Polyurethane Laminating Adhesives and Food Safety: A Smart Alliance

Dr. Claudia Meckel-Jonas
Henkel Company China Ldt.

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Flexible packaging
Sustainable packaging system

Environment Resources

Packaging with adhesives

Social
- Meet customer expectations
  - Product protection
  - Safety
  - Handling
  - Information

Economy
- Cost for production distribution, merchandizing of goods

Source: incpen
PAA in food!

So called “Danish food scandal”
Laminating adhesives
Polyurethane (PUR) chemistry

R-NCO + HO-R' → R-NH-CO-O-R'
Urethane

- Advantages
- Performance
- Price
- Availability
- Established equipment

- Disadvantages
- Interaction with films/inks/additives
- Curing needs time
**Physical Curing**

Production stage:
- **high performance**
- **medium performance**
- **standard performance**

Curing time:
- **1st lamination**
- **slitting**
- **heat sealing**
- **boiling resistance**
- **retort resistance**

safe for food contact?
We have to get the chemical curing of the adhesives & the physical requirements balanced for a sustainable and safe packaging.
Curing mechanism of 2-c polyurethane adhesives

- **First curing step:** Reaction of NCO with OH

![Chemical reaction diagram]

Polyurethane prepolymer after first curing step
Curing mechanism of 2-c polyurethane adhesives

- **Final curing (1): Reaction of NCO with H$_2$O**

![Chemical reaction diagram]

\[
\begin{align*}
\text{O=C=NN} & \rightarrow \text{O=C=NN} + \text{H}_2\text{O} \\
\text{N=C=O} & \rightarrow \text{N=C=O}
\end{align*}
\]

- Completely cured polyurethane adhesive
Flexible packaging in contact with food

Adhesive in indirect food contact

<table>
<thead>
<tr>
<th>Outer Layer</th>
<th>Adh.</th>
<th>Sealing Layer</th>
<th>Food</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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</tbody>
</table>

E.g.:  
NCO + Water $\Rightarrow$  
Aromatic Amines  
“PAA”  
Suspected to be carcinogenic  
ONLY present in not fully cured PUR-adhesives!
Migration of aromatic amines in screening test – cited in BfR XXVIII

Sample from reel

Make pouch (200cm²) + 100ml acetic acid

Store in oven 2h@70°C

Chemistry!

Derivatisation of filling

UV-Detection
PAA-Migration: Photometric Test (BfR)

- Colour intensity corresponds to level of migration of non-reacted NCO-monomer!
- Detection limit: 2 ppb!
Chemical Curing - Conventional

PAA Migration Level

Conventional System

- High performance
- Medium performance
- Standard performance

Days

Curing time

1st lamination

Slitting

Heat sealing

Oiling resistance

Retort resistance

Chemical Curing - Conventional
Cure mechanism of a modified 2-component PUR with smart chemistry

Cure mechanism

NCO/OH > 1
based on mix ratio

\[
\text{OCN} \quad \textit{---NCO} \quad + \quad \text{HO} \quad \textit{-----OH} \\
\text{with free MDI-monomer}
\]

\[
\text{OCN} \quad \textit{---------urethane---------NCO} \\
\text{no retain NCO-monomer} \quad \rightarrow \quad \text{safe for indirect food contact}
\]

\[
\text{OCN} \quad \text{n-----urea-----urethane-----urea-----} \\
\text{---fully cured PUR}
\]

\[
\text{step 1: fast} \\
\text{+ water} \\
- \text{carbon dioxide}
\]

\[
\text{step 2: slow}
\]
Chemical Curing - Smart

PAA Migration Level

Conventional System

Smart System

1st lamination

slitting

heat sealing

Oiling resistance

retort resistance

Curing time

Days

0
EC Regulations for safe food packaging

EC 1935/2004 framework

- 82/711 + amendments time/temp.
- 85/572 food simulants

2002/72/EC Plastic directive
(90/128 + amendments)

- amendments
  - 2004/1/EC
  - 2004/19/EC
  - 2005/79/EC
  - 2007/19/EC

- 5th amendment 2008/39/EC
### Flexible packaging in food contact

#### Legal requirements

<table>
<thead>
<tr>
<th>Country</th>
<th>Regulations/Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>FDA § 175.300 (direct food contact), FDA § 175.105 (indirect food contact), FDA § 177.1395 (40°C – 120°C), FDA § 177.1390 (&gt; 120°C)</td>
</tr>
<tr>
<td>Germany</td>
<td>LFGB, BedGgstV, BfR Recommendation XXVIII for cured polyurethanes as adhesive layers for food packaging</td>
</tr>
<tr>
<td>China</td>
<td>GB 9685-2008</td>
</tr>
</tbody>
</table>

- FDA § 175.300: Direct food contact
- FDA § 175.105: Indirect food contact
- FDA § 177.1395: 40°C – 120°C
- FDA § 177.1390: > 120°C
- Framework regulation 1935/2004/EC
- LFGB
- BedGgstV
- BfR Recommendation XXVIII for cured polyurethanes as adhesive layers for food packaging
- GB 9685-2008
Framework Regulation
1935/2004/EC

EC 1935/2004 (replaced 89/109), Article 3:
Packaging materials have to be manufactured in a way that under the conditions of use no components will be transferred into the food, which

- are a potential hazard to the human health
- change the food composition or
- influence the organoleptic properties
EC migration limit for aromatic amines & BfR-method - Conclusion

We recommend to use the BfR-method for compliance testing using a limit of 2ppb

Otherwise there will be the risk of non-conformity with EU-legislatives!
Limitations of „BfR-test“

- **SUMMARIZING method**
  - All PAA are measured at once
- **Known to give false positive results!!!**
  - No distinction between PAA and other substances possible.
  - Problematic in presence of additives (films/ink)
  - Results for retort applications & higher temperatures are doubtful and have to be cross-checked

⚠️ A specific method is required for cross-check!
Summary: Compliance testing for PAA

4th amendment of 2002/72/EC: 2007/19/EC
DL = 0.01 mg/kg (aniline, without analytical tolerance)

Screening method
BfR photometric test
considers lower response factors of real PAA vs aniline
threshold of action limit 0.002 mg/kg

Specific method
HPLC-UV
if >0.002 mg/kg
DL = sum PAA <0.01 mg/kg
Factors Influencing Migration Time

- Adhesive system
  - free monomeric isocyanate content
  - Curing mechanism (most important)
  - coating weight
  - Mix ratio
- Laminating AND storing conditions
  - Temperature
  - Humidity
  - Thickness of rolls
  - Width of rolls
- Film
  - Type
  - Thickness
  - Additives (e.g. copolymers (EVA), pigments..)
  - Type of film for outer layer
Conclusion

- Laminates should not be used for food packages until physical AND chemical curing is completed!

- Packages, that do not comply with legislatives endanger human health.

- The answer is....
...responsible care
...training and information of converters
...the choice of the smart & appropriate adhesive!

Henkel CAC India and Liofol

will help to meet the demands of safe food packaging!!