Wann und warum klebt Gummi
- Wann klebt es nicht.

DKG – Nord: Herbsttagung 2012
"Gummi klebt, Hamburg lebt"
H&R Ölwerke Schindler GmbH

Dr. Hans-Joachim Graf
Wann und warum klebt Gummi? - wann klebt es nicht?

- Introduction
- Principles of Adhesion
  - What can we learn from Nature?
  - Which forces are enable Adhesion
- What makes rubber sticky
  - Examples
- What the hint to stickiness of rubber
  - Examples
- Conclusion / summary
### Introduction: Adhesives History

<table>
<thead>
<tr>
<th>Adhesives for broken pottery</th>
<th>~6000 years ago</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tar like glue (for ivory)</td>
<td>~6000 years ago</td>
</tr>
<tr>
<td>Animal glue (tombs – Aegypt)</td>
<td>~3500 – 3000 years ago</td>
</tr>
<tr>
<td>First reference in literature for making animal glue</td>
<td>~ 2200 years back</td>
</tr>
<tr>
<td>Animal glue for wood marquetries, fish glues, egg white to glue gold leaf, Natural ingredients for glues developed like: blood, bones, hide, milk, cheese, vegetables and grains</td>
<td>~2000-1500</td>
</tr>
<tr>
<td>Bows (Genghis Khan) from laminated lemon wood and bullhorn, but formula is lost!!</td>
<td>~ 1000 years ago</td>
</tr>
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<td>First factory for animal glue in NL</td>
<td>~ 1000 years ago</td>
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<tr>
<td>First Glue Patent GB – Fish Glue)</td>
<td>1750</td>
</tr>
<tr>
<td>Adhesives industrialized from NR, fish, bones, starch, milk protein</td>
<td>After 1750</td>
</tr>
<tr>
<td>Phenolic Resin (after invention of Bakelite)</td>
<td>~1910</td>
</tr>
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</table>
1763 P.I. Macquer and L.A.M. Herissaut discovered the solubility of caoutchuc in ether and benzene. After evaporation of the solvent, the rubber hold its properties as before. Macquer spread rubber solutions on wax mold and made rubber hoses and shoes (1765)

1783 The British physicist J.A.C. Charles impregnated textiles with this solution, which was used to manufacture the first Hot Air Balloon of the brothers Montgolfiere.
Introduction: Adhesives History

- Vulcanization (Goodyear, Hankok) 1840
- Rubber – Fabric (Macintosh) 1823
- Ebonite - Compound (Rollers) Late 1800
- Brass plating (Tire Steel Cord) Since 1900
- Phenolic Resin (C.H. Meyer) 1902
- Phenol-Formaldehyde (Textil) 1930
- Isocyanate Adhesive 1945
- Chemlok 220/205 (Hughson/Lord) 1956

Structure of Phenolic Resin
Source ChiUZ. 3/2010
The three principles of adhesion

- Contact
- Reaction
- Diffusion
Principles of Adhesion

The three principles of adhesion

- Contact
- Reaction
- Diffusion

Adhesion on the boundary surface in contact

<table>
<thead>
<tr>
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<th>Bond length [nm]</th>
<th>Bond energy [kJ/mol]</th>
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<tr>
<td>Molecular interactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Van der Waals forces</td>
<td>0,4 – 0,5</td>
<td>2 – 15</td>
</tr>
<tr>
<td>Hydrogen Bridges</td>
<td>0,2</td>
<td>20 – 30</td>
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Source: Schuster, DIK
Principles of Adhesion

Criteria for intimate wetting

- Surface must be free of foreign particles. Weak layer or contaminants (H₂O, organic vapor, nitrates, ketones, alcohols, amines) has to be removed.
  - A large interfacial area of intimate contact
  - Thermodynamically, a high surface-energy surface is the most conductive to good wetting, particularly if adhesive contains polar functional group.
  - Surface energy of the adherent (reinforcement substrate) should be greater than surface energy of the adhesive (matrix top coat).
  - Creation or addition of chemical groups in the adhesive
  - Variation in surface topography (mechanical interlocking)

Influencing parameters

- Surface chemistry
- Surface topography
- Mechanical properties
Principles of Adhesion
What can we learn from nature?

- In nature bonding is the most dominant joining technology
- Adhesives found in nature
  - More powerful than any known synthetic glue – especially in the presence of water.

“Firmly Stuck” Barnacles

Peptide unit belonging to the adhesive substance found in mussels.

Dihydroxyphenylalanine (DOPA)
Functional group in adhesive substance found in mussels.

Source: CEN
Gecko–like adhesives

Pictures by K. Autum, Lewis & Clark College (Portland Oregon, USA) and S. Gorb, MPI für Metallforschung, Stuttgart, Germany
Forces create Adhesion

**Adsorption theory**
- Ordinary Van der Waals forces can be responsible for adhesive strength, if sufficiently intimate contact is achieved
- Hydrogen bonding can enhance adhesion

The attraction only due to dispersion forces:
- Theoretical: 100 MPa !!
- Experimental: Strength of most joints much smaller

**Why**
- Air voids, cracks, geometric defects acting as stress raisers, when the joint is loaded.
- Impurities like water, organic vapor, nitrates, ketones, alcohol, and amines can weaken adhesion.
Principles of Adhesion

The three principles of adhesion

- Contact
- Reaction
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The three principles of adhesion

- Contact
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<td>0.1 – 0.2</td>
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<tr>
<td>Metallic</td>
<td>0.3 - 0.4</td>
<td>100 – 400</td>
</tr>
<tr>
<td>Ionic</td>
<td>0.2 – 0.3</td>
<td>400 – 800</td>
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Source: Schuster, DIK
The three principles of adhesion

- Contact
- Reaction
- Diffusion

Precondition for Reactions in between the surfaces:

- Intimate contact
- Cleanliness!!
  - No foreign material
  - Functional groups
  - Weak hydrogen (in case of peroxide)
    - Absence of radical chain transfer / deactivation groups
Chain segments get in Interaction with a solid surface
Rubber - metal
Rubber, crystalline synthetic material

Side valency strengths determine the adsorption enthalpy (warmth)
- Dipoles and induced dipoles
- Hydrogen bridge relationships (Polarizability)

Introduction of functional groups
- Chemical or physical
- Pretreatment of the solid area
- Chemical modification of the polymer

Roughness of the solid surface
Principles of Adhesion

The three principles of adhesion

- Contact
- Reaction
- Diffusion

Source: Schuster, DIK
Principles of Adhesion

Source: Metten; Thesis 2002
Principles of Adhesion

Inter diffusion of different polymeric chains

Entanglement of chains in the Boundary layer (mechanical adhesion)

Influence of parameters on diffusion

Thermodynamic Compatibility

Process parameter P, T

Molecular dynamics, Chain mobility

Bond strength

Source: Schuster, DIK
Principles of Adhesion

The three principles of adhesion

- **Contact**
- **Reaction**
- **Diffusion**

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Forces:
- A little bit of everything!
- But in a broader layer!

Source: Schuster, DIK
Example 1: Rubber to metal

Source: DOW

Surface Energy $\rightarrow$ 72 dyne/cm

Metal surface treated
Example 1: Rubber to metal

Source: DOW

Surface Energy $\sim 72$ dyne/cm (Hydrophilic)

Metal surface treated
Example 1: Rubber to metal

Source: DOW

Top Coat

Primer

Surface Energy $\sim 72$ dyne/cm
(Hydrophilic)

Chlorinated Rubbers + Crosslinker

Metal surface treated
Example 1: Rubber to metal

Source: DOW

Surface Energy ~> 72 dyne/cm (Hydrophilic)

Top Coat

Primer

NBR / NR / EPDM Compound

Chlorinated Rubbers + Crosslinker

Metal surface treated
Example 1: Rubber to metal

Source: DOW

- **Surface Energy**: $\sim 72$ dyne/cm (Hydrophilic)
- **Primer**: Chlorinated Rubbers + Crosslinker
- **Top Coat**: NBR / NR / EPDM Compound
- **Rubber**
Example 1: Rubber to metal

What is the game?

Surface Energy $\sim$ 72 dyne/cm (Hydrophilic)

Wetting + Chemical Reaction

Diffusion + Chemical Reaction

Primer

Top Coat

Rubber

NBR / NR / EPDM Compound

Chlorinated Rubbers + Crosslinker

Metal surface treated
Example 1: Rubber to metal

Source: G. Polaski, et al., Lord Corp

Fig. 11: Pergut application: Rubber-to-metal bonding
Rubber rollers, engine bearings, shock absorbers, clutches etc.

Source: Bayer, Pergut brochure

Figure 2
Interfacial dynamics of a rubber-to-metal bond
Example 2: Corner Moulding

Profiles made of compounds based on EPDM
- EPDM Compounds bound with EPDM compounds
- TPV proven to bound on EPDM compounds
  - TPV: PP/EPDM base

Source: Toyoda Gosei

Dr. Hans-Joachim Graf
Example: Corner Moulding

Injection of Corner Moulding Compound based on EPDM

- Injection conditions
  - Compound has ~ 100°C
  - Mold Temperature ~ 170°C
  - Thermal expansion result pressure

- Vulcanization time

- Diffusion
  - Reaction eventually possible

Hot – low viscosity

Flow direction

Corner Moulding Compound

EPDM Profile

Cold + crosslinked solid
Example 2: Corner Moulding

Injection of Corner Moulding Compound based on TPE-V

- Injection conditions
  - Compound has ~ 200°C
  - Mold Temperature ~ 50°C
  - Thermal shrinkage result pressure, compensated with after pressure

- Allow time to cool

Some times called “Fusion Bonding”

- Diffusion
  - Reaction eventually possible

Hot – low viscosity

Flow direction

Corner Moulding Compound

EPDM Profile

Cold + crosslinked solid
Example 2: Corner Moulding

➤ Injection of Corner Moulding Compound
   • And then no bond!
   • Condition: profile stored in plant for a couple of days
   • No Diffusion

➤ What might hint the bonding?

Hot – low viscosity

- Corner Moulding Compound
- EPDM Profile

Cold + crosslinked solid

Flow direction
Example 2: Corner Moulding

Injection of Corner Moulding Compound (EPDM or TPV)
- And then no bond!
- Condition: profile stored in plant for a couple of days
- No Diffusion

What might hint the bonding?
- Water layer on surface
- Water absorption change polarity
  - Drying with heat result oxidation!?
  - Plasma to remove water?

Hot – low viscosity

Flow direction

Corner Moulding Compound

EPDM Profile

Cold + crosslinked solid
**Example 2: Corner Moulding**

- **Injection of Corner Moulding Compound (EPDM or TPV)**
  - Little change in surface energy prevents diffusion
  - Effect is large, due to pressure and time constraints
  - No Diffusion

**Diagrams:**
- Hot – low viscosity
- Flow direction
- Corner Moulding Compound
- EPDM Profile
- Cold + crosslinked solid
Example 3: Coating

System:
- EPDM Adherent
- PUR / VMQ Coating

Wetting with Plasma
- Introducing of OH groups in the surface
- Important: Must be the „right“ amount.

Reaction with OH groups
- Well known PUR chemistry

Source: Acheson/Henkel
Example 4: TP - Rubber

Injection Molding of a thermoplast "Vestoran" and Rubber

- Project TP-Rubber Part for the K'86 Fair in Düsseldorf (Jadamus, Richter)

U.S. 4835063 and subsequent patents

- Vestoran – SBR rubber manufactured with moving platen technology
  - Investigation of Diffusion
  - Worked, as long Rubber was compounded with SBR / SBR Blend
# Example 4: TP-Rubber

Thermodynamically compatible blend

Interactions:
1) between aromatic rings
2) Styrene ether groups

<table>
<thead>
<tr>
<th>H, W combine</th>
<th>Processing-compatibility</th>
<th>Creation boundary layer</th>
<th>Self adhesion</th>
<th>Crosslinking layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 PPE - SBR</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>2 PPE - SBR/NR</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>3 PPE - SBR/NBR</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>4 PPE - SBR/EPDM</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>5 PPE - EPDM</td>
<td>no-one</td>
<td>very low</td>
<td>no-one</td>
<td>Peroxide</td>
</tr>
</tbody>
</table>

Cohesive rips through physical or chemical phase connection

Source: Schuster, DIK
What help we get from this knowledge?

- **Rubber to metal**
  - Cleaning
  - Contamination
  - Surface structure
  - Selection of Primer / Cement
  - Layer Thickness
  - Temperature-Time during loading
  - Cavity Pressure
  - Forces during unloading

- **Rubber - Rubber**
  - Compatibility
  - Production with no delay time
  - Temperature - Time
  - Cavity pressure

- **TP - Rubber**
  - Environmental influences
  - Bleaching / Blooming of Ingredients
  - Incompatibility
  - Contamination

Dr. Hans-Joachim Graf
Rubber adheres with cohesive failure and high forces, if at least we have:

- Contact + reaction
- Contact + diffusion
- Contact + diffusion + reaction

It can have adhesion, if there is only contact, but the forces remain low.