicity, corrosivity
- Fire penetration
- Pollution

“Reaction-to-fire”
FR act here

“Fire Resistance”
Intumescents can act here

Source: EFRA
Fire Safety Notions

- Reaction-to-Fire: characterizes the burning behaviour of a material under certain defined conditions:
  - Ability to ignite (easy, difficult)
  - Burning rate, spread of flame (slow, quick)
  - Heat release (rate of heat release, peak heat release)
  - Smoke density
  - Smoke toxicity
  - Smoke acidity
  - Formation of droplets (burning and/or non-burning)

- May be performed on material or final part
- May be small, large or in a few cases full scale fire tests
- May be binary (“pass / fail”) or based on numerical value (e.g. heat release, toxic gases)
- Results are dependant on the testing conditions, thus each fire test has its own “truth”
Fire safety Notions

- Fire Resistance: ability of a part or product, regardless its composition (organic, inorganic) and its reaction-to-fire, to **maintain its function for a given time** in the event of a **fully developed fire**.
  - Fire resistant doors
  - Air ducts
  - Load bearing beams or column
  - ...

- FRT requirements can range from 15’ up to 8 h

- The related fire tests are typically **large scale**

Source: www.warringtonfire.net
1. **Building / Construction**
   - The use of fire rated (reaction-to-fire) and fire resistant materials is regulated by:
     - National building codes
     - Some countries, like Germany, have even regional building codes
       (Note: not sure if fire safety requirements are different)
   - For Construction Products (CE marking, CPD or ETAG), the test and classification systems are now harmonized, but the requirements may differ from country to country.
     - E.g. for the same application, Euroclass B may be required in Germany and C in Spain

2. **Electrical & Electronic (E&E) applications**
   - Main fire test: UL 94 vertical (5VA, 5VB, V-0, V-1, V-2) and horizontal burning (HB)
   - Sometimes subject to further (different) fire tests, such as glow wire, needle flame test etc.
   - Certain cables have also fire resistance requirements and other specific tests
Regulations

Other applications that typically require flame retarded products

3. **High safety areas** (mostly country specific):
   - Mining and milling sites, chemical sites, offshore platforms
   - Hospitals, retirement homes, jails

4. **Transportation**
   - Cars: FMVSS 302, increasingly completed by OEM specifications
   - Trains: Harmonized TS 45545 (calorimetry + smoke) will replace national standards
   - Planes: FAR 25.853 (Boeing), ABD 031 (Airbus) incl. fire + smoke (density/toxicity)
   - Busses: Directive EC/95/28 will probably be subject to modifications

5. **Furniture**
   - Mainly UK & Ireland (BS 5852:2)
   - Rest of Europe: discussions about upholstered furniture, but no short term changes expected

6. **Toys**: EN 71:2  *(Any polyurea used in toys??)*
Common Fire Tests

(focus on Europe and relevant application areas for polyurea)

Source: FTT, WarringtonFire, Currenta
Materials regulated by the Construction Products Directive (89/106/EEC) or by European Technical Agreement Guideline (ETAG), and subject to CE marking, are tested according to:

- EN ISO 1182:1999 Non-combustibility test
- EN ISO 1716:1999 Determination of gross calorific value
- EN ISO 11925-2:1999 Ignitibility test
- EN ISO 9239-1 Radiant panel test for floor coverings (only)
- EN 13823:2002 Single Burning Item (not for floor coverings)
- ISO 9705 Full scale room test for surface products (Reference Scenario)

Results are: Euroclasses (A₁, A₂, B, C, D, E, F) respectively Bₘ, Cₘ etc. for floorings

Pending: EU harmonization for roofing applications (currently 4 different tests resulting in Bₐ₀ rfl - Eₐ₀ rfl)
Expected not before 2013
Small flame test (EN ISO 11925-2 – very similar to DIN 4102 B2)
- Vertical flame test used prior to SBI and Flooring testing
- Application of flame (edge and surface) for 30 sec (SBI: class B-D) or 15 sec (flooring test + SBI: class E)
- Destroyed area must be <150 mm
- Considers burning droplets (d0, d1)
Floor covering test (EN ISO 9239-1)
- Radiant panel with heat flux 11 to 1 kW/m²
- Horizontal test on specimen 1050 x 230 mm
- Duration: until flames extinguish or max. 30’
- Classification is based on Critical Heat Flux (CHF) below which flame spread is no longer occurring.
- Additional classification based on smoke density (s0, s1, s2)

- $B_{fl}$: CHF > 8 kW/m² + FS < 150 mm within 20s
- $C_{fl}$: CHF > 4,5 kW/m² + FS < 150 mm within 20s
- $D_{fl}$: CHF > 3 kW/m² + FS < 150 mm within 20s
- $E_{fl}$: FS < 150 mm within 20s
**Building/Construction**

- **SBI**: Single Burning Item (EN ISO 13823)
  - Two specimen (0,5x1,5m and 1x1,5m) mounted as vertical corner
  - Tested three times each
  - Exposed to 30 kW gas burner for 20’
  - Classification based on Fire Growth Rate (FIGRA), Total Heat Release after 10’ ($\text{THR}_{600}$) and maximum Flame Spread
  - Additional classification based on Smoke Growth Rate (SMOGRA), Total Smoke Production ($\text{TSP}_{600}$) and droplets/particles

- **B**: $\text{FIGRA} < 120$ W/s + Lateral FS<edge of specimen + $\text{THR}_{600} < 7,5$ MJ + FS <150 mm within 60s (EN 11925-2)
- **C**: same except FIGRA < 250 W/s and $\text{THR}_{600} < 15$ MJ
- **D**: FIGRA < 750 W/s + FS <150 mm within 60s (30s flaming)
- **E**: FS < 150 mm within 20s (15 sec flaming)
Materials used in building/construction, but not subject to CPD / CE Marking, are subject to local regulations based on national tests. Main ones are:

- **BS 476-7:**
  - 6 specimen (885 x 270 mm) tested for 10’
  - Radiant panel (35 kW/m²) + pilot flame (1 cm)
  - Classification (Class 1-3) based on lateral flame spread

- **DIN 4102-15 (German “Brandschacht”):**
  - 4 specimen (1000x190 mm) vertically oriented (chimney effect)
  - Ring burner for 10’
  - Classified B1 if Tmax of gases < 200°C and rest length > 150 mm and B2-test passed (cf. EN 11925-1)
Building/Construction

- NF P 92501 (French “Epiradiateur”) for rigid materials and flexible materials >5mm:
  - 5 specimen (400 x 300 mm)
  - Radiant panel (30 kW/m²) at 45° with butane pilot flame
  - 20’ testing
  - Classification (M1-M4, n.c.) calculated as an equation between:
    - Time to ignition (1st flame > 5s)
    - Maximum flame height
    - Total burning times
Other tests

- Furniture
  - UK: BS 5852-2, standardized seat structure tested with different sources, the most frequent one being Crib 5 (5 levels of wood)
  - Rest of EU: no to little requirements, limited to furniture in public places (cinemas, theatres etc)
    - EN 1021-1: cigarette test
    - EN 1021-2: match test

- Marine Applications: IMO Resolution MSC.61(67)

  Fire tests depending on final applications
  - Upholstered furniture: resolution A.652 (16)
  - Bulkhead, ceiling and deck: resolution A.653 (16)
  - Primary deck coverings: resolution A.687 (17)
  - Plastics: ISO 5659-1:1996 (Smoke density)
Fire Resistance Tests

- Determination of the Fire Resistance Time (FRT), as the time needed to reach failure, when exposed to a defined fire scenario.
- Different Time-Temperature curves may apply. The main applied ones are:
Fire Resistance Tests

- Important point to consider for Polyurea coatings

- Polyurea coatings (until now) mostly have requirements in regard to their reaction-to-fire (e.g. Euroclass B, or German B1), but not (yet) in regard to fire resistance.

- BUT

- If coatings are applied on existing load bearing structures (such as concrete or steel), one should carefully check if the coating does not degrade the FRT of the substrate!

- A good reaction-to-fire does not ensure fire resistance properties (this applies to inorganic materials as well).
Flame Retardants?

- The term “Flame Retardant” describes the function of these additives, but gives no hint about their chemical or physical nature, or their mode of action.
- There are in fact more than 170 single substances, which can act as FR.
- They can be liquid (plasticizing) or solid / organic or inorganic.
- They can be additive or reactive (= grafted into the polymer backbone).
- They have different environmental and toxicity profiles (substance specific).
- They have different mode of actions.
- They have different price-performance profiles.
Flame Retardants?

- The Fire Triangle (Emmons)

- Fire is sustained only when the three parameters are given at once.
- However, dynamics of combustion depends on exact decomposition path, which is polymer specific
- FR, depending on their nature, act by different means on one or more parameters
### Flame Retardants?

<table>
<thead>
<tr>
<th></th>
<th>Halogenated FR</th>
<th>Phosphorus FR</th>
<th>Nitrogen FR</th>
<th>Mineral FR</th>
<th>Intumescents</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mode of action</strong></td>
<td>Chemical</td>
<td>Chemical + Physical</td>
<td>Physical</td>
<td>Physical</td>
<td>Chemical + Physical</td>
</tr>
<tr>
<td><strong>Place of action</strong></td>
<td>Gas phase (flame)</td>
<td>Mostly solid phase</td>
<td>Gas phase</td>
<td>Gas phase</td>
<td>Solid phase</td>
</tr>
<tr>
<td><strong>Mechanism</strong></td>
<td>Release of HBr or HCl traps H-radicals in the flame</td>
<td>Formation of a carbon rich layer which prevents access of oxygen</td>
<td>Release of non-flammable nitrogen, dilute oxygen content</td>
<td>Release of water vapour, cool down and dilute smoke</td>
<td>Formation of an insulative foam at the surface</td>
</tr>
<tr>
<td><strong>Compatibility</strong></td>
<td>+</td>
<td>0</td>
<td>0</td>
<td>(o)</td>
<td>0</td>
</tr>
<tr>
<td><strong>Effectiveness</strong></td>
<td>+</td>
<td>+</td>
<td>0</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td><strong>Fire side effects</strong></td>
<td>-</td>
<td>+</td>
<td>(+)</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td><strong>Cost-performance</strong></td>
<td>+</td>
<td>0</td>
<td>0</td>
<td>++</td>
<td>0</td>
</tr>
</tbody>
</table>
Flame Retardants?

- **High performance**
  - 8 - 40 EUR / kg
  - ex. DOPO, Oxa, RP, Phosphazene

- **Performance**
  - 3 - 8 EUR / kg
  - ex. APP, EDAP, MPP, phosphonates, HBCD, BrPS, Deca-BDO, ZnBorate

- **Commodities**
  - 0.50 - 3 EUR / kg
  - ex. Triaryl-, Trialkyl-phosphates, ATH, Mg(OH)2, MC, TCPP, TEP, TBBP-A, Cl-Paraffins, RDP, BDP, Sb2O3 (synergist to Br/Cl)
The FR Controversy

- FR save lives and properties, this is undisputed.
- However, concerns are raised about environmental impact and toxicity of certain FRs
  - Scientific studies e.g. in Germany, Nordics, UK and Switzerland
  - Topics: Persistence, Bioaccumulation, Toxicity (PBT)
  - Potential formation of halogenated dioxins & furans
  - FR findings in the Environment, Biota, Indoor Air and dust
- Discussion mainly focuses on halogenated FR, but also a few phosphorus FR
- Highly controversial discussions, e.g. Deca-BDO
- Political agenda: EU risk assessments of 13 high volume FR, REACH implementation
- Increasing role of Ecolabels and Public Green Procurement Policies
- In consumer products, OEM increasingly adopt proactive “halogen-free” stance
Chemicals & Environment

Analytical Chemists in the Wild West

Don't move or I'll fill you full of 98% lead, 1% antimony, 0.75% silver, 200 ppm nickel, with trace amounts of cobalt, and other components below their respective detection limits!!!

Wait a minute! Are those values certified??

REACH
The FR challenge

- Selection of FR and formulation work is a complex, empirical process (“trial and error”)
- Often subject to difficult compromises

Compatibility with host polymer and processing

FR efficiency vs. Fire test

Cost

Eco-tox aspects
Summary

- Flame Retardants are an essential part of passive fire safety in a world made of plastics.
- Their use is dictated by a complex framework of different regulations (national laws and/or industry standards).
- Material testing is subject to a variety of different fire tests (depending on final use and related fire scenarios) which in turn affect the FR strategy.
- The use of FR in polyurea is relatively recent and therefore not extensively explored.
- Systems exist but most of them are subject to further improvements.
- Many R&D activities ongoing, expected to result in improved formulations (i.e. processing, new fire standards).
- Headaches?
  *Seek advice from your raw material producer, formulator or FR supplier.*
Thanks!

- Thank you for your attention!

- Special thanks to Dr. Volker Butz (Thor GmbH) for his contribution and his promising, ongoing R&D works

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  3rd Edition (2004), Hanser Publishers
  www.troitzsch.com

- For any question, feel free to contact me:
  jdb@thor.com  - Cell: +49 160 908 51 935