Influence of silicone elastomer recyclate on the processing with silicone rubber and resulting mechanical properties

UNIpace
Polymer Application Center

Timo Hofmann, R.-U. Giesen, H.-P. Heim
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Short introduction Unipace

- Founded in 2013 as Polymer Application Centre by B BRAUN SHARING EXPERTISE UNIKASSEL VERSITÄT
- Integrated in the subject area of plastics technology (Prof. Heim)
- Link between university and industry
- Research & development in the field of silicone processing
- Selection of research areas

Thermoplastic – LSR Injection moulding

Compounding and extrusion of high consistency silicone rubber (HCR)

Materials testing of elastomers

- Currently 9 employees (4 scientific, 2 technical, 3 student assistants)
- Turnover approx. 1.1 million € (public funding/industry 60%/ 40%)

Why recycling?

- Increasing regulation from the European Union
  - EU Packaging Directive - 55 percent of plastic packaging must be recycled from 2030
  - EU Single-Use Plastics Directive - some single-use products have been banned in the EU since 2021
  - Action plan for the circular economy - for electronics, batteries, vehicles, plastics, textiles....

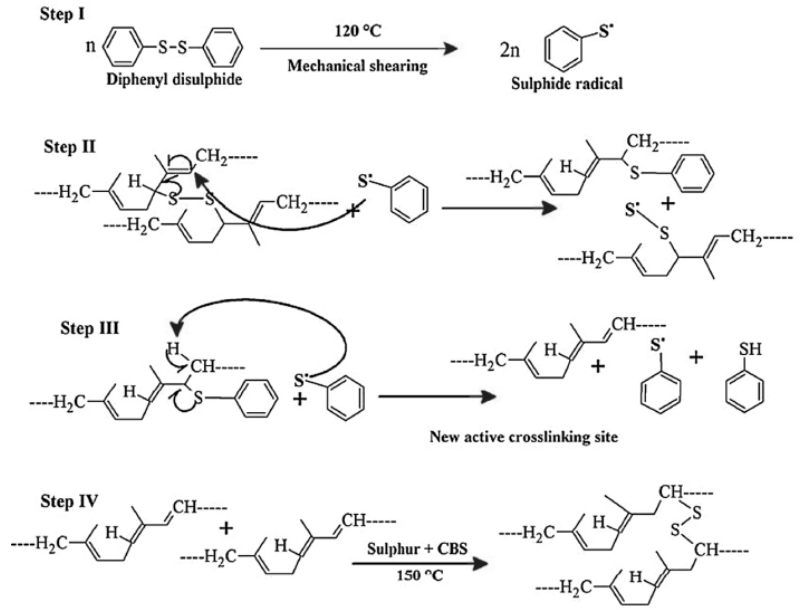
- Specification by end customer/government order
  - Increasing environmental awareness among end customers
  - Recycling necessary to fulfill the CO^2 balance

- Until now no industrial use of the recycling processes

Possibilities of recycling I

- Mechanical recycling of rubber
  - Grinding of the waste (crygonic, wet)
  - Producesses filler material

- Chemical recycling of rubber
  - Devulcanisation of the crosslinked rubber
  - Generally combined with thermal or mechanical energy to speed up the process
  - Using chemical agents that breaks the carbon- sulfur or sulfur- sulfur bonds

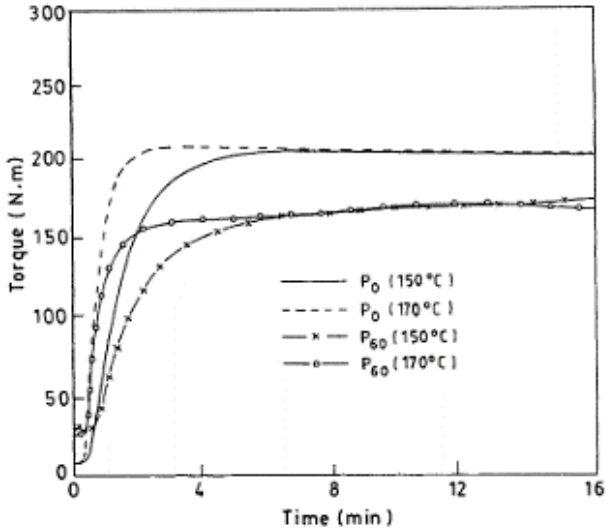


[1]

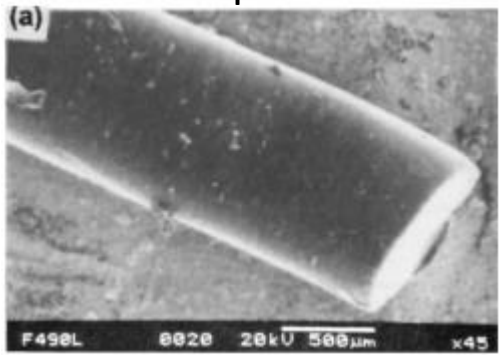
- Some more ultrasonic, ultrawave method….

Possibilities of recycling II

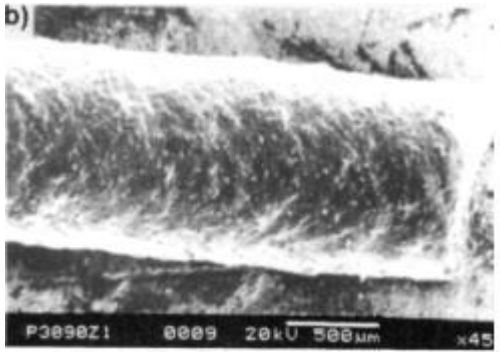
- Mechanical recycling of silicone rubber
  - Crushing and grinding the vulcanized rubber
- Previous findings from research
  - Adding the recyclate increases the viscosity
  - The addition of recyclat changes the cross-linking speed
  - Change in the surface morphology of extruded profiles



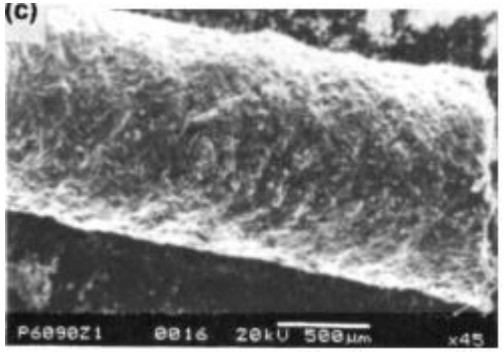
0 phr



30 phr



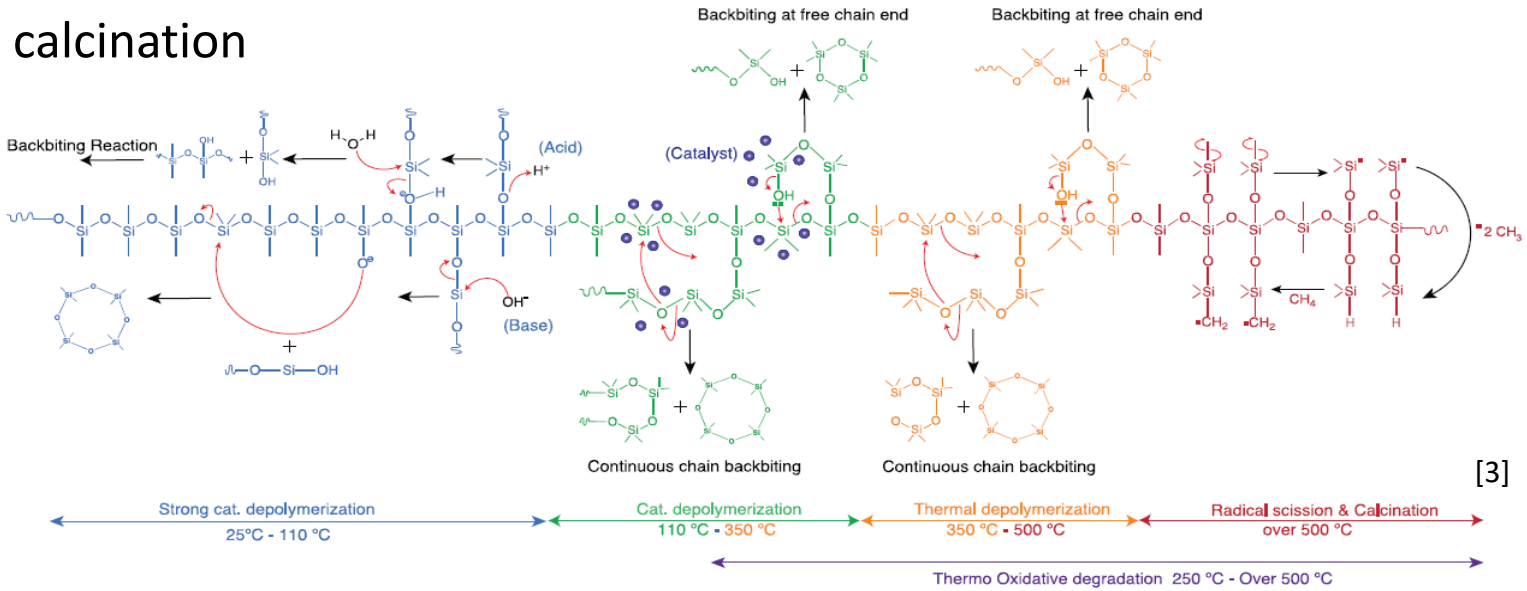
60 phr



[2]

Possibilities of recycling III

- Subdivision of chemical recycling into 4 areas
  - Catalytic controlled depolymerization by strong acids or bases
  - Use of nucleophiles or electrophiles with catalysts
  - Thermal depolymerization
  - Radicals cause cleavage and calcination



[3]

- Current fields of reasearch
  - Recycling with tetramethylammoniumhydroxid (Japan) [4]
  - Fluoride-Catalyzed Depolymerization (USA) [5]

Current issues in the context of recycling

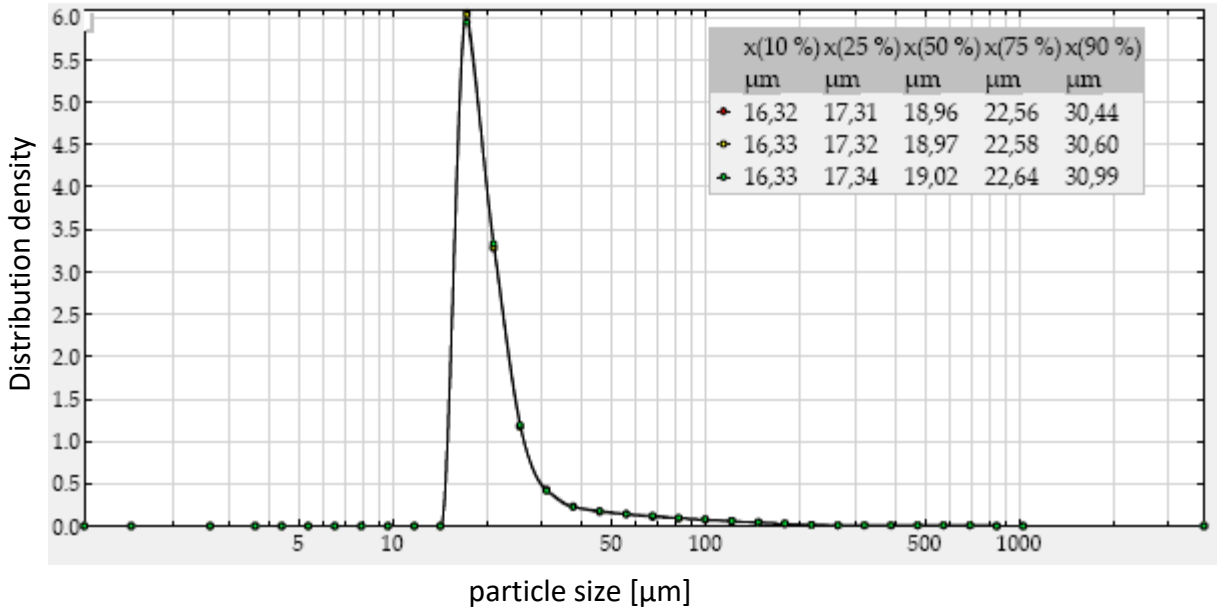
- How do the decomposition products of chemical blowing agents behave when using the recyclate is used
  - Very important for the use of addition curing systems (interesseting point for chemical and mechanical recycling)
- What influence has the recycling content on the mechanical properties of our endproduct
  - High impact of the used recyclat (Shore Hardness and fillers, particle size, post curing)
- What filler contents can be processed with the usual processing methods?
  - Limitation of the component thickness by the recyclat size with extrusions tools
  - Does the sprue have to be adjusted for injection molds due to the recyclate?

→ How would a cycle economy look like in this field?

Focus at mechanical recycling at UNIpace I

- Procedure of the mechanical recycling: crushing and grinding of silicone elastomers with an external service provider
- Achieving very small grain sizes

HCR, LSR, RTV…



Focus at mechanical recycling at UNIpace II

- Cutting mill at Unipace
  - Goliath Plus from Digicolor
  - Sizes from 4 mm to approx. 0.5 mm depending on the sieve used

- Industrial grinding with a mill
  - Use of disk mills or turntable mills
  - Use of different screening systems to achieve the desired quality

Source: Pallmann

Processing & testing of the HCR with recyclat content

Compounding

Mixing of HCR 401-40 with 1,5 phr Crosslinker and recyclat content

Crosslinker

HCR

Recyclat

Processing

Extrusion

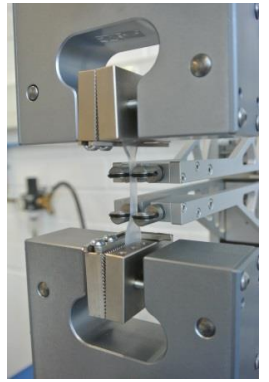
Temperature IRUnit : 500 & 600°C
Speed of the screw: 10 & 15 [u/min]

Press

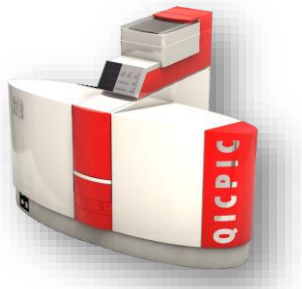
Processing:
170°C for 10 min
Tempering:
200°C for 4h

Analysing & testing

Shore Hardness



Tensile test



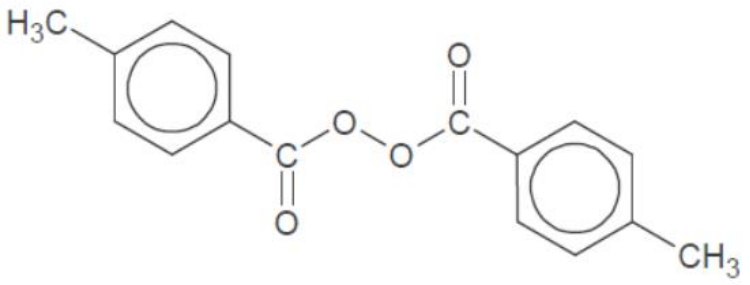
Particle size distribution

Used materials for extrusion

- Base rubber was a Wacker 401-40 S
  - Good flexibility, high transparence and mechanical properties
- Crosslinker Pergan Peroxan PMB Paste 50 SI
  - Di-(4-methylbenzoyl)-peroxide
  - Peroxide content approx. 50%
  - Crosslinking temperature (t90): 110°C

Used compounds for the extrusion

Base rubber	Amount of crosslinker [phr]	Recyclat content [phr]
401-40	1,5	0
401-40	1,5	10
401-40	1,5	30
401-40	1,5	50



Structural formula of Di-(4-methylbenzoyl)-peroxide

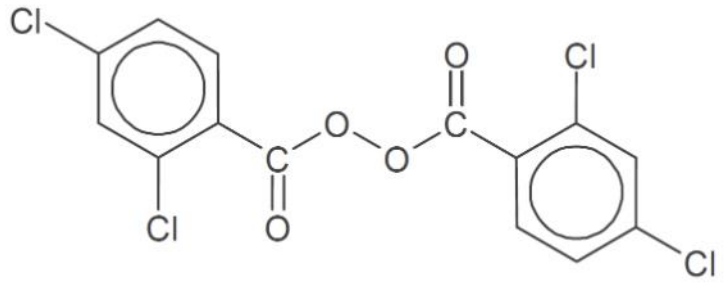
Source: Pergan

Used materials for press

- Base rubber was a Wacker 401-40 S
  - Good flexibility, high transparence and mechanical properties
- Crosslinker Pergan Peroxan BD Paste 50 SI
  - Di-(2,4-dichlorobenzoyl)-peroxides
  - Peroxide content approx. 50%
  - Crosslinking temperature (t90): 90°C

Used compounds for the press

Base rubber	Amount of crosslinker [phr]	Recyclat content [phr]
401-40	1,5	0
401-40	1,5	10
401-40	1,5	20
401-40	1,5	30

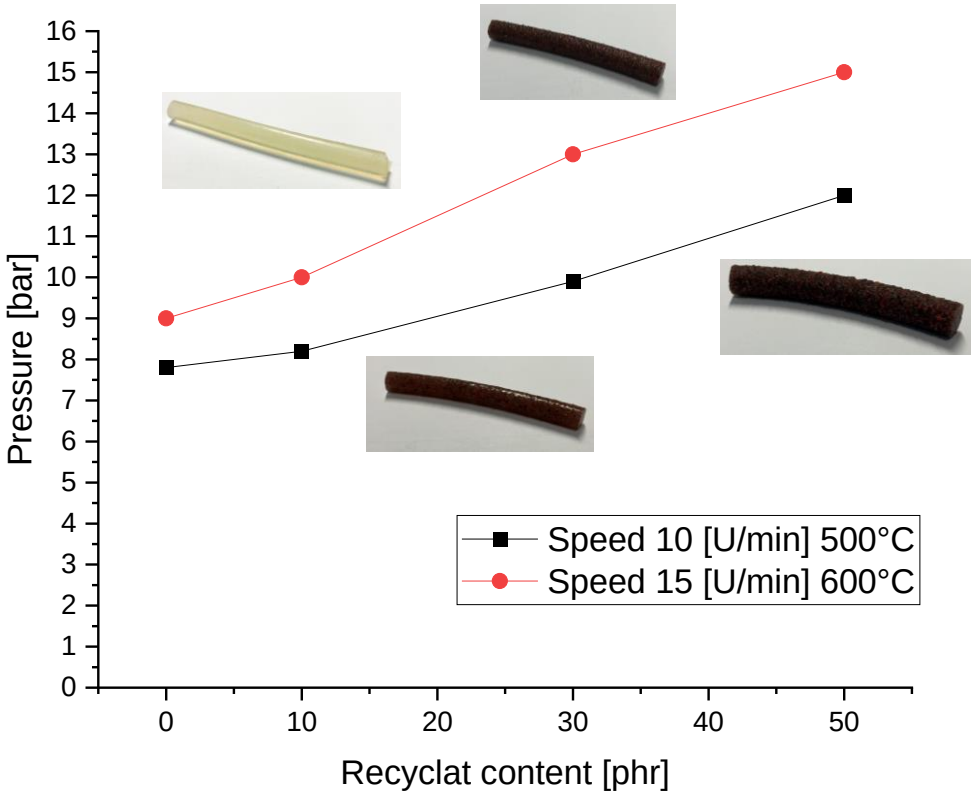


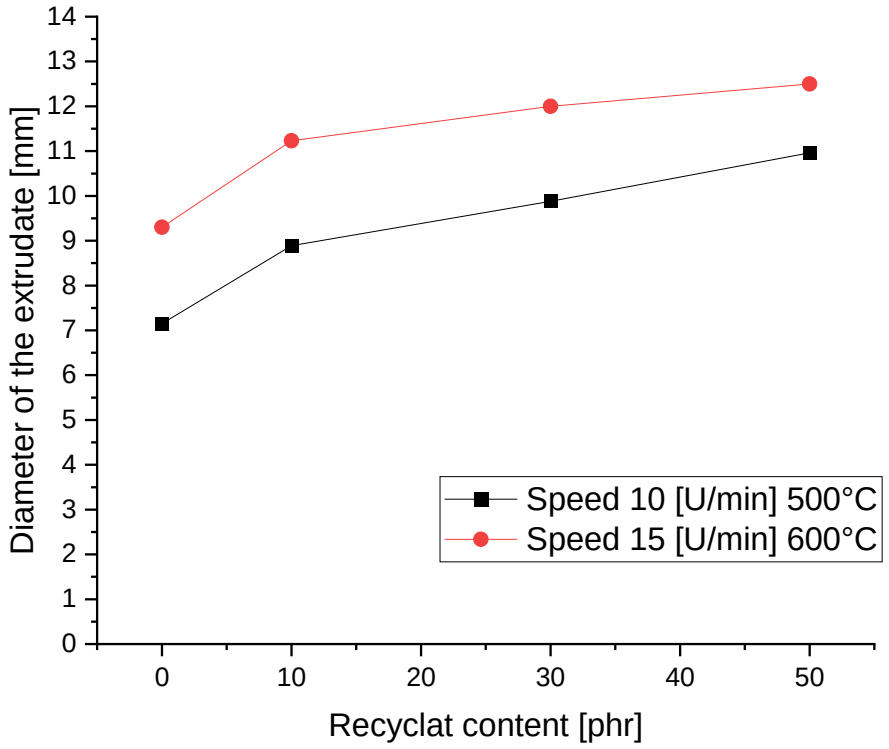
Structural formula of Di-(2,4-dichlorobenzoyl)-peroxide

Source: Pergan

Influence of the recyclat content by the extrusion of HCR

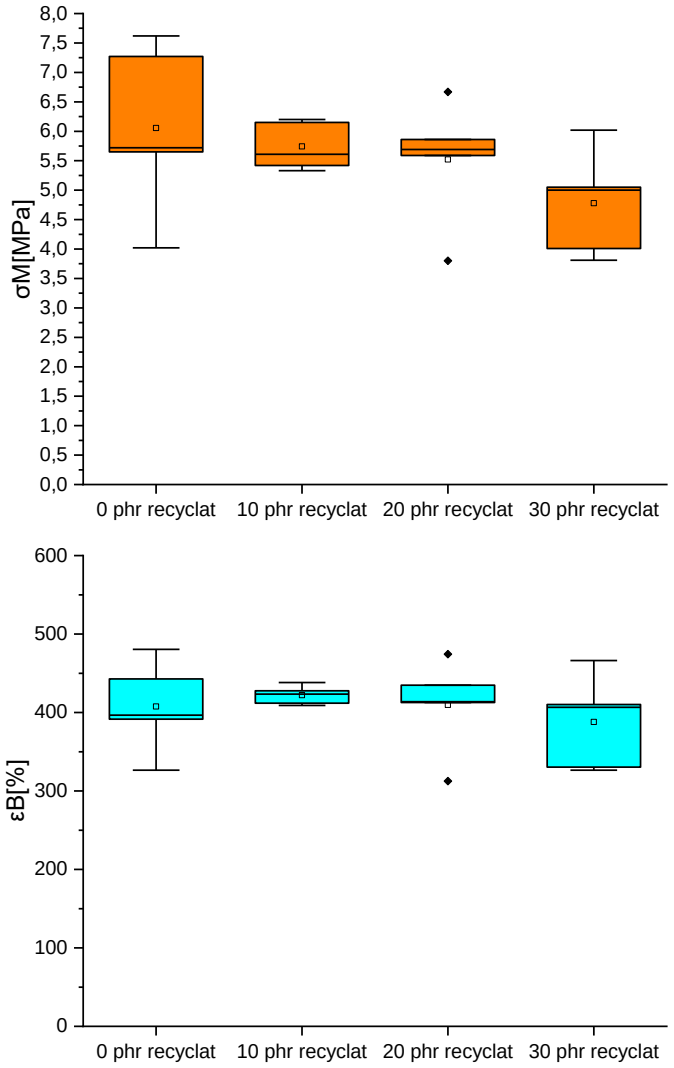
- Extrusion at two speeds and temperatures with different recyclate contents
- Significant influence of the recyclat content on the melt pressure in the extruder
- Increase of the extrudat diameter with rising recyclat content





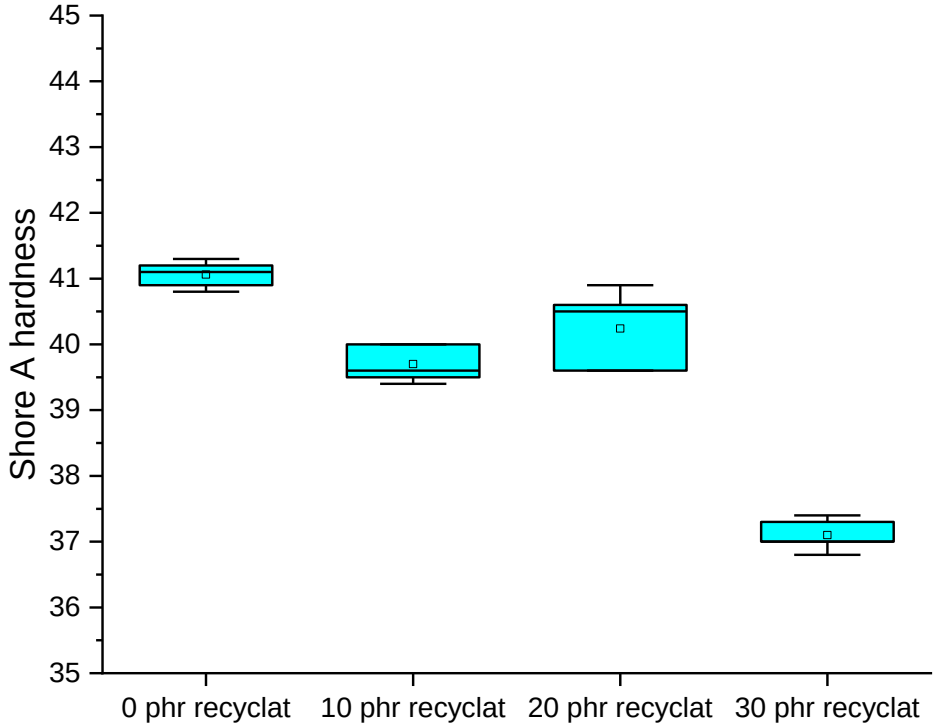
Influence of the recyclat content on testet pressed plates I

- Tensile test
  - a decrease in the maximum force with increasing recyclate content can be seen in the tension
  - Low influence of the recyclate on the elongation at break independent of the recyclate content



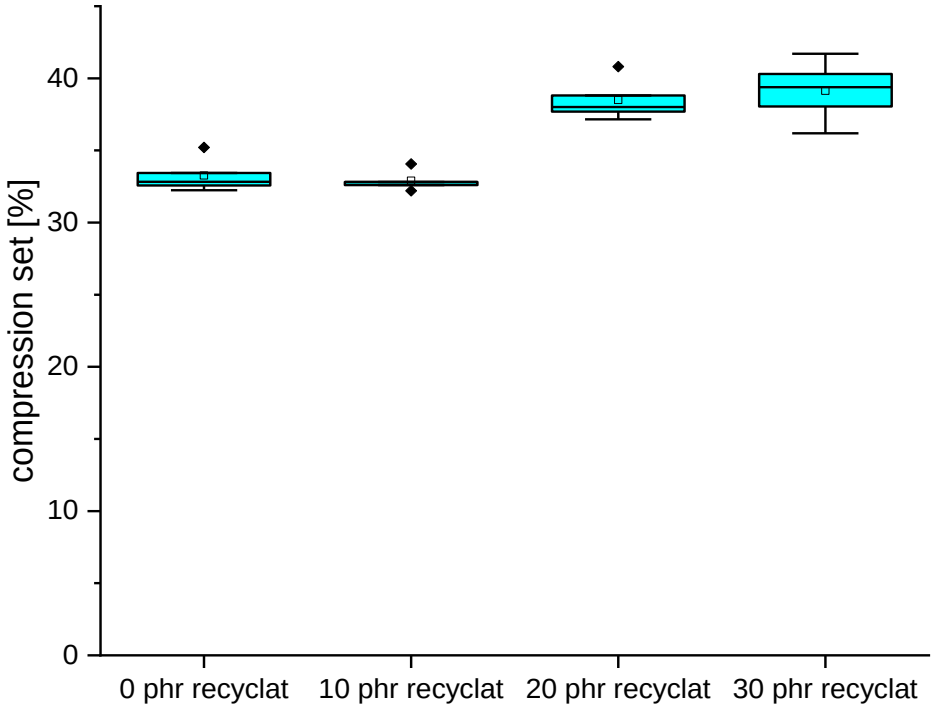
Influence of the recyclat content on testet pressed plates II

- Shore hardness
  - Initially, an increase in the measured value scatter and a reduction in the hardness due to the filler material can be observed
  - If the recyclate content is increased from 20 to 30 phr, the influence of the recyclate composition increases noticeably



Influence of the recyclat content on testet pressed plates III

- Compression set
  - increase in scattering from a recyclate content of 20 phr
  - slight deterioration in compression set with increasing recyclate content from 20 phr



Short excursion on LSR injection molding

- Previous tests with a Arburg 270S and tension test tool have yielded the following results:
  - Increase of the injection pressure with rising recyclat content
  - sprayability of tensile rods with a 0.8 nozzle up to 15 phr recyclat content
  - With increasing recyclat content we see a decrease of the crosslinking because of the higher content of catalyst poisens

Source: Arburg

Summary

- Recycling of silicone rubbers is possible using various processes, although no industrial processes are yet available
- The use of mechanical recycling allows the use of recyclate powder in small quantities (up to 20 phr) when using peroxide, depending on the subsequent application
- When using addition crosslinkers, it must be ensured that, if possible, no catalyst poisons are present in the recyclate.
- Most important: Building a circular economy

Outlook

- HCR injection molding mit recyclat content
  - Offers great potenzial through to the use of peroxides

- Use of recyclat in the 3d printing technolgie
  - The challenge her is to use the smallest possible particele sizes
  - Furthermore there should be no catalysator poisen inside of the recyclat

Timo Hofmann, M. Sc.
Research Associate

☎ +49(561)804-7961

t.hofmann@uni-kassel.de

www.ifw-kassel.de

https://archive.org/services/img/QuestionMark

Sources

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- [2] Ghosh, A., Rajeev, R.S., Bhattacharya, A.K., Bhowmick, A.K. and De, S.K. (2003), Recycling of silicone rubber waste: Effect of ground silicone rubber vulcanizate powder on the properties of silicone rubber. Polym Eng Sci, 43: 279-296. https://doi.org/10.1002/pen.10024
- [3] Rupasinghe, Buddhima & Furgal, Joseph. (2021). Degradation of Silicone-based Materials as a Driving Force for Recyclability. Polymer International. 71. 10.1002/pi.6340.
- [4] Ikeda, Yuko & Huang, Wei & Oku, Akira. (2003). Recycling of monomers and fillers from high-temperature-vulcanized silicone rubber using tetramethylammonium hydroxide. Green Chem.. 5.
- [5] Rupasinghe, Buddhima & Furgal, Joseph. (2021). Full Circle Recycling of Polysiloxanes via Room-Temperature Fluoride-Catalyzed Depolymerization to Repolymerizable Cyclics. ACS Applied Polymer Materials. 3. 10.1021/acsapm.0c01406.