Adhesive Polyester Polyols with inherent Flame Retardancy

Gabriele Brenner, Dr. Christina Diehl, Sabine Thüner
Izmir, 2013-09-13
Polyester Polyols as Building Block System for RHM Formulations

RHMs are reaction products of solid polyol mixtures with excess diisocyanates (e.g. MDI).

Building block systems of
- amorphous
- liquid
- crystalline Polyester grades
allow a precise formulation of the RHM.

Formulation example

To adjust RHM setting time:
- 40 ppw - amorphous grade A 7150
- 30 ppw - liquid grade L 7250
- 30 ppw - crystalline grade C 73XX
 & 4,4’ MDI [OH/NCO 1/2.2]
Markets and Applications for Reactive Hot Melts

Reactive Hot Melts are mainly used in:

- **Automotive Industry**
  (e.g. Automotive interior parts, Door panels, Windshield bonding)

- **Woodworking Industry**
  (e.g. Edge banding, Profile wrapping, Flat lamination, Parquet floors)

- **Packaging Industry and Graphic Arts**
  (e.g. Folding Boxes, Bookbinding)

- **Construction Industry**
  (e.g. Flat Lamination, Sandwich construction)

- **Textile Industry**
  (e.g. Protection wear, Sports wear, Medical applications, Health care)
Specific Applications for Flame Retardant Adhesives

Even non-flammable materials can be rendered flammable by bonding materials that use a standard adhesive. This is why – in addition to adhesive properties – high flame resistance often is an additional requirement particularly in:

- **Public buildings**
  - Technical textiles (e.g. curtains, carpeting)

- **Public transport**
  - Textile adhesives in vehicles

- **Aircraft construction**
  - Bonding materials for textiles and leather

- **Clothing industry**
  - Lamination of protective clothing and outdoor clothing

- **Boat building**
  - Lamination of paneling and textile adhesives

- **Electronic industry**
  - Lamination of metal foils and plastic films (e.g. for flexible flat cables)
Flame Retardants: Mode of Action

Activation

Flame retardants act during the initial stage of a fire and are activated by thermal decomposition

Task

- Avoid or hinder flammability
- Slow down flame propagation

Physical

- Cooling by endothermic processes or liberation of water
- Formation of protective barrier on surface
- Dilution by inert substances

Chemical

- Carbonization and formation of char barrier on surface
- Inhibition of radical chain reaction (gas phase)
- Formation of a foam insulation barrier (intumescence)

Barrier for heat and mass (emissions, oxygen) transfer

Isolating Carbon Layer

reduce smoke emission

Plastic (PE, PP) + Organo phosphorus FR-system
Types of Flame Retardants

**Anorganic metal hydroxides**
e.g. aluminium trihydroxide

- Mainly physical modes of action
- Very high loadings required
- Low thermal stability
- Low amounts of smoke

**Halogenated flame retardants**

- Radical inhibitors in gas phase
- High emission (e.g. CFCs)
- Formation of corrosive gases
- Highly effective

**Phosphorus-containing flame retardants**

- Catalysis of carbonization
- Highly effective in oxygen-containing polymers
- Non-toxic
- Broad range available

**Flame retardants worldwide 2011**

- Aluminium Trihydroxide: 34%
- Brominated FR: 12%
- Organo phosphorus FR: 7%
- Chlorinated FR: 8%
- Antimon Oxides: 18%
- Others: 21%

*) Source: SRI Consulting, Flame Retardants 2011

2013/09/13 | Adh. Polyester Polyols with inherent flame retardancy, G. Brenner
General Market Trends for Flame Retardants in Adhesives

Requirements on safety enhance the consumption of flame retardants

**Consumption of FR in A&S**

- Total Consumption (EU / 2010) = 19,7 kt
- Dominating systems: Aluminium Trihydrate and brominated FR
- Only small volumes for organo phosphorus FR in A&S

**Trends for FR in A&S**

- Adhesives have to be free of toxic elements (e.g. halogens or antimony)
- Adhesive properties should not be affected when adding a FR while some FR systems have negative influence due to very high concentrations (e.g. ~40 wt.% Aluminium Trihydrate in PU-Adhesives)

**Outlook**

Organo phosphorus FR-systems grow and will benefit from A&S trends

*) Source: SRI Consulting, Flame Retardants 2011

---

2013/09/13 | Adh. Polyester Polyols with inherent flame retardancy, G. Brenner
Development of a Polyester with inherent Flame Retardancy

**Problem**
State-of-the-art adhesives contain flame retardants as additives which lead to significantly reduced adhesion performance

**Challenge**
Find a reactive phosphorus-based organic flame retardant as monomeric building block

**Literature research**
- Learn about flame retardants in general
- Find reactive phosphorus based ones

**Market screening**
- Check on availabilities
- Check on prices

**Development**
Check of suitability for polyester synthesis with regard to:
- thermal stability
- reactivity
- purity

**Polymer design**
Chemical incorporation of flame retardant during polyester synthesis

**Results**
Development of first prototype successful: patent application filed
Flame Retardant Polyester for RHM: DYNACOLL® EP 455.04 FR

<table>
<thead>
<tr>
<th>Polyester data</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>-</td>
<td>pasty</td>
</tr>
<tr>
<td>Hydroxyl number</td>
<td>mgKOH/g</td>
<td>35</td>
</tr>
<tr>
<td>Acid number</td>
<td>mgKOH/g</td>
<td>1</td>
</tr>
<tr>
<td>Glass transition temperature (DSC)</td>
<td>°C</td>
<td>55</td>
</tr>
<tr>
<td>Softening point (R&amp;B)</td>
<td>°C</td>
<td>35</td>
</tr>
<tr>
<td>Viscosity at 80°C</td>
<td>Pa.s</td>
<td>1</td>
</tr>
</tbody>
</table>

**Lab insight:** This flame retardant polyester-polyol shows excellent compatibility to conventional amorphous, liquid as well as crystalline polyesters!

<table>
<thead>
<tr>
<th>RHM data</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction product of DYNACOLL® EP 455.04 FR with 4,4'-MDI as a ratio of OH/NCO = 1/2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity at 100°C / 120°C</td>
<td>Pa.s</td>
<td>6 / 3</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>N/mm²</td>
<td>15</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>%</td>
<td>1100</td>
</tr>
</tbody>
</table>
Flammability characteristics are tested according to UL-94, which determines the material’s tendency to spread the flame once the specimen has been ignited, i.e. tests have to be fulfilled by the polymer itself, not the bonded substrate.

<table>
<thead>
<tr>
<th>Criteria conditions of UL 94</th>
<th>V-0</th>
<th>V-1</th>
<th>V-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total flaming combustion for each specimen</td>
<td>≤ 10s</td>
<td>≤ 30s</td>
<td>≤ 30s</td>
</tr>
<tr>
<td>Total flaming combustion for all 5 specimens of any set</td>
<td>≤ 50s</td>
<td>≤ 250s</td>
<td>≤ 250s</td>
</tr>
<tr>
<td>Flaming and glowing combustion for each specimen after second burner flame application</td>
<td>≤ 30s</td>
<td>≤ 60s</td>
<td>≤ 60s</td>
</tr>
<tr>
<td>Cotton ignited by flaming drips from any specimen</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Glowing or flaming combustion of any specimen to holding clamp</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>

- UL 94 V-0 Vertical Burn; Burning stops within 10 seconds, NO flaming drips are allowed
- UL 94 V-1 Vertical Burn; Burning stops within 30 seconds, NO flaming drips are allowed
- UL 94 V-2 Vertical Burn; Burning stops within 30 seconds, Flaming drips ARE allowed
RHM Properties: inherent vs. external Flame Retardancy

Reaction products with MDI OH/NCO ratio 1/2.2 based on…

- RHM 1: DYNACOLL® EP 455.04FR
- RHM 2: Conventional pasty polyester
- RHM 3: Conventional pasty polyester with additive liquid flame retardant
- RHM 4: Conventional pasty polyester with additive powder flame retardant

…were tested according to UL 94 burning test. The results:

<table>
<thead>
<tr>
<th>RHM data</th>
<th>Unit</th>
<th>RHM 1</th>
<th>RHM 2</th>
<th>RHM 3</th>
<th>RHM 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 100°C / 120°C</td>
<td>Pa.s</td>
<td>6/ 3</td>
<td>11/ 6</td>
<td>7/ 4</td>
<td>8/ 4</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>N/mm²</td>
<td>15</td>
<td>25</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>%</td>
<td>1100</td>
<td>1100</td>
<td>1300</td>
<td>1250</td>
</tr>
<tr>
<td>Flammability testing UL 94</td>
<td></td>
<td><strong>V-0</strong></td>
<td><strong>V-2</strong></td>
<td><strong>V-0</strong></td>
<td><strong>V-2</strong></td>
</tr>
</tbody>
</table>
Comparison of RHM based on Polyester with inherent vs. additive FR

Adhesion Properties

Shear adhesion [MPa]

Reactive Hot Melts based on:
- Polyesters with inherent flame retardant
- Polyesters with flame retardant additives
- Conventional Polyester

- PVC
- ABS
- PET
- PMMA
- PC
Chemical and Heat Resistance

**Chemical Resistance**
- Method: Determination of soluble components after extraction in boiling acetone

**Heat Resistance**
- Method: According to WPS 68

Reactive Hot Melts based on
- Polyesters with inherent flame retardant
- Polyesters with flame retardant additives
- Conventional Polyester
## RHM based on Polyester Mixtures: Flammability Results

### Flame retardant Polyester: Required amount in RHM composition

<table>
<thead>
<tr>
<th>RHM composition</th>
<th>20</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>DYNACOLL® EP 455.04 FR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conventional pasty Polyester with additive FR</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conventional crystalline Polyester</td>
<td>100</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>4,4’-MDI [OH/NCO]</td>
<td>1/2.2</td>
<td>1/2.2</td>
<td>1/2.2</td>
</tr>
<tr>
<td>Flammability testing UL 94</td>
<td>V-2</td>
<td>V-2</td>
<td>V-0</td>
</tr>
</tbody>
</table>

### Result

**Only 20 ppw of flame retardant polyester are needed!**
Hydrolysis Resistance

Reaction products with MDI OH/NCO ratio 1/2.2 based on crystalline polyesters and pasty or liquid components 80/20 ppw.

- RHM 5: DYNACOLL® EP 455.04FR
- RHM 6: Conventional pasty polyester
- RHM 7: Conventional pasty polyester with additive liquid flame retardant
- RHM 8: Conventional liquid polyester

![Tensile strength after exposure to water at 60°C (N/mm²)]
Influence of isocyanate grade

Excellent melt stability with monomer-free isocyanate prepolymers

Melt Stability of RHM based on Flame Retardant Polyester

Influence of mixtures on RHM’s melt stability based on MDI

Lab tests show

Lower application temperatures avoid side reactions

Influence of isocyanate grade

Lab tests show

Excellent melt stability with monomer-free isocyanate prepolymers

Increase of viscosity [%]

Decreasing amount of FR in RHM composition

110°C /24h
100°C /24h

Increase of viscosity [%]

RHM 1
RHM 1a
based on MDI
based on Prepolymer

120°C /24h
110°C /24h
100°C /24h

500 400 300 200 100 0
Flame retardant DYNACOLL®: Your Benefits

Discover the benefits of...

...our flame retardant solutions:

- Highly effective flame retardant properties
- Excellent adhesion performance
- Improved chemical and heat resistance
- Adequate hydrolysis resistance
- Adjustable melt stability
- Very good compatibility with various polyester polyols