THE ADHESION OF LSR AND POLYPROPYLENE TYPES AFTER STORAGE

Dipl.-Ing. A. Rüppel, M. Hartung, M. Sc., Dr.-Ing. R.-U. Giesen, Prof. Dr.-Ing. H.-P. Heim
University of Kassel, Institute of Material Engineering
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Objectives

Production of Liquid-Silicone-Rubber (LSR) - Polypropylene Composites

- Adhesion of LSR and Polypropylene only possible with surface activation of PP-component
- Self-bonding LSR types only suitable for PA and PBT
  - No self-bonding LSR-types für bulk plastics (PP, PE) currently on the market

→ Generation of an Adhesion of LSR and Polypropylene
→ Surface activation of thermoplastic component
→ Long therm stability of the surface activation
Properties of LSR-TP-Composite Materials

○ ○ ○ **LSR-Thermoplastic Composite Materials**
  • hard-soft composites of thermoplastic and LSR
  • sample production by multi-component injection molding

○ ○ ○ **Advantages by using LSR Thermoplastic Composite Materials**
  • cycle time saving production (LSR is direct overmoulded on TP)
  • production is carried out in one step
  • for production only one machine and one tool is needed
  • merging of the materials to a synergetic component
  • use of several positive properties by 2c-composites
Adhesion

**Mechanical Adhesion**

Mechanical adhesion by surface texture by
- Surface roughness
- Hollows
- Pores

**Specific Adhesion**

**Chemiesorption**
Chemical primary valency bonds (covalent, ionic, metal)

**Diffusion Theory**
Diffusion of the molecular chains into the other component

**Adsorption Theory**
Formation of secondary valence bonds
→ good wettability necessary
Silane Coupling Agent

Generation of Adhesion between LSR-TP: Selfbonding LSR \(\rightarrow\) compatible for PA and PBT

Reactive groups
\(\rightarrow\) form chemical bond with inorganic material (silicone, glass, metal)
- Methoxy groups
- Ethoxy groups
- ..... 

\(\rightarrow\) connection of epoxy groups with functional groups of activated PP
\(\rightarrow\) connection of methoxy-functionalized silane group with the LSR

Ref.: ShinEtsu: Silane Coupling Agents, Product Outlines, (2011)
### Experimental

#### Material selection

**Selfbonding LSR**

Elastosil LSR 3071/40 (Wacker Chemie AG)

- **component A:** contains platinum catalyst
- **component B:** contains crosslinker & inhibitor

→ mixing ratio: 1:1

**Polypropylene:**

<table>
<thead>
<tr>
<th>Material</th>
<th>Brand Name</th>
<th>Company</th>
<th>Properties</th>
</tr>
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<tbody>
<tr>
<td>Polypropylene</td>
<td>PP Sabic 575P</td>
<td>Sabic</td>
<td>Suitable for food contact application, toys and houseware articles</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>PP Purell HP571P</td>
<td>LyondellBasell</td>
<td>Medical devices</td>
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<tr>
<td>Polypropylene</td>
<td>Altech PP-HA A 2020/100 GF 20</td>
<td>Albis Plastic</td>
<td>Glass-fiber reinforced PP, applications in furniture industry</td>
</tr>
</tbody>
</table>
Experimental

Production of polypropylene components by injection molding process
(full-electric Arburg 370A 600-70/70 Alldrive)

Multicomponent TP-/LSR tool
I & II: cooled areas for TP
III & IV: for LSR component
IV is changable
Experimental

Surface activation

No adhesion between PP and selfbonding LSR → functional groups for interaction

due to surface activation
→ functional groups for interactions
→ allow hydrogen bonds for adhesion
Experimental

Surface activation by flame treatment (silicatization)

○ Flame pyrolytic deposition of amorphous silicate
○ Layer thickness 20-40nm
○ Precursor (silicon-containing substances)
○ Formation of Si-OH groups
  → Connection of functional groups (e.g. amino groups) to increase the adhesion
○ Formation of a very thin, chemically highly reactive layer (glass layer)

Experimental

Surface activation by flame treatment (silicatization)

Used Parameters: Flame distance: 15mm; activation speed: 0,4m/s

With increasing flame distance
→ aggregation of coating particles
→ less reactivity of larger particles
→ removal of particles in gas flow
→ no involvement in layer deposition

- Mobile table to control flame distance and speed of activation
- Partial storage of thermoplastics before further overmolding with LSR
- Direct overmolded with LSR → Composite storage at room temperature of LSR-PP
Experimental

Experimental Plan → 2 ways

After surface activation → storage of PP and examination of:
- Wetting behavior by Contact Angle Measurement (DSA-Method)
- Surface roughness by Confocal Scanning Laser Microscopy
- Formation of chemical bonds by FTIR-Spectroscopy

<table>
<thead>
<tr>
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<th>0 days</th>
<th>1 day</th>
<th>7 days</th>
<th>14 days</th>
<th>28 days</th>
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<tr>
<td>No activation</td>
<td></td>
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After surface activation → overmolding with LSR and storage of compound

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Contact angle measurement by Drop Shape Analysis (DSA-Analysis) → Wetting Behaviour of PP

→ a drop of water is applied on the PP surface
→ measurement of contact angle
→ 4 samples and 3 drops every batch were measured
Experimental

Confocal Scanning Laser Microscopy (LEXT, OLS 3100/OLS3000) → Surface Roughness of PP

- Scanning of the sample by focusing laser
- Investigation of stored and direct activated samples
- No sample preparation needed
- Magnification: 500x
- 3 samples per batch
FTIR Spectroscopy (Schimadzu, IRAffinity -1S) → Chemical Bonds

- Investigation of stored and direct activated samples
- Examination by Attenuated Total Reflection (ATR)
- Total reflection at the boundary between two optically different media (crystal and specimen)
- Crystal: Zinc selenide (ZnSe, 45°)

Experimental

After Storage → Overmoulding of TP with selfbonding LSR

○●● PP was inserted into the machine by hand → overmolding with LSR

○●● Temperature of 140°C for 60s during injection molding process for both components
Peel-Test according to VDI 2019 (Hegewald & Peschke, 5kN, testing speed: 100mm/min.)

- Force-stroke diagram [mm]
  - curve with force peaks
  - wavy curve
  - cohesive failure at LSR
  - cohesive failure at LSR after peeling (50%)

A: peeling of the LSR component without residue (adhesive peeling)

B: residue (1-50%) of LSR on thermoplastic component (cohesive peeling)

C: residue (51-99%) of LSR on thermoplastic component (cohesive peeling)

D: no peeling of the LSR component ➔ cohesion crack (Ws max)
Results and Discussion
significant reduction of the values after surface activation for all materials

→ increase of the contact angle after storage time

→ reversible process of flame treatment, but lower values of contact angle than materials without surface activation
Confocal Laser Scanning Microscopy

- PP Sabic 575P
  - Without activation [Rz: 1]
  - With activation [Rz: 0.51]

- PP + 20% GF
  - Without activation [Rz: 1.8]
  - Without activation [Rz: 0.9]

○ ○ ○ reduction of surface roughness after silicatization → increase of the values after storage
○ ○ ○ But lower values than materials without surface activation
FTIR-Spectroscopy
Example: PP after silicatization

- Significant changes after silicatization visible
- Formation of silicon bonds (Si-O-Si, area 1090-1030)
- Si-NH₂ bonds in the range of 1250-1100 (Amino-group)
- After 28 days storage → decrease of the bondings of PP

→ rotation of polymer chains → they are not available for further interactions
- no adhesion without surface activation
- strong adhesion (cohesive peeling) after silicatization
- decrease of peel-resistance after storage time but still a strong adhesion up to 1 week (failure type: B & C)

→ Overmoulding of test samples within one week
No adhesion without surface activation

Increase of the values up to 7 days

Increase of the values by post-crosslinking of the silicone component and possibly an interdiffusion due to temperature storage

Reduction of the values after 2 weeks → post-crystallisation of the PP component and the resulting embrittlement
No adhesion without surface activation

Increase of the values up to 3 days

In comparison with 100°C composite storage → faster reduction of the peel-resistance from 7 days up to 28 days

Post-crystallisation leads to embrittlement in the material → less adhesion after storage time
Conclusion
Dependence between adhesion and storage of Polypropylene before overmolding with LSR exemplified by PP Sabic 575P

- Decrease of surface roughness after silicatization → increase of the values after storage time → deterioration of adhesion depending on storage time
- Improvement of wetting behaviour after surface activation → storage time leads to an increase in contact angle → decrease of the peel-resistance depending on storage time
Conclusion

- Peel-Test according to VDI 2019 (Storage of the whole compound at 100°C & 120°C)
  - 100°C: increase of values up to 7 days & a reduction of peel-resistance from 2 weeks → post-crystallization of PP
  - 120°C: increase of values up to 3 days → significant reduction in adhesion from 7 days (HDT & post-crystallization)

Due to surface activation...

- Generation of a very good adhesion between LSR an PP (no adhesion without activation)
- Very strong compounds even after storage of the PP component bevor overmolding
- Very strong compound after storage of LSR/PP-compound up to one week (especially for 100°C)
Thank you for your attention

A gecko can run overhead on all surfaces by perfect matched properties of the soles of his feet

www.unipace.de

Ref.: http://jacobs.physik.uni-saarland.de/forschung/gecko.htm
Back Up
Overview of Silicone Rubber

Silicone Rubber

**High Temperature Vulcanized (HTV)**

- **High-Consistency Rubbers (HCR)**
  - 1-c peroxide cured
  - 2-c addition cured

- **Liquid Silicone Rubber (LSR)**
  - 2-c addition cured

**Room Temperature Vulcanized (RTV)**

- **Single- component (1-c)**
  - 1-c condensation cured

- **Dual- component (2-c)**
  - 2-c condensation cured
  - 2-c addition cured
Differential Scanning Calorimetry of PP after Storage

- Heating up the sample from 0°C to 200°C (10K/min.) → Changes of the heat flow in endothermic direction
- Constant melting temperature for PP reference and the stored thermoplastics
- Increasing melting enthalpy with storage time especially at 120°C → post-crystallization of the material
- Post-crystallization could lead to a reduction of the adhesion → embrittlement in the thermoplastic component