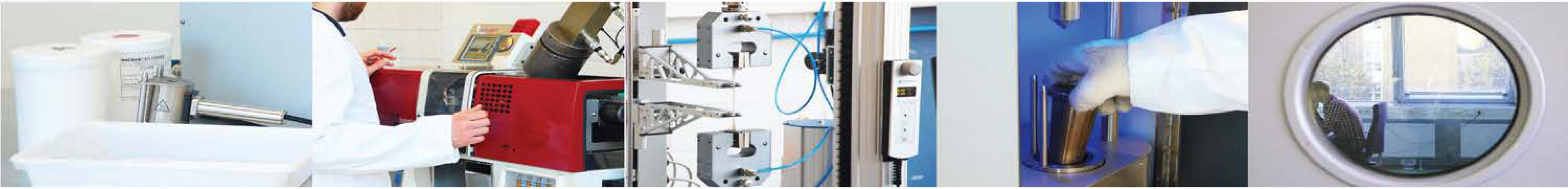

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2017

THE ADHESION OF LSR AND POLYPROPYLENE TYPES AFTER STORAGE

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University of Kassel, Institute of Material Engineering

Content

- Objectives
- Properties LSR-TP-Composite Materials
- Adhesion
- Experimental
- Results and Discussion

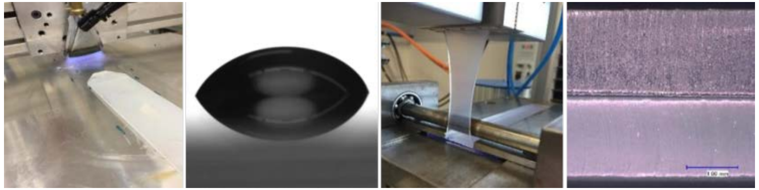
Objectives

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

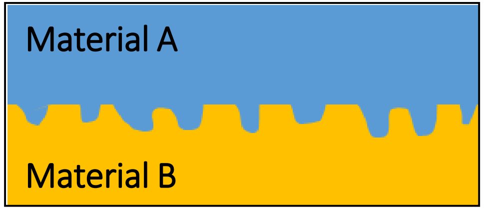
- hard-soft composites of thermoplastic and LSR
- sample production by multi-component injection molding

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



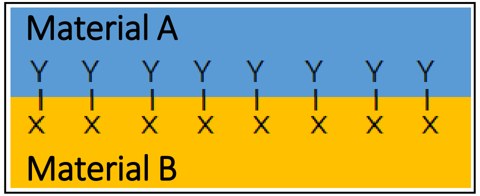
Mechanical adhesion by surface texture by

- Surface roughness
- Hollows
- Pores

Specific Adhesion

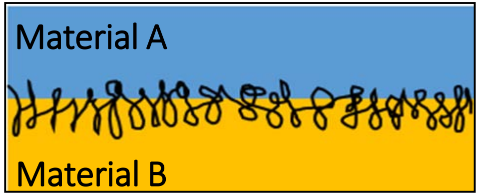
Chemiesorption

Chemical primary valency bonds (covalent, ionian, metal)



Diffusion Theory

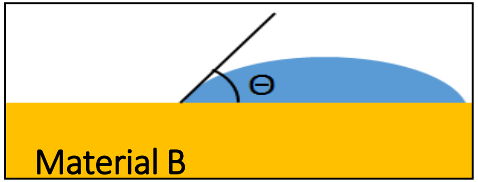
Diffusion of the molecular chains into the other component



Adsorption Theory

Formation of secondary valence bonds

→ *good wettability necessary*

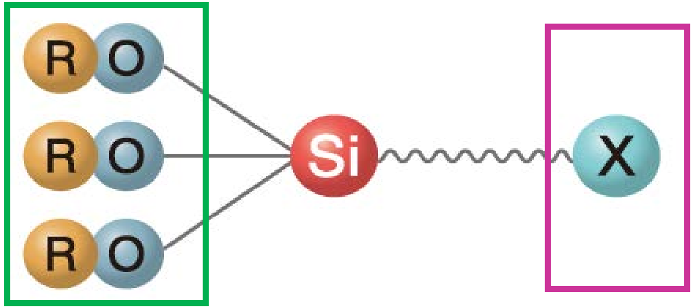


Silane Coupling Agent

Generation of Adhesion between LSR-TP: Selfbonding LSR → compatible for PA and PBT

Reactive groups
→ form chemical bond with inorganic material (silicone, glass, metal)

- Methoxy groups
- Ethoxy groups
- .....



Reactive groups
→ form chemical bond with organic material (thermoplastics)

- Vinyl grups
- Epoxy groups
- Amino groups
- .....

→ connection of epoxy groups with functional groups of activated PP

→ connection of methoxy-functionalized silane group with the LSR

Ref.: Baumgart, C. et al.: Hitzebeständige 2K-Verbunde, Kunststoffe (2014)10, 134-137
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

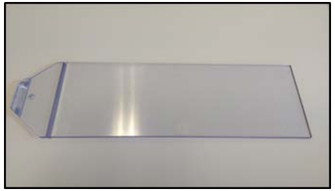
Polypropylene:

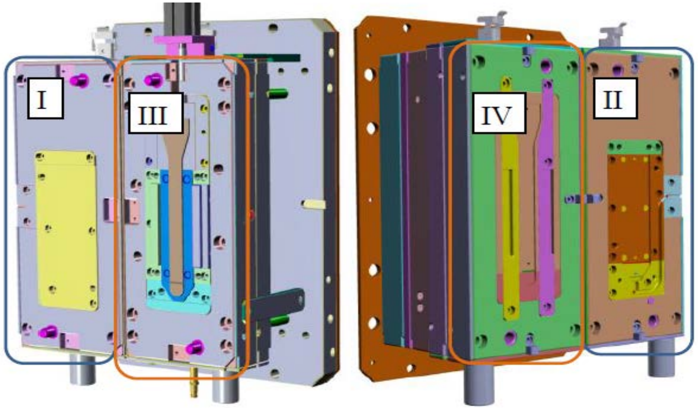
Material	Brand Name	Company	Properties
Polypropylene	PP Sabic 575P	Sabic	Suitable for food contact application, toys and houseware articles
	PP Purell HP571P	LyondellBasell	Medical devices
	Altech PP-HA A 2020/100 GF 20	Albis Plastic	Glass-fiber reinforced PP, applications in furniture industry

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

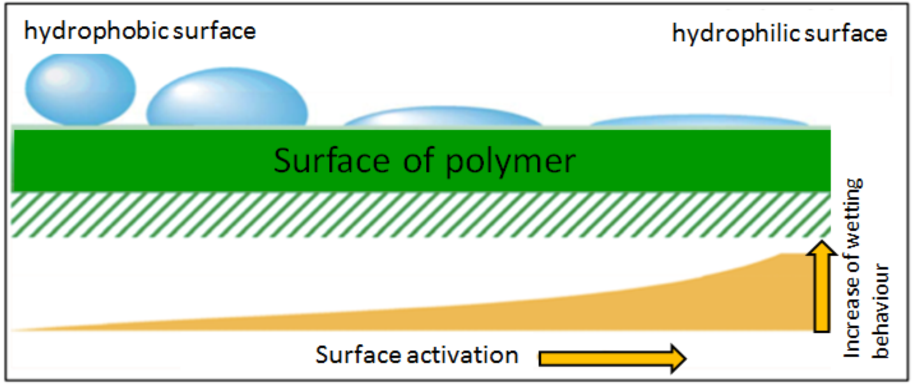
III & IV: for LSR component

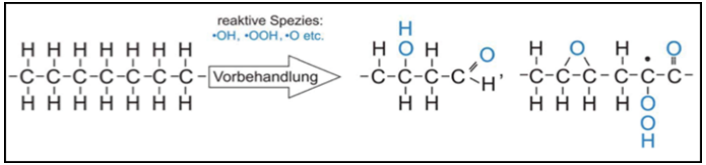
IV is changable

Experimental

Surface activation

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





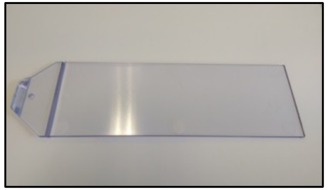
due to surface activation
→ functional groups for interactions
→ allow hydrogen bonds for adhesion

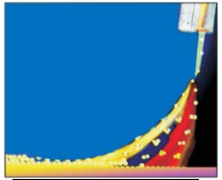
Experimental

Surface activation by flame treatment (silicatization)

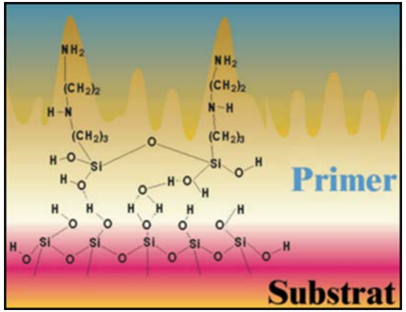
- Flame pyrolytic deposition of amorphous silicate
- Layer thickness 20-40nm
- Precursor (silicon-containing substances)
- Formation of Si-OH groups

  → Connection of functional groups (e.g. amino groups) to increase the adhesion
- Formation of a very thin, chemically highly reactive layer (glass layer)





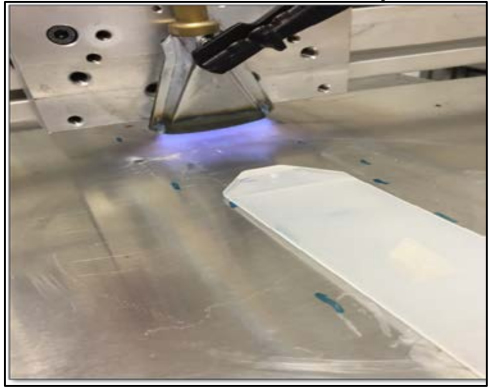
silicatization

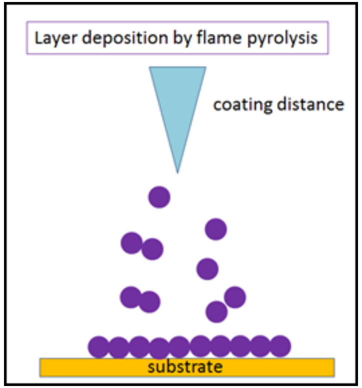


Reference: SURA Instruments GmbH: Produktinformationen – Pyrosil®-Verfahren, 09/2004

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

Reference: SURA Instruments GmbH: Produktinformationen – Pyrosil®-Verfahren, 09/2004

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

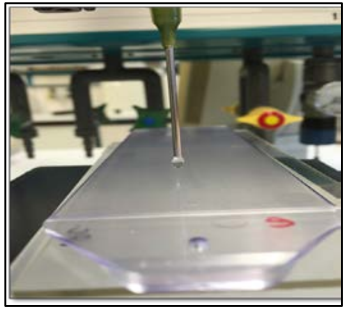
No activation	0 days	1 day	7 days	14 days	28 days

After surface activation → overmolding with LSR and storage of compound

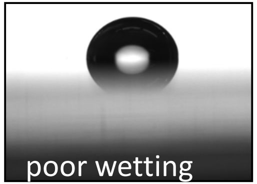
No activation	0 days	1 day	7 days	14 days	28 days

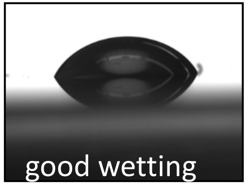
Experimental

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

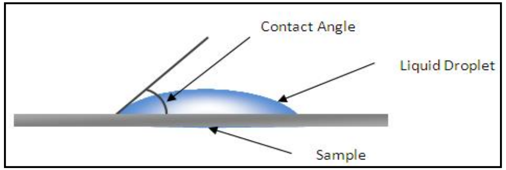


→



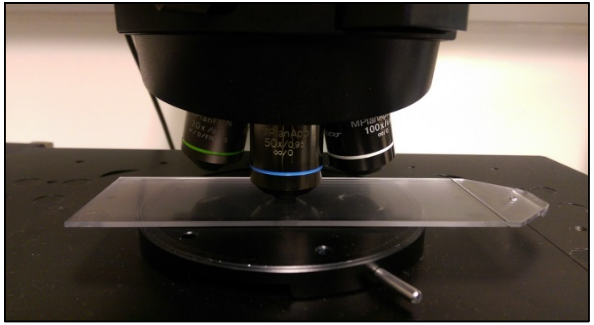


→ a drop of water is applied on the PP surface
→ measurement of contact angle
→4 samples and 3 drops every batch were measured

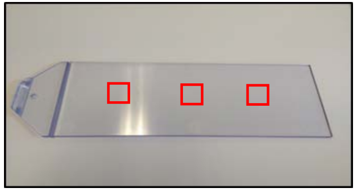


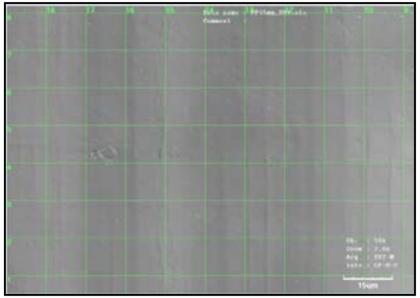
Experimental

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



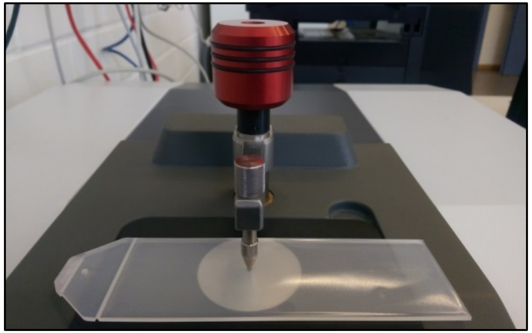
- Scanning of the sample by focusing laser
- Investigation of stored and direct activated samples
- No sample preparation needed
- Magnification: 500x
- 3 samples per batch



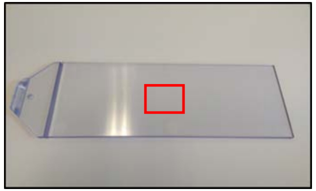


Experimental

FTIR Spectroscopy (Schimadzu, IRAffinity -1S) → Chemical Bonds



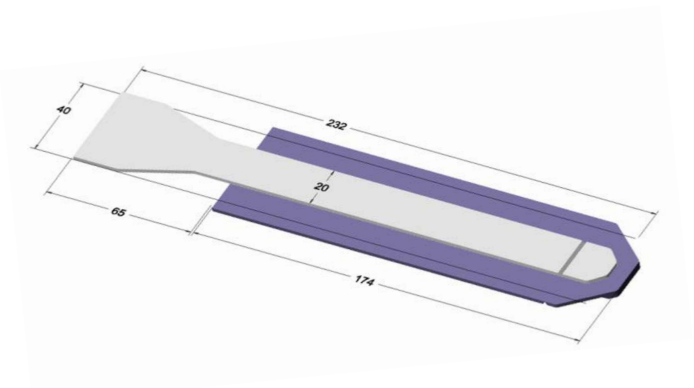
- Investigation of stored and direct activated samples
- Examination by Attenuated Total Reflection (ATR)
- Total reflection at the boundary between two optically different media (crystal and specimen)
- Crystal: Zinc selenide (ZnSe, 45°)



Ref.: http://www.inspect-online.com/topstories/automation/3d-oberflaechenanalyse-mit-uv-laser-mikroskopie

Experimental

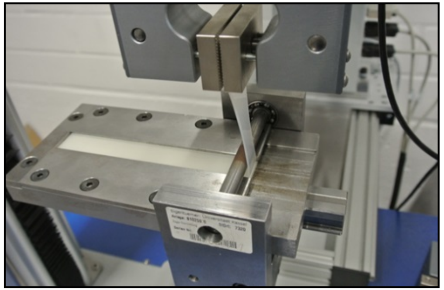
After Storage → Overmoulding of TP with selfbonding LSR

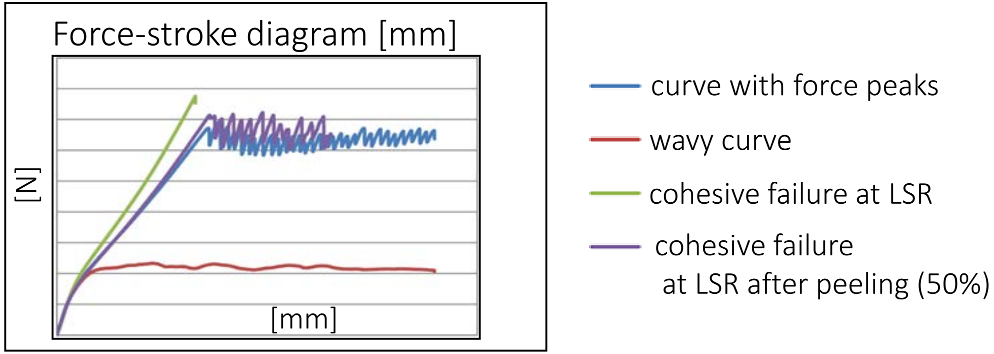


- PP was inserted into the machine by hand → overmolding with LSR
- Temperature of 140°C for 60s during injection molding process for both components

Experimental

Peel-Test according to VDI 2019 (Hegewald & Peschke, 5kN, testing speed: 100mm/min.)





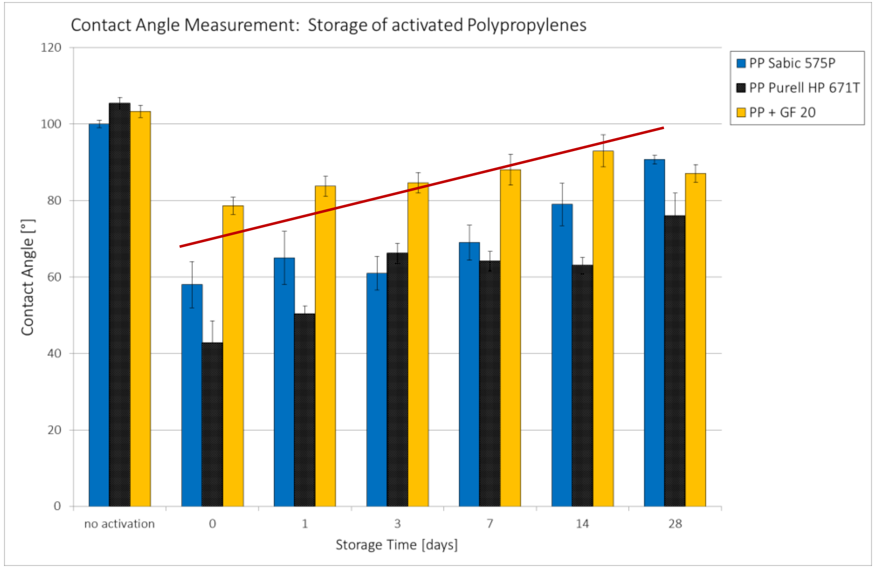
A: peeling of the LSR component without residue (adhesive peeling)

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

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

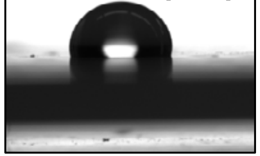
D: no peeling of the LSR component → cohesion crack (Ws max)

Results and Discussion

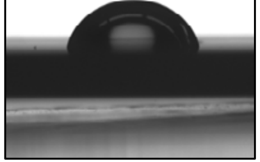


Contact Angle after silicatization

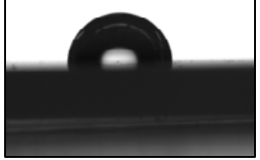
no activation [100°]



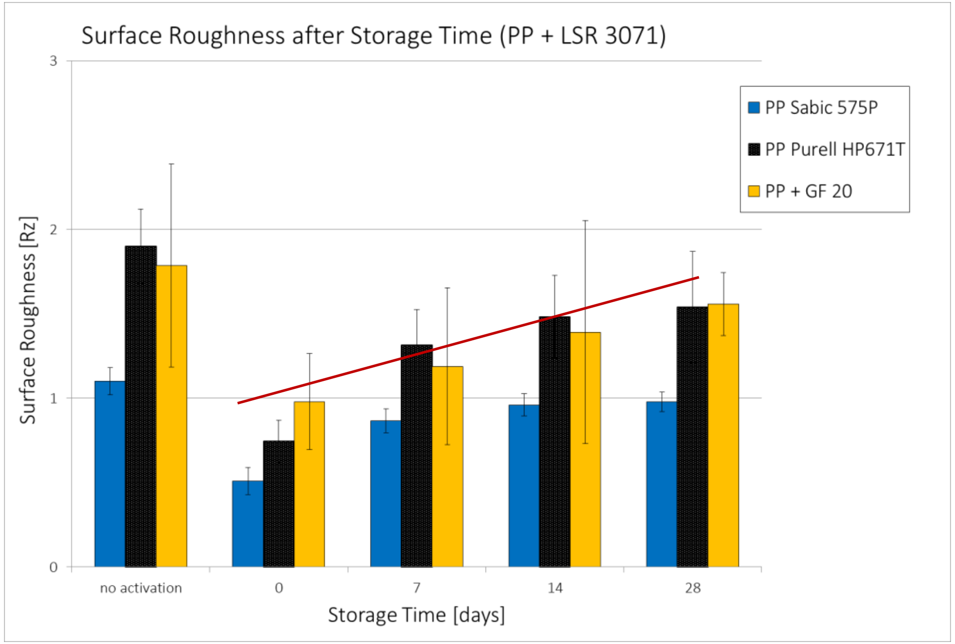
direct [58°]



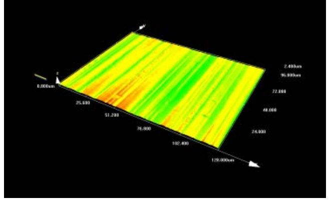
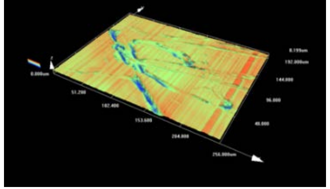
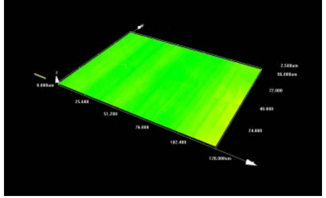
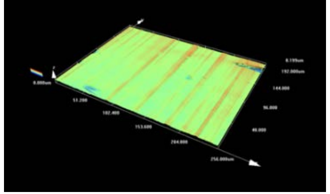
28 days stored [93°]



- 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



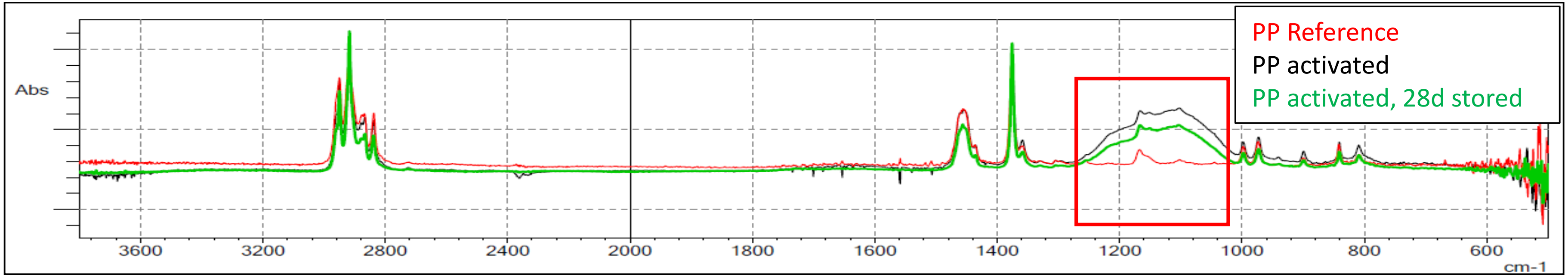
Confocal Laser Scanning Microscopy

PP Sabic 575P	PP + 20% GF
Without activation [Rz: 1]	Without activation [Rz: 1,8]
	
With activation [Rz: 0,51]	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

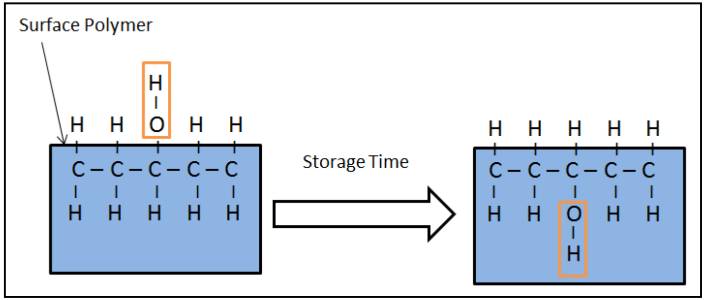


Significant changes after silicatization visible

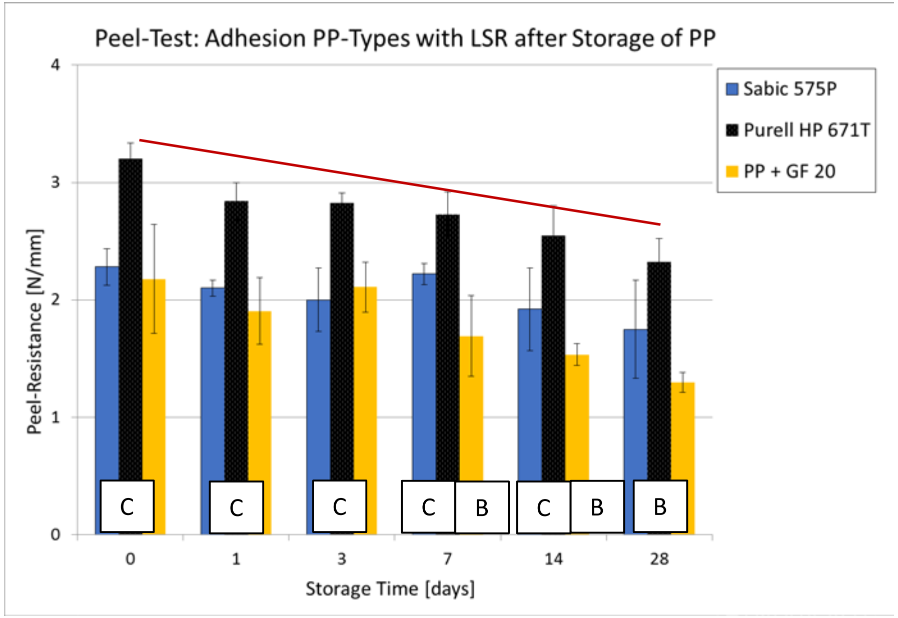
→ Formation of silicon bonds (Si-O-Si, area 1090-1030)

→ Si-NH_2 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

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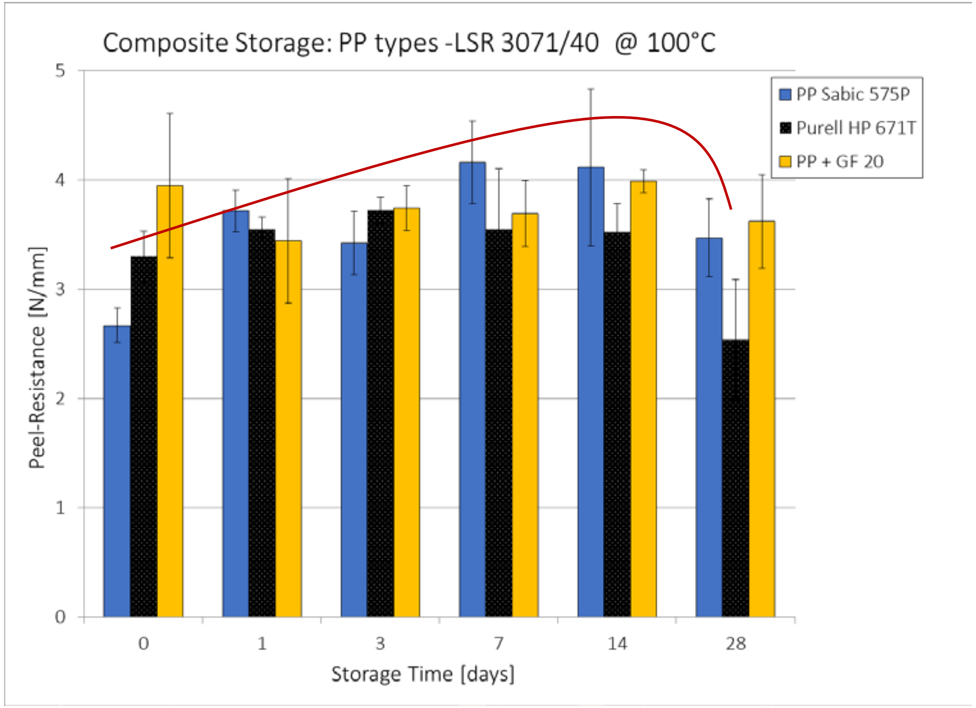
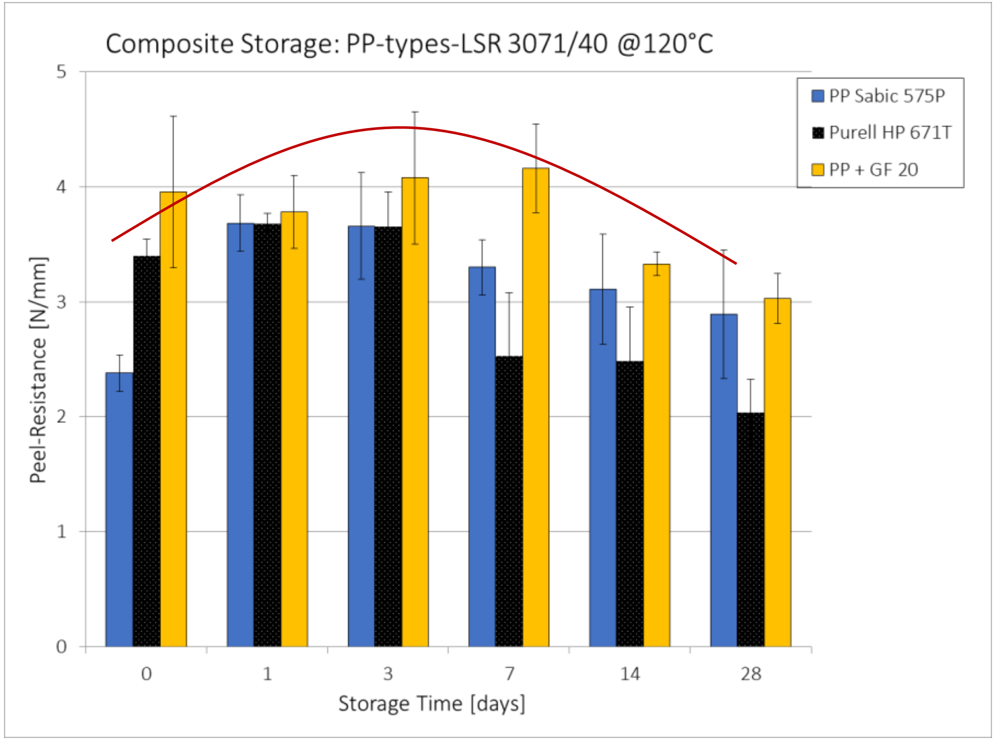


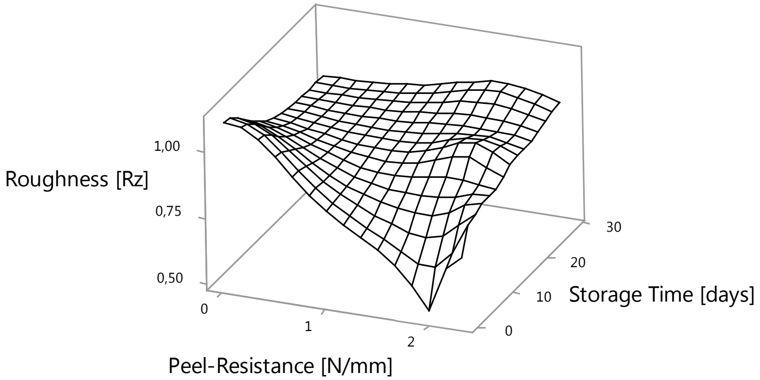
- No adhesion without surface activation
- Increase of the values up to 7 days
- Increase of the values by post-crosslinking of the silicone component and possibly an interdiffusion due to temperature storage
- Reduction of the values after 2 weeks → post-crystallisation of the PP component and the resulting embrittlement

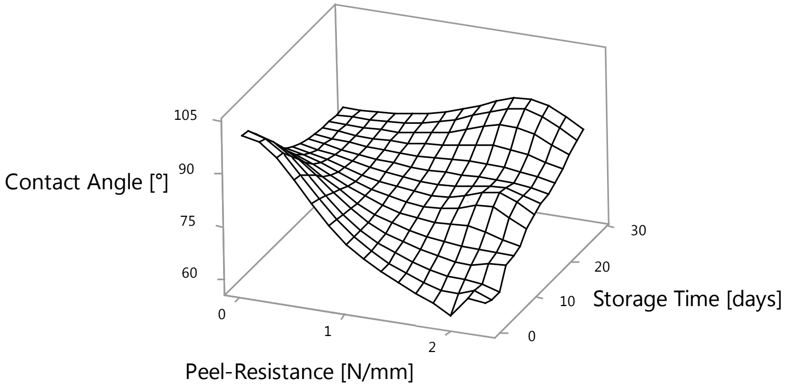


- No adhesion without surface activation
- Increase of the values up to 3 days
- In comparison with 100°C composite storage → faster reduction of the peel-resistance from 7 days up to 28 days
- Post-crystallisation leads to embrittlement in the material → less adhesion after storage time

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

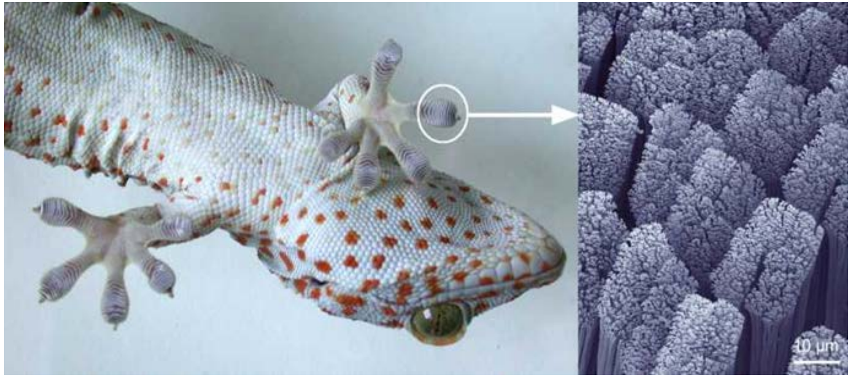
Conclusion

- 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

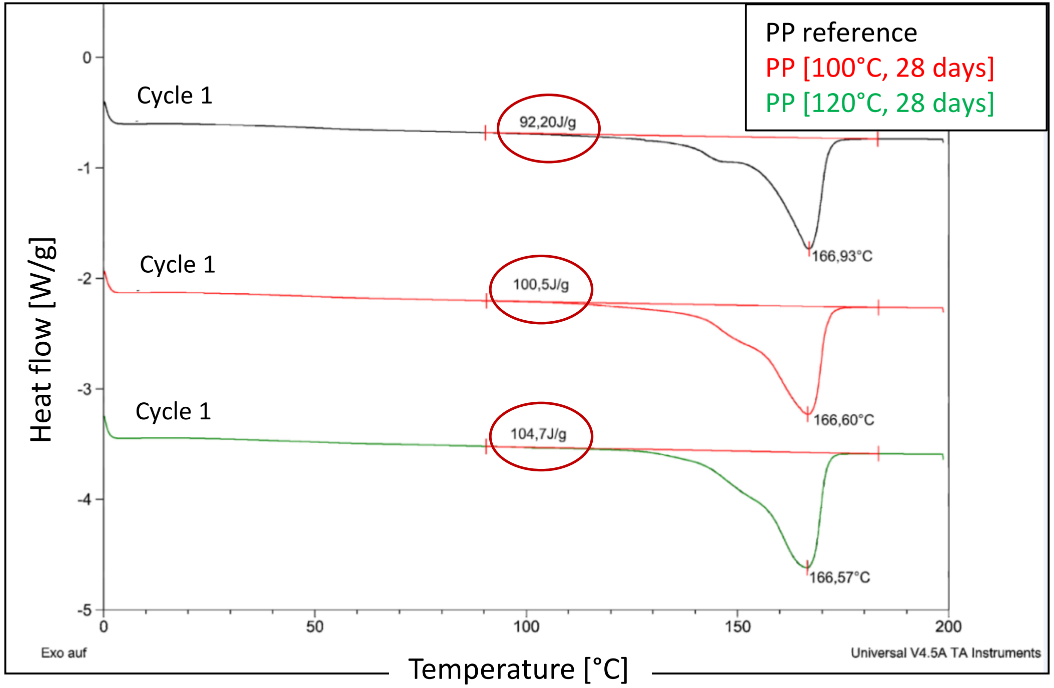
Ref.: http://jacobs.physik.uni-saarland.de/forschung/gecko.htm

Back Up

Overview of Silicone Rubber

- Silicone Rubber
  - **H**igh **T**emperature **V**ulcanized (HTV)
    - **H**igh-**C**onsistency **R**ubbers (HCR)
      - 1-c peroxide cured
      - 2-c addition cured
    - **L**iquid **S**ilicone **R**ubber (LSR)
      - 2-c addition cured
  - **R**oom **T**emperature **V**ulcanized (RTV)
    - single- component (1-c)
      - 1-c condensation cured
    - dual- component (2-c)
      - 2-c conden-sation 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