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

Adhesives for broken pottery	**~6000 years ago**
Tar like glue (for ivory)	**~6000 years ago**
Animal glue (tombs – Aegypt)	**~3500 – 3000 years ago**
First reference in literature for making animal glue	**~ 2200 years back**
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**	**~2000-1500**
Bows (Genghis Khan) from laminated lemmon wood and bullhorn, but formula ist lost!!	**~ 1000 years ago**
First factory for animal glue in NL	**~ 1000 years ago**
First Glue Patent GB – Fish Glue)	**1750**
Adhesives industrialized from NR, fish, bones, starch, milk protein	**After 1750**
Phenolic Resin (after invention of Bakelite)	**~1910**

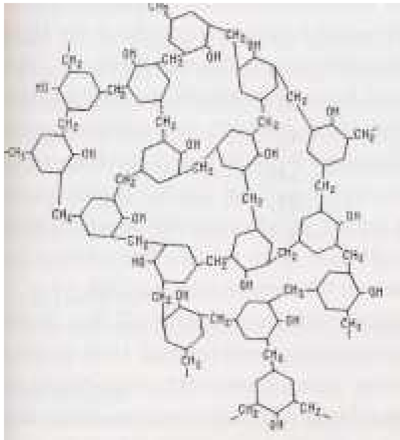
Introduction:
Adhesives History

Source: Internet

- 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 itsproperties 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

Principles of Adhesion

➨ **The three principles of adhesion**

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

Principles of Adhesion

Source: Schuster, DIK

➡ The three principles of adhesion

- Contact
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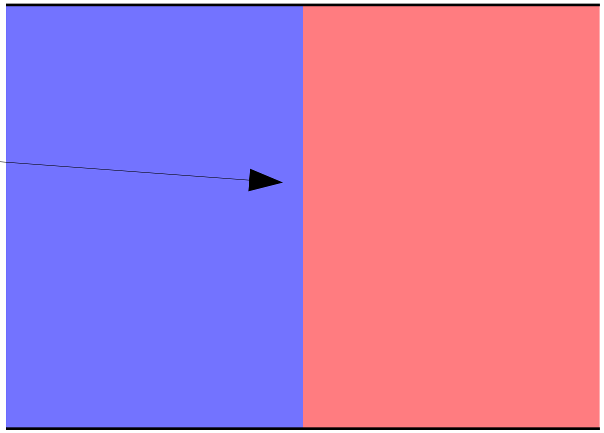


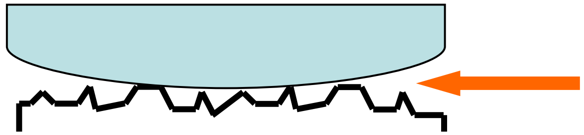
Adhesion on the boundary surface in contact

	Bond length [nm]	Bond energy [kJ/mol]
Molecular interactions		
Van der Waals forces	0,4 – 0,5	2 – 15
Hydrogen Bridges	0,2	20 – 30

Principles of Adhesion

Criteria for intimate wetting

- **Surface must be free of foreign particles. Weak layer or contaminants (H_2O, 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

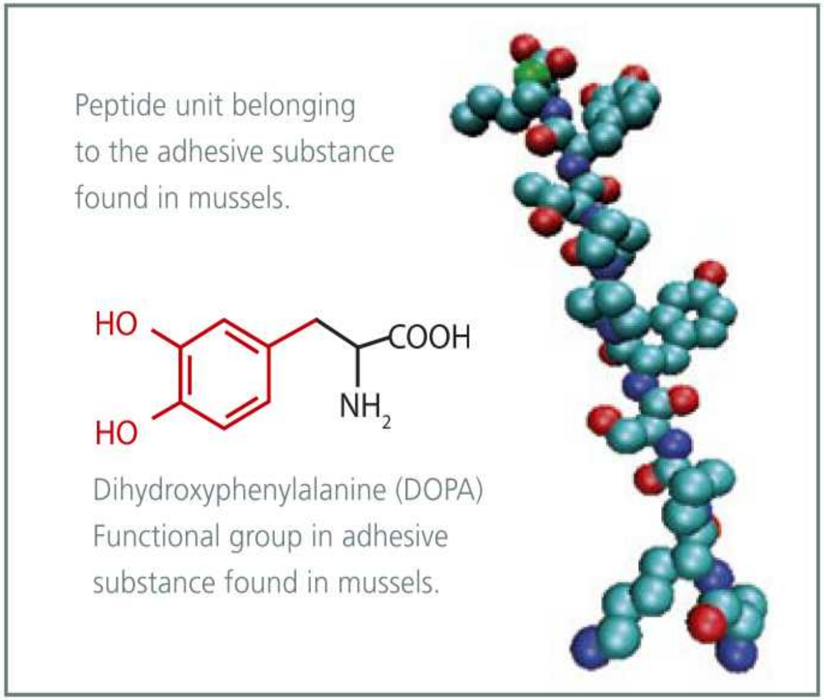
Surface chemistry
Surface topography
Mechanical properties

Principles of Adhesion

What can wie from natur?

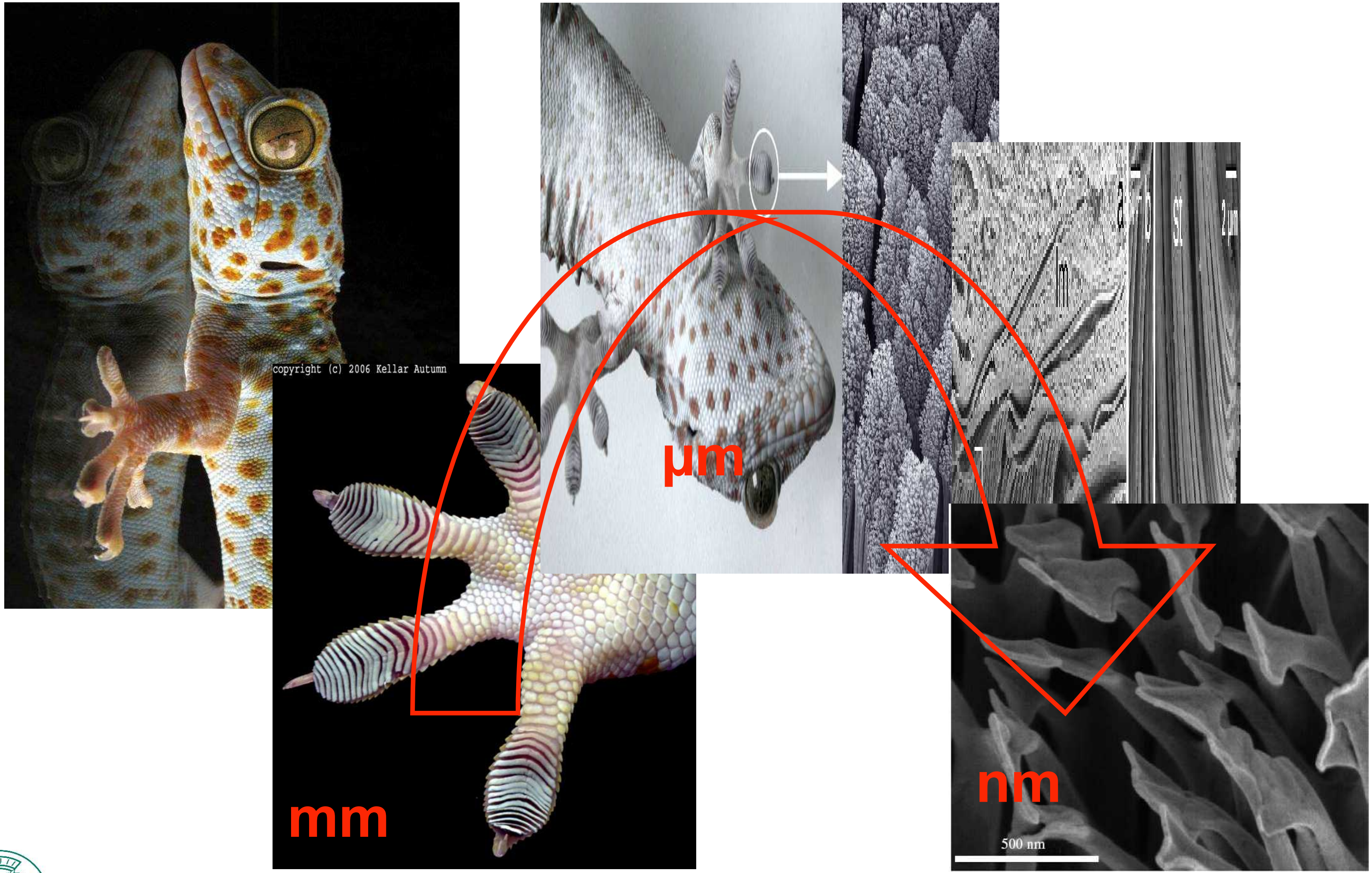
Source: CEN

- 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

Gecko–like adhesives

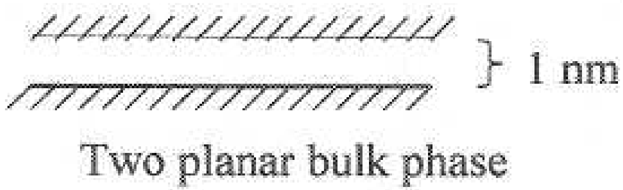


Pictures by K. Autum, Lewis & Clark College (Portland Oregon, USA) and S. Gorb, MPI für Metallforschung, Stuttgart, Germany

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

Source: Schuster, DIK

➨ The three principles of adhesion

- Contact
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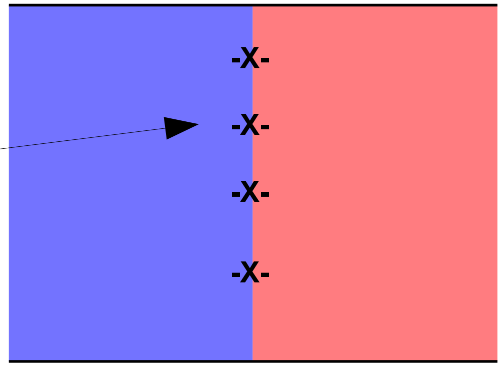
- Diffusion



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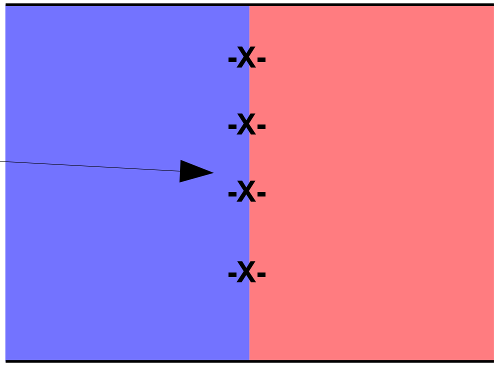


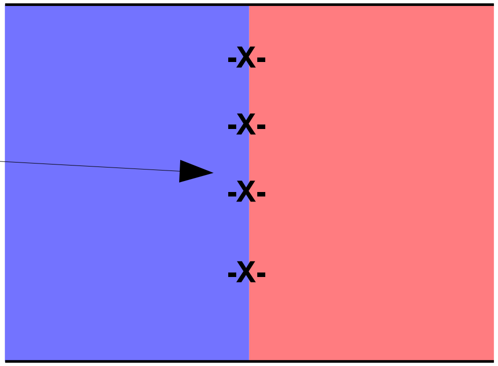
	Bond length [nm]	Bond energy [kJ/mol]
Chemical Bond		
Covalent	0,1 – 0,2	150 – 950
Metallic	0,3 - 0,4	100 – 400
Ionic	0,2 – 0,3	400 – 800

Principles of Adhesion

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

Principles of Adhesion

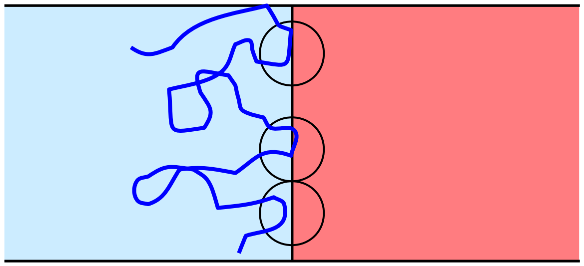
Source: Schuster, DIK

- **Chain segments get in Interaction with a solid surface**
  Rubber - metal
  Rubber, crystalline synthetic material

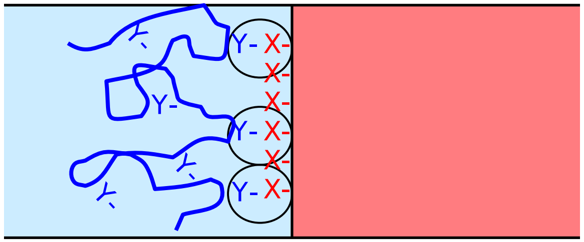
- **Side valency strengths determine the adsorption enthalpy (warmth)**
  - Dipoles and induced dipoles
  - Hydrogen bridge relationships
  (Polarizability)

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

- **Roughness of the solid surface**



Solid



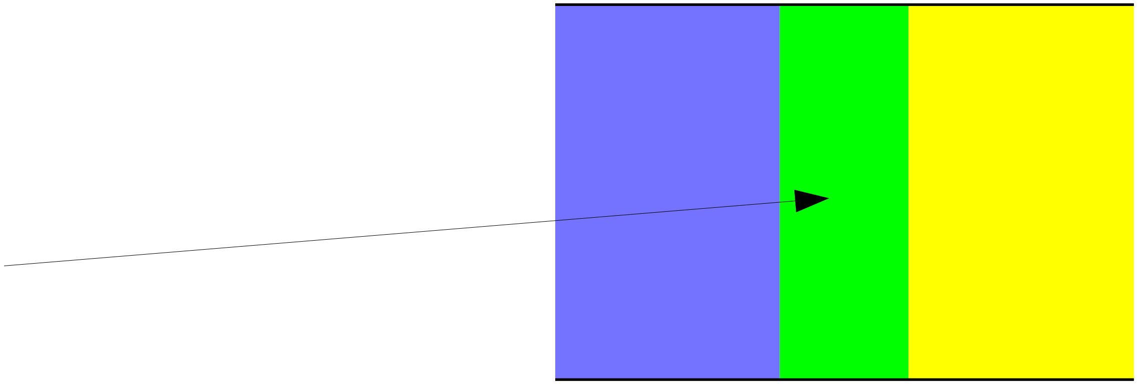
Solid

Prinziples of Adhesion

Source: Schuster, DIK

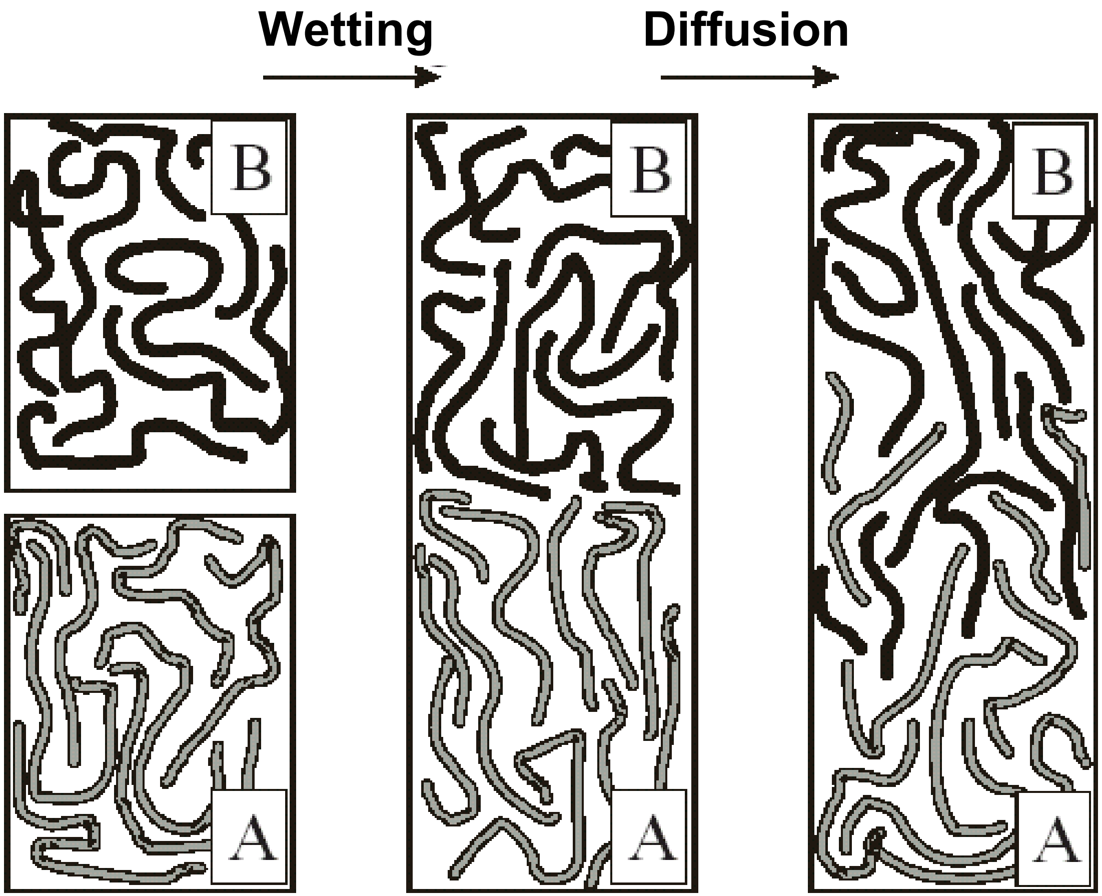
➡ The three principles of adhesion

- Contact
- Reaction
- Diffusion



Principles of Adhesion

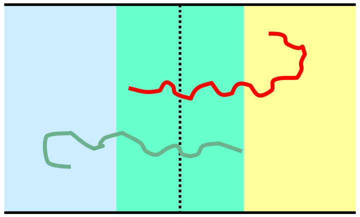
Source: Metten; Thesis 2002



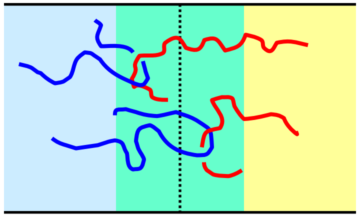
Principles of Adhesion

Source: Schuster, DIK

- 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

Principles of Adhesion

Source: Schuster, DIK

➡ The three principles of adhesion

- Contact
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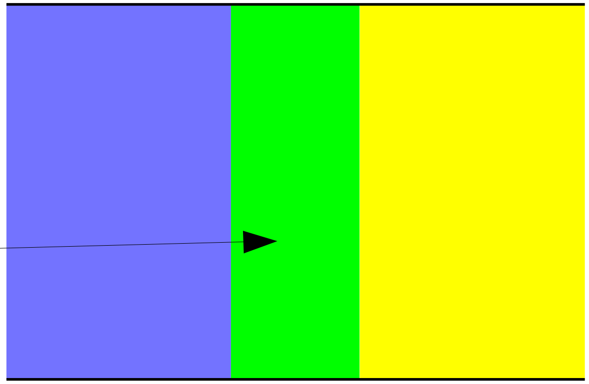


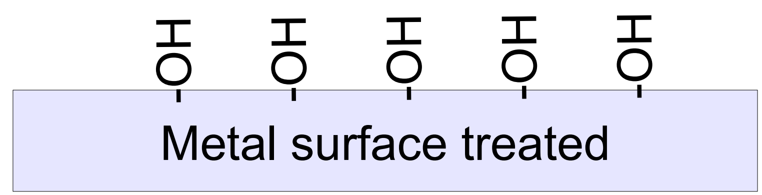
	Bond length [nm]	Bond energy [kJ/mol]
Chemical Bond		
Covalent	0,1 – 0,2	150 – 950
Molecular interactions		
Van der Waals forces	0,4 – 0,5	2 – 15
Hydrogen Bridges	0,2	20 – 30

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

Example 1: Rubber to metal

Source: DOW

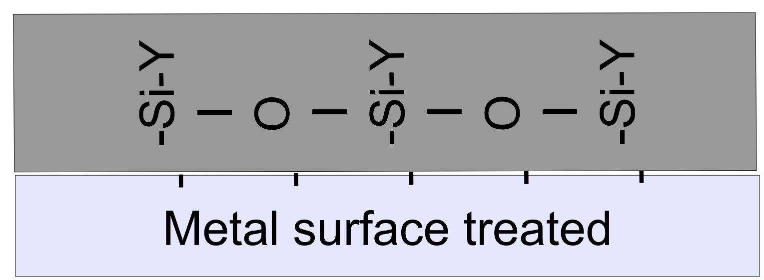
Surface Energy ~> 72 dyne/cm



Example 1: Rubber to metal

Source: DOW

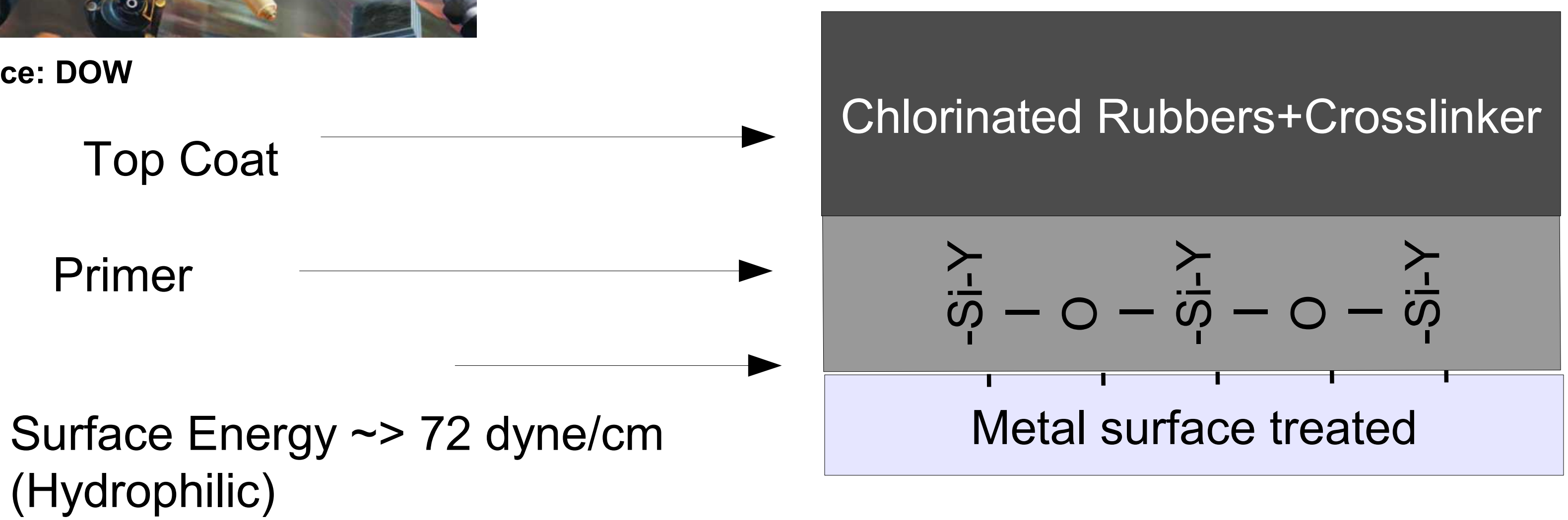
Primer



Surface Energy ~> 72 dyne/cm
(Hydrophilic)

Example 1: Rubber to metal

Source: DOW



Example 1: Rubber to metal

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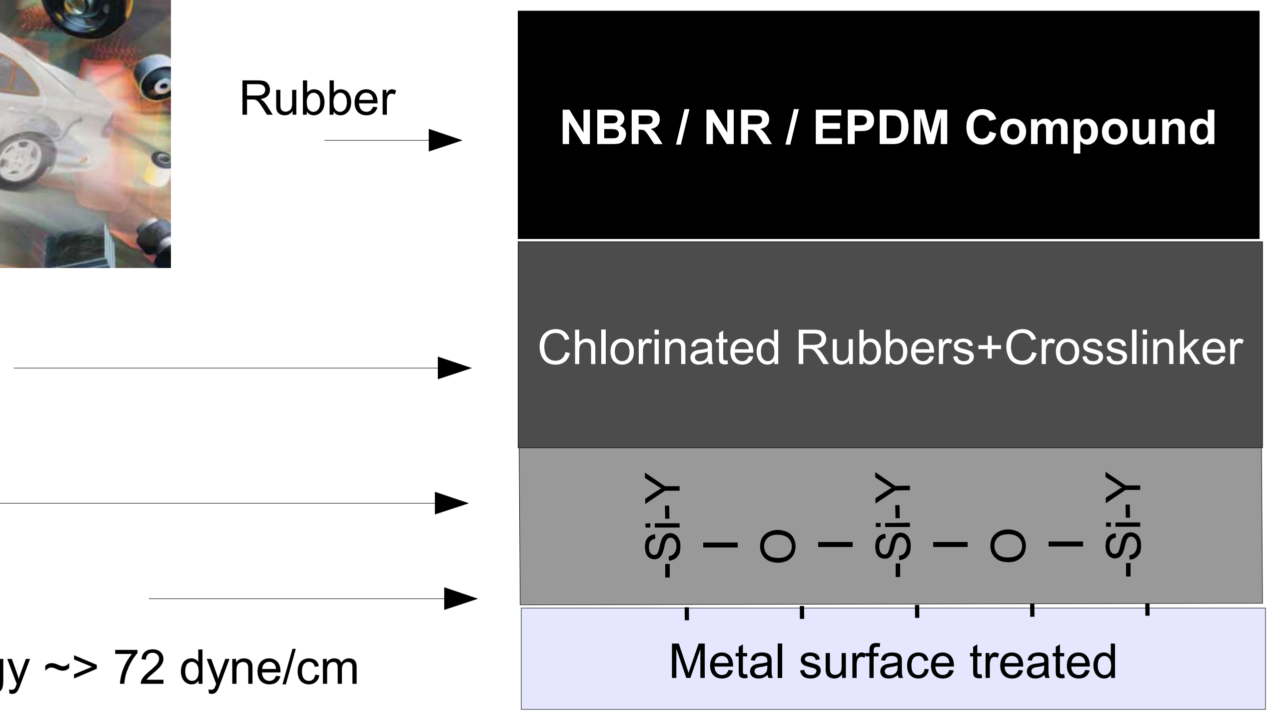


Example 1: Rubber to metal

Source: DOW

Rubber → **NBR / NR / EPDM Compound**

Top Coat → Chlorinated Rubbers+Crosslinker

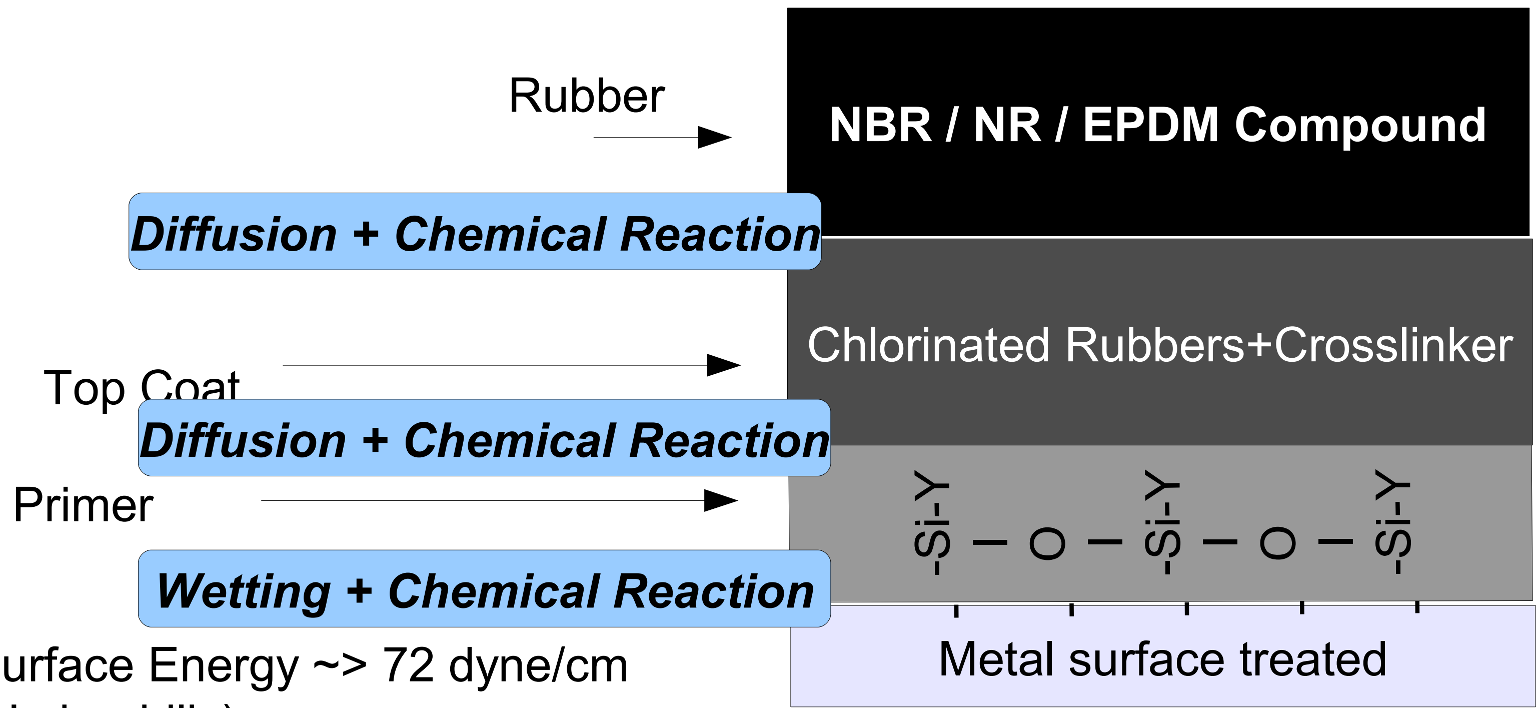
Primer → -Si-Y – O – -Si-Y – O – -Si-Y

→ Metal surface treated

Surface Energy ~> 72 dyne/cm
(Hydrophilic)

Example 1: Rubber to metal

What is the game?



Surface Energy ~> 72 dyne/cm
(Hydrophilic)

Example 1: Rubber to metal

Source: G.Polaski, et all, Lord Corp

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

Source: Bayer, Pergut broshure

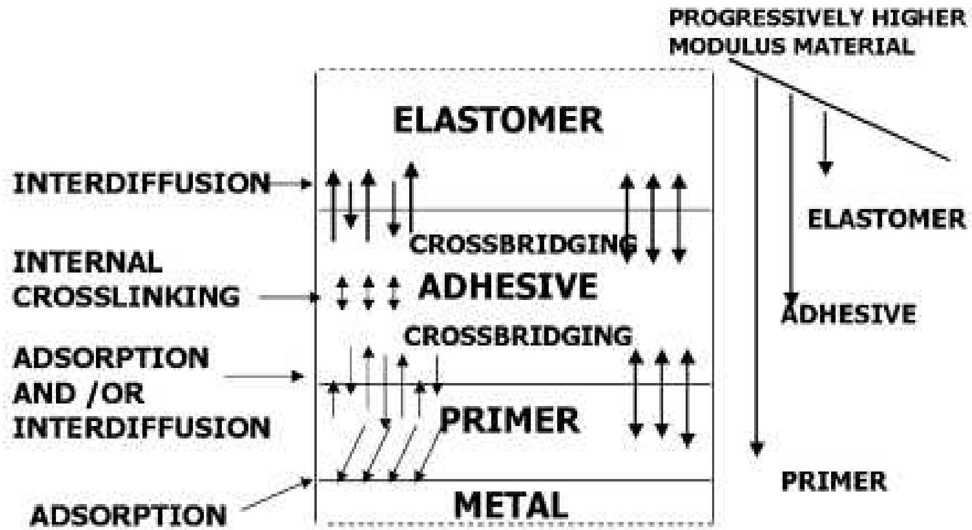
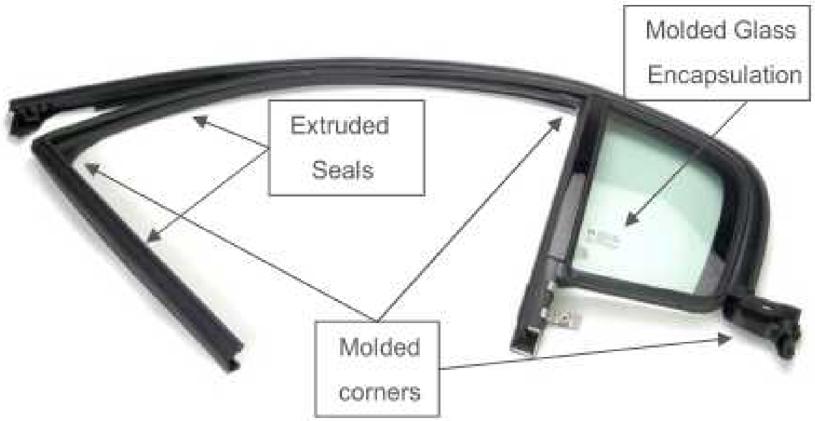
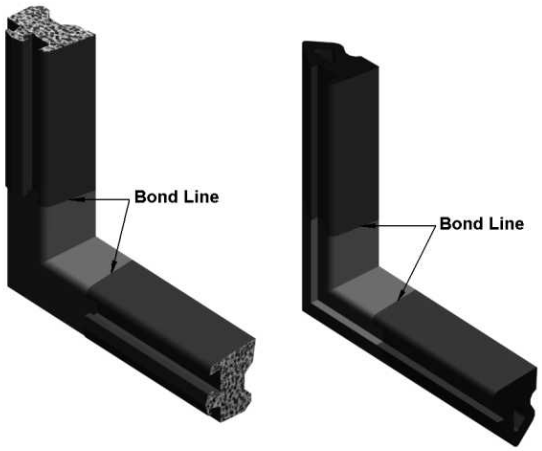


Figure 2

Interfacial dynamics of a rubber-to-metal bond

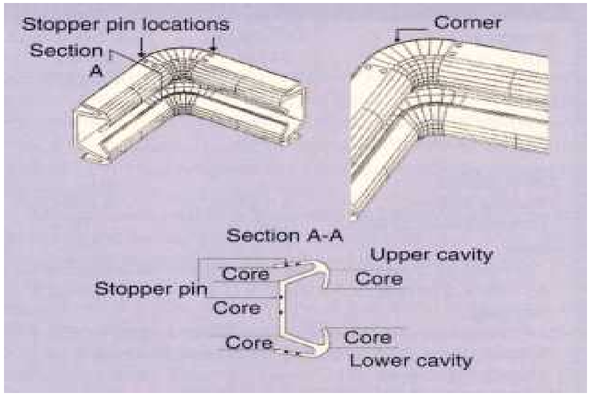
Example 2: Corner Moulding





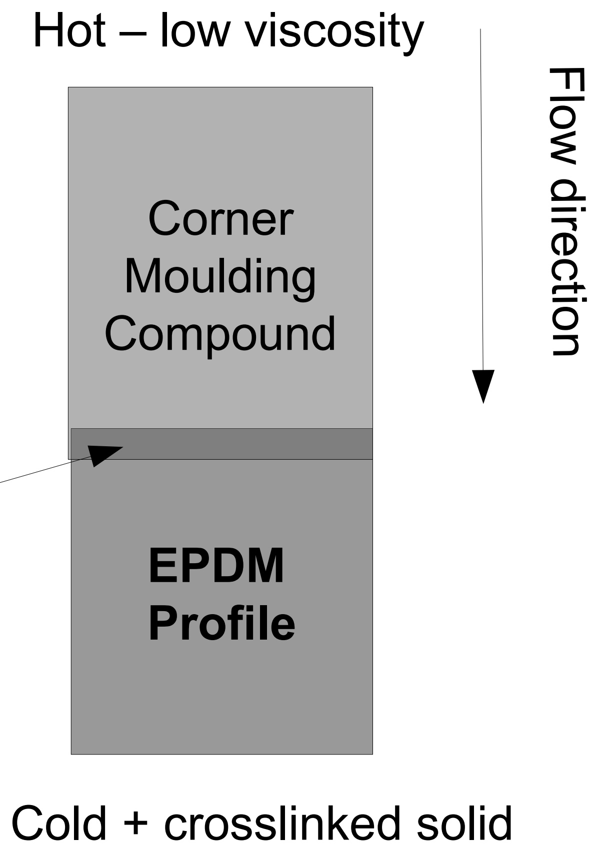
Source: Toyoda Gosei

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



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**

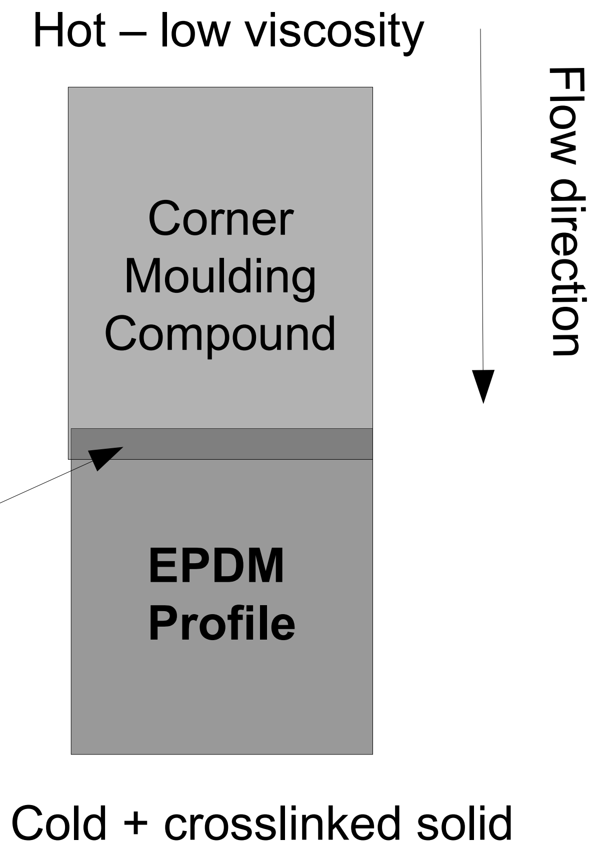


- **Diffusion**
  - **Reaction eventually possible**

Example 2: Corner Moulding

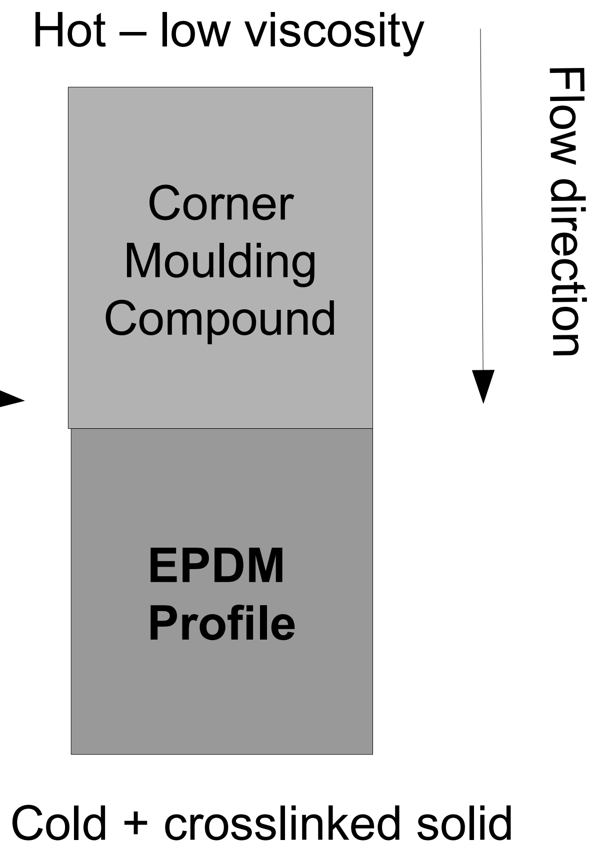
- **Injection of Corner Moulding Compound based on TPE-V**
  - **Injection conditions**
    - **Compound has ~ 200°C**
    - **Mold Temperature ~ 50°C**
    - **Thermal shrinkage result pressure, compensated with after pressure**
  - **Allow time to cool**

- **Some times called "Fusion Bonding"**
  - **Diffusion**
    - **Reaction eventually possible**



Example 2: Corner Moulding

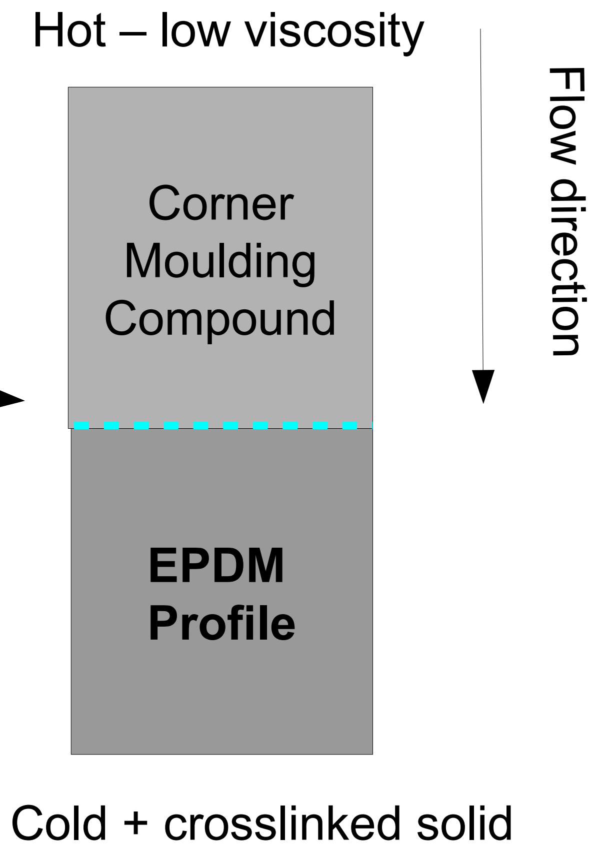
- **Injection of Corner Moulding Compound**
  - **And then no bond!**
  - **Condition: profile stored in plant for a couple of days**
- **No Diffusion**



- **What might hint the bonding?**

Example 2: Corner Moulding

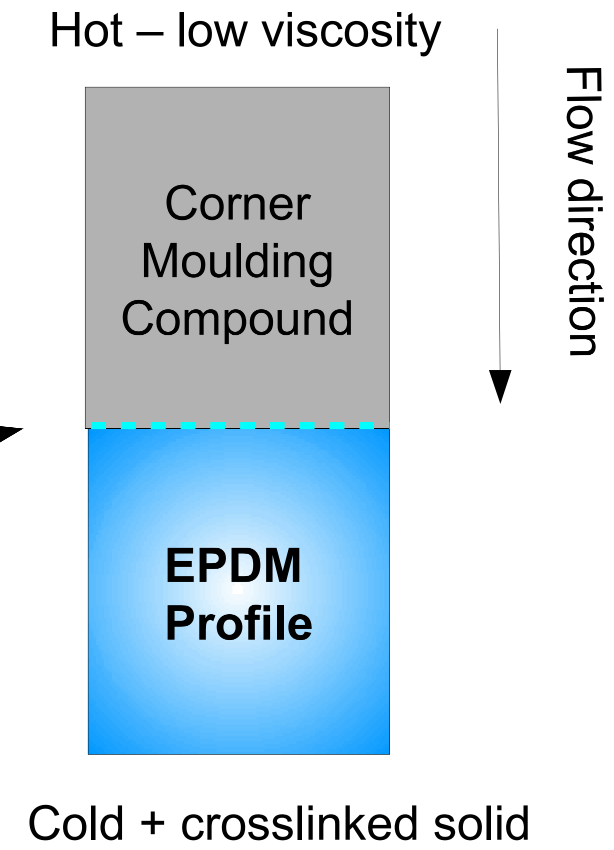
- **Injection of Corner Moulding Compound (EPDM or TPV)**
  - **And then no bond!**
  - **Condition: profile stored in plant for a couple of days**
  - **No Diffusion**
- **What might hint the bonding?**
  - **Water layer on surface**
  - **Water absorption change polarity**
    - **Drying with heat result oxidation!?**
    - **Plasma to remove water?**



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**



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**

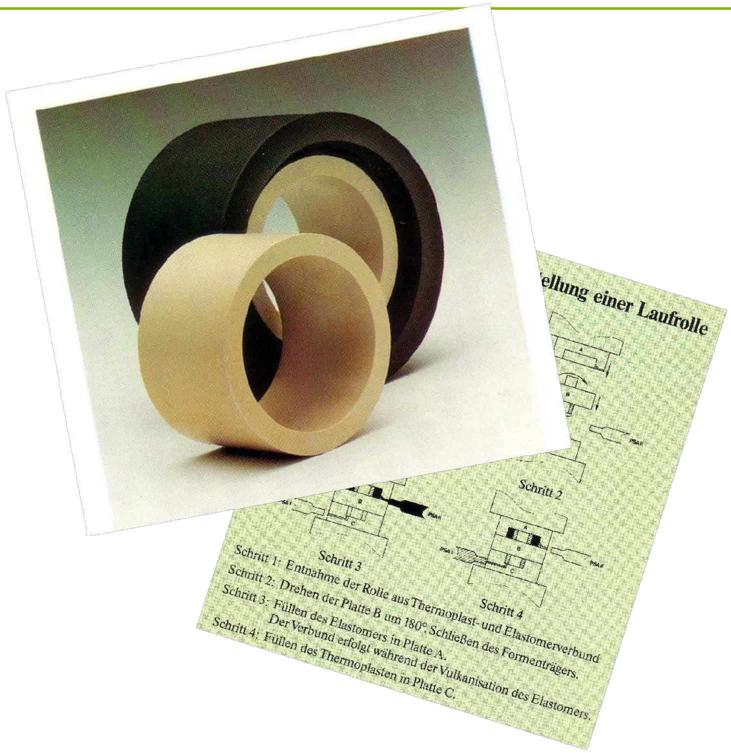
Source: Acheson/Henkel

In der Aufstellung fehlen die
Coulomb-Kräfte

Example 4: TP - Rubber

Source: Graf, DESMA

- **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**



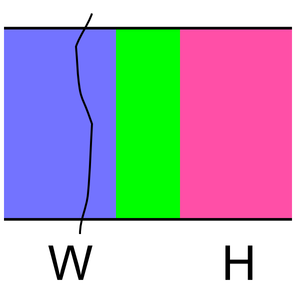
Example 4: TP-Rubber

Source: Schuster, DIK

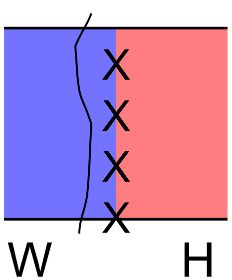
PPE-PS

Thermodynamically compatible blend
Interactions: 1) between aromatic rings
2) Styrene ether groups

H, W combine	Processing-compatibility	Creation boundary layer	Self adhesion	Crosslinking layer
1 PPE - SBR	+	+	+	-
2 PPE - SBR/NR	+	+	+	-
3 PPE - SBR/NBR	+	+	+	-
4 PPE - SBR/EPDM	+	+	+	-
5 PPE - EPDM	no-one	very low	no-one	Peroxide



Cohesive rips through physical or chemical phase connection



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
TP - Rubber

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

- Environmental influences
- Bleaching / Blooming of Ingredients
- Incompatibility
- Contamination

Summary / Conclusion

➨ **Rubber adheres with cohesive failure and high forces, if at least we have**

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

- **It can have adhesion, it there is only contact, but the forces remain low**