IMPREGNATION OF POLYCARBONATE SURFACES WITH SILVER NITRATE USING COMPRESSED CARBON DIOXIDE

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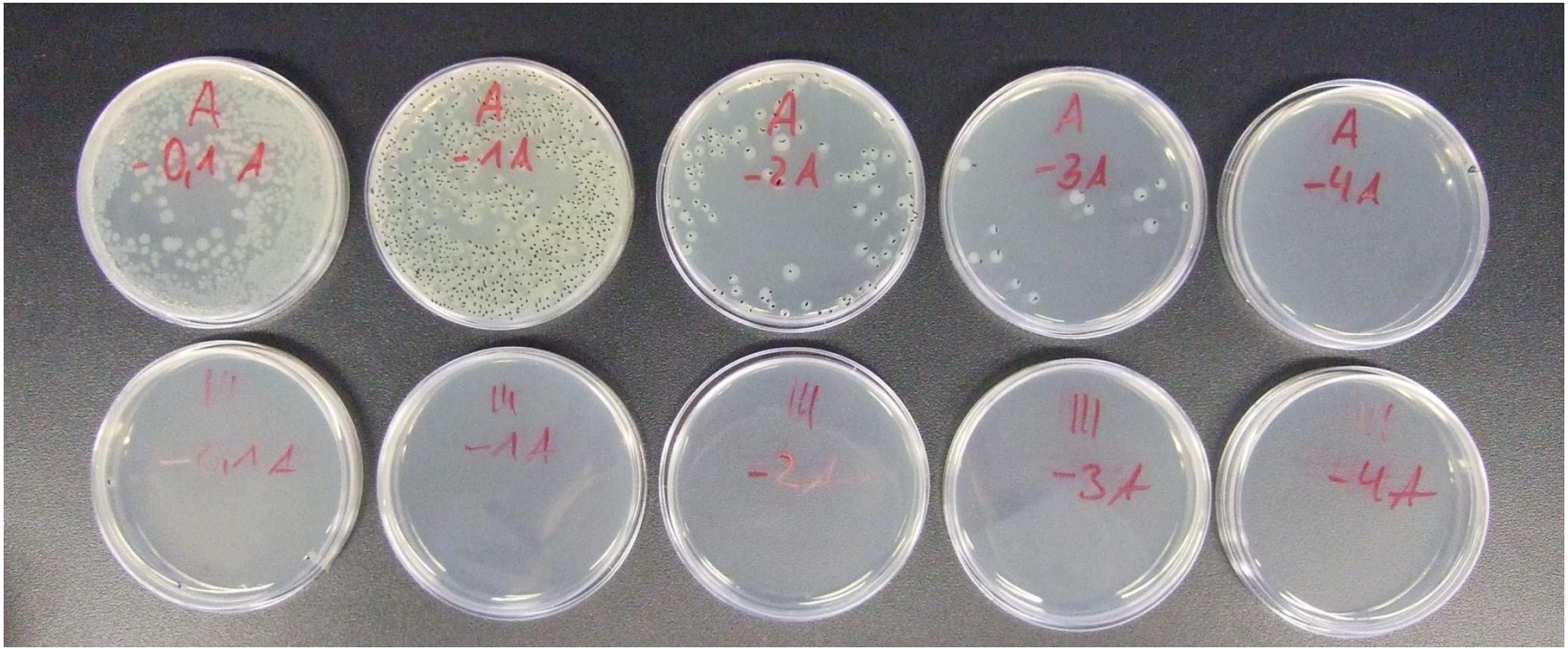

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Motivation

- Reducing bacterial growth on polymer surfaces which are touched frequently like
  - Switches
  - Buttons
  - etc.
- State of the art processing includes
  - Injection moulding: filling the complete part with additives
  - Coating: bonding is challenging

(http://bit.ly/1K5yvPA)

(http://bit.ly/1PMzYH6)

Approach

- Using compressed CO_2
  - Well known process for CO_2 soluble dyes[1,2]
  - Transfer the process on CO_2 insoluble silver nitrate
  - Avoids disadvantages of state of the art
- Simulating the daily use by
  - Scratch test
  - Radiation test
  - Leaching test

➡ Focus on industrial implementation

(http://bit.ly/1K5yvPA)

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[1] Joachim von Schnitzler; 2001; Der Stofftransport in Färbeprozessen von Polymeren mit überkritischem CO_2 ; Shaker Verlag

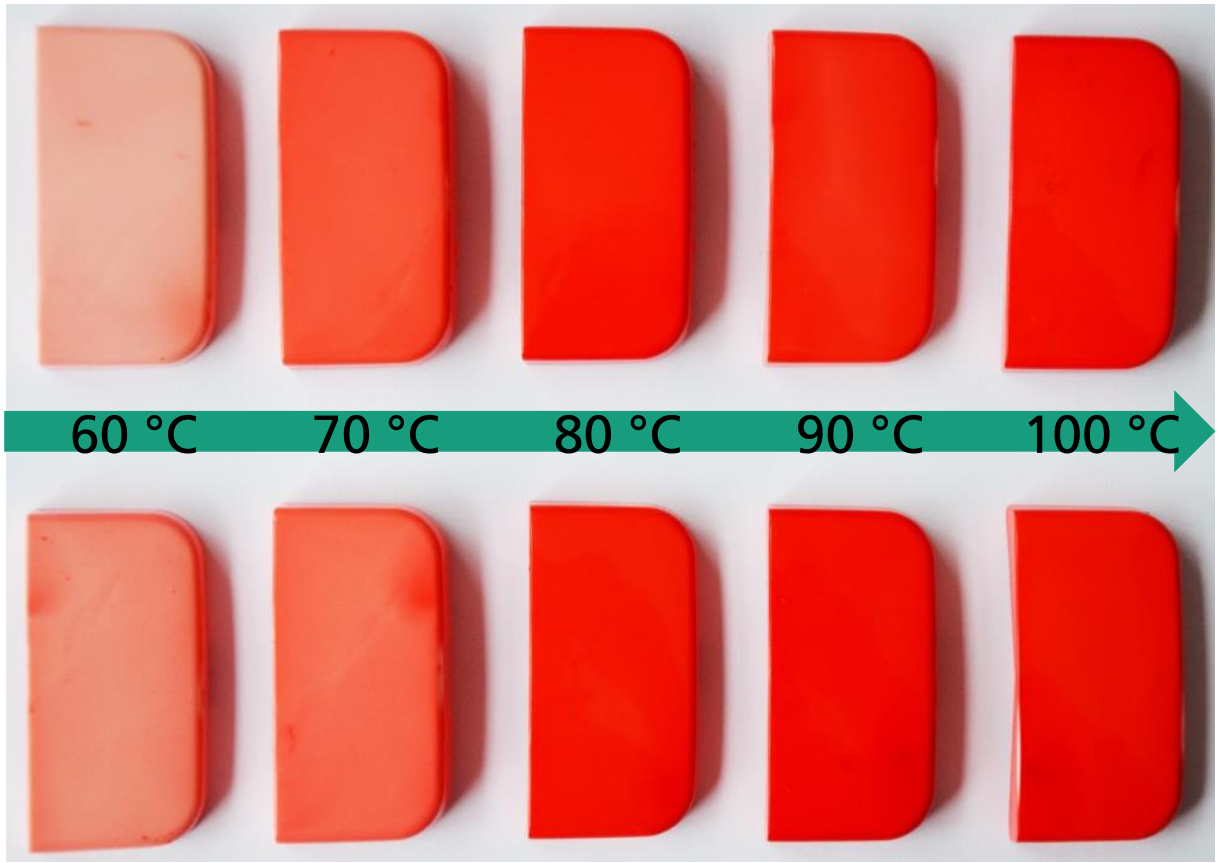
[2] Elke Bach, Ernst Cleve and Eckhard Schollmeyer; 2002; Past, present and future of supercritical fluid dyeing technology – an overview; Rev. Prog. Color.; Vol. 32

Silver nitrate | Facts and mechanism

- Crystalline appearance
- Good solubility in water
- Fair solubility in ethanol
- No solubility in compressed CO_2 (usage of cosolvent)

- Mechanism of action of silver ions
  - Deactivation of enzymes
  - Damaging the cell wall
  - Disorder the DNA replication
- In comparison to antibiotics no resistance formation possible

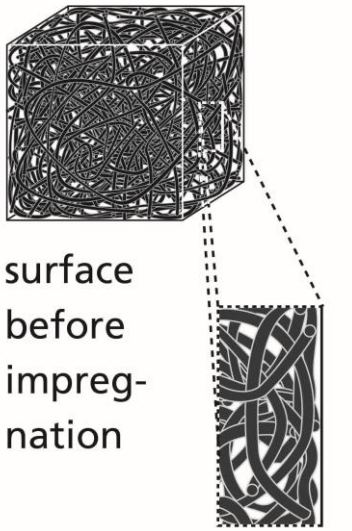
Impregnation with compressed CO_2 | Screening method



➡ Huge influence of temperature | No shape changes

Transport phenomena | Insoluble impregnates

t_0 | 0 bar



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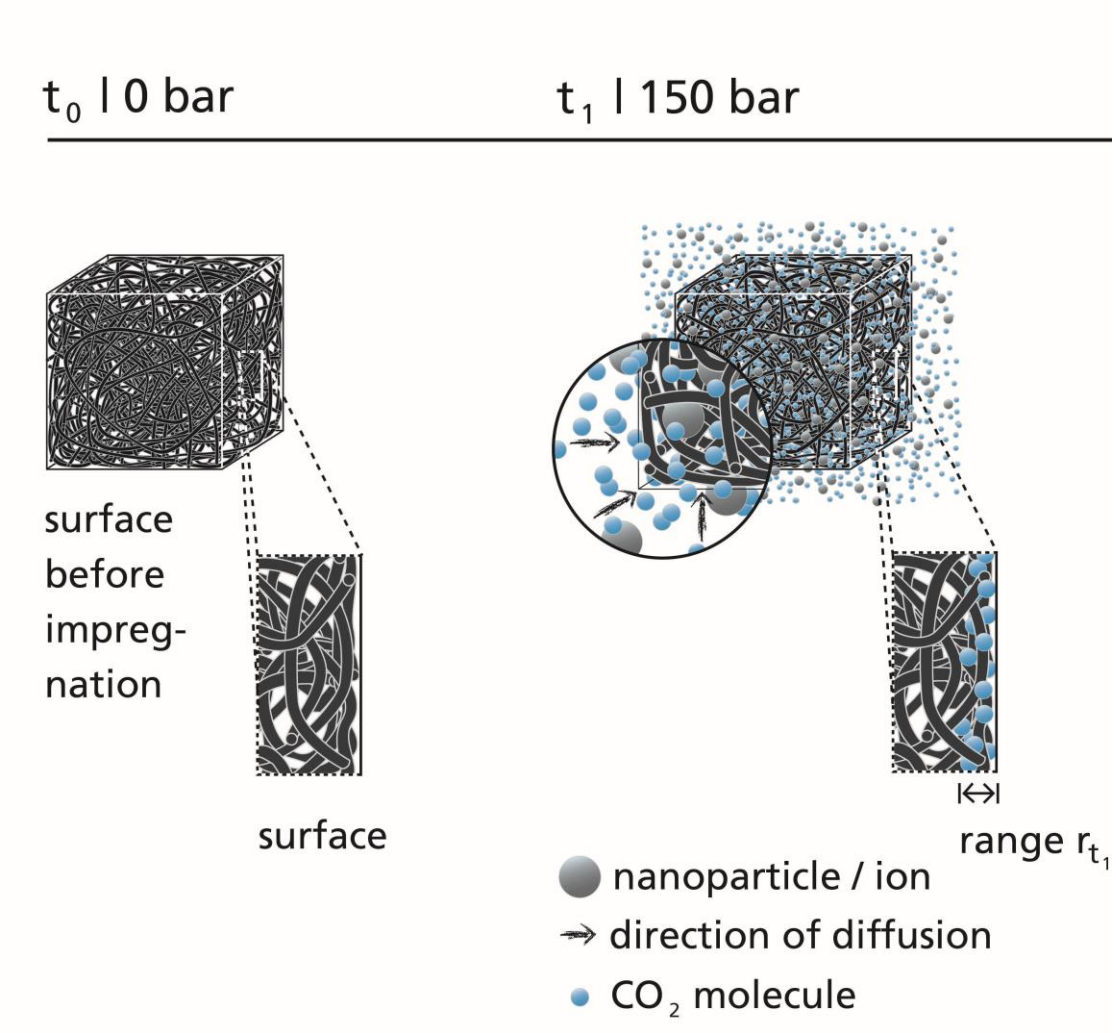
Transport phenomena | Insoluble impregnates



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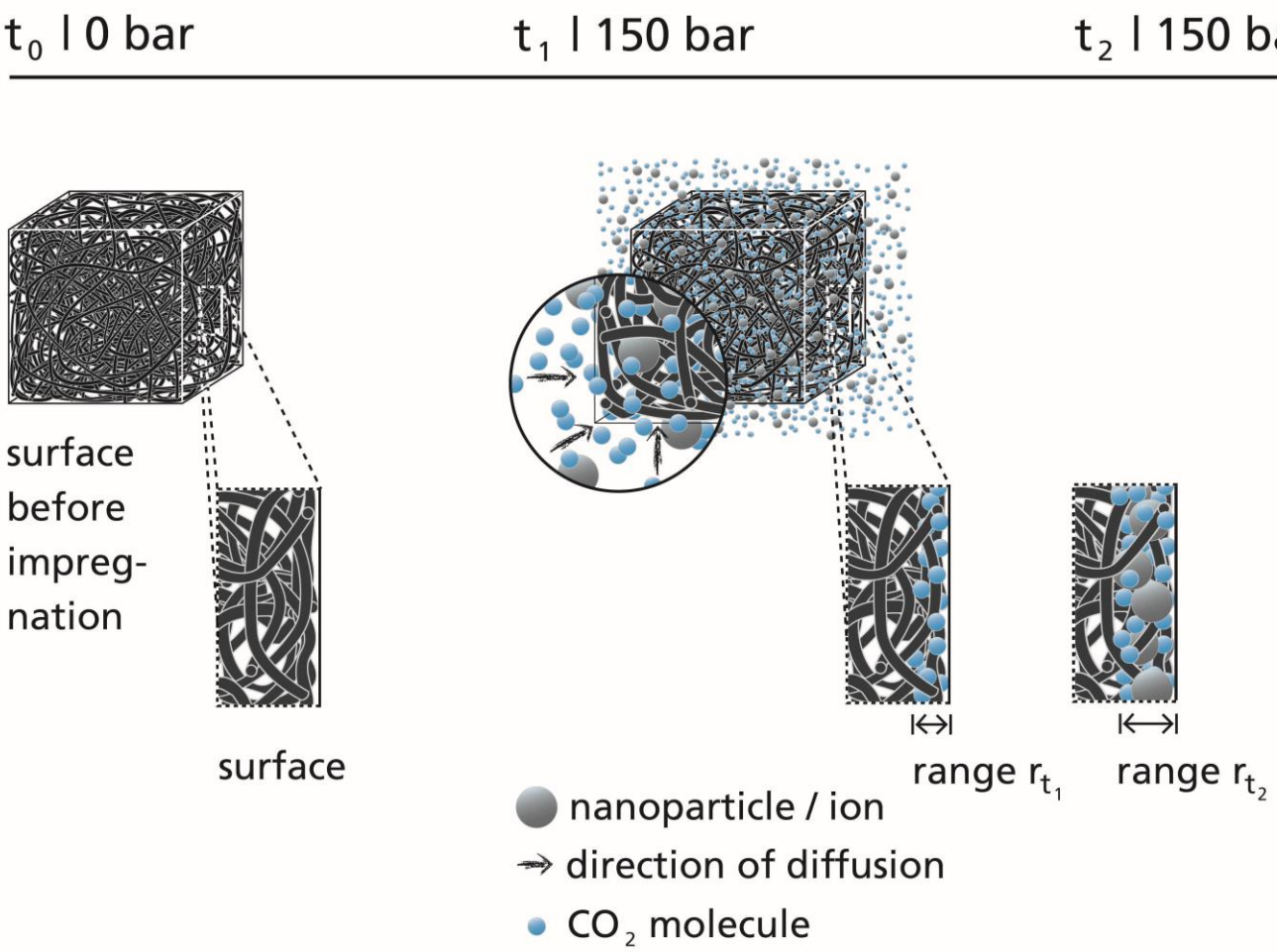

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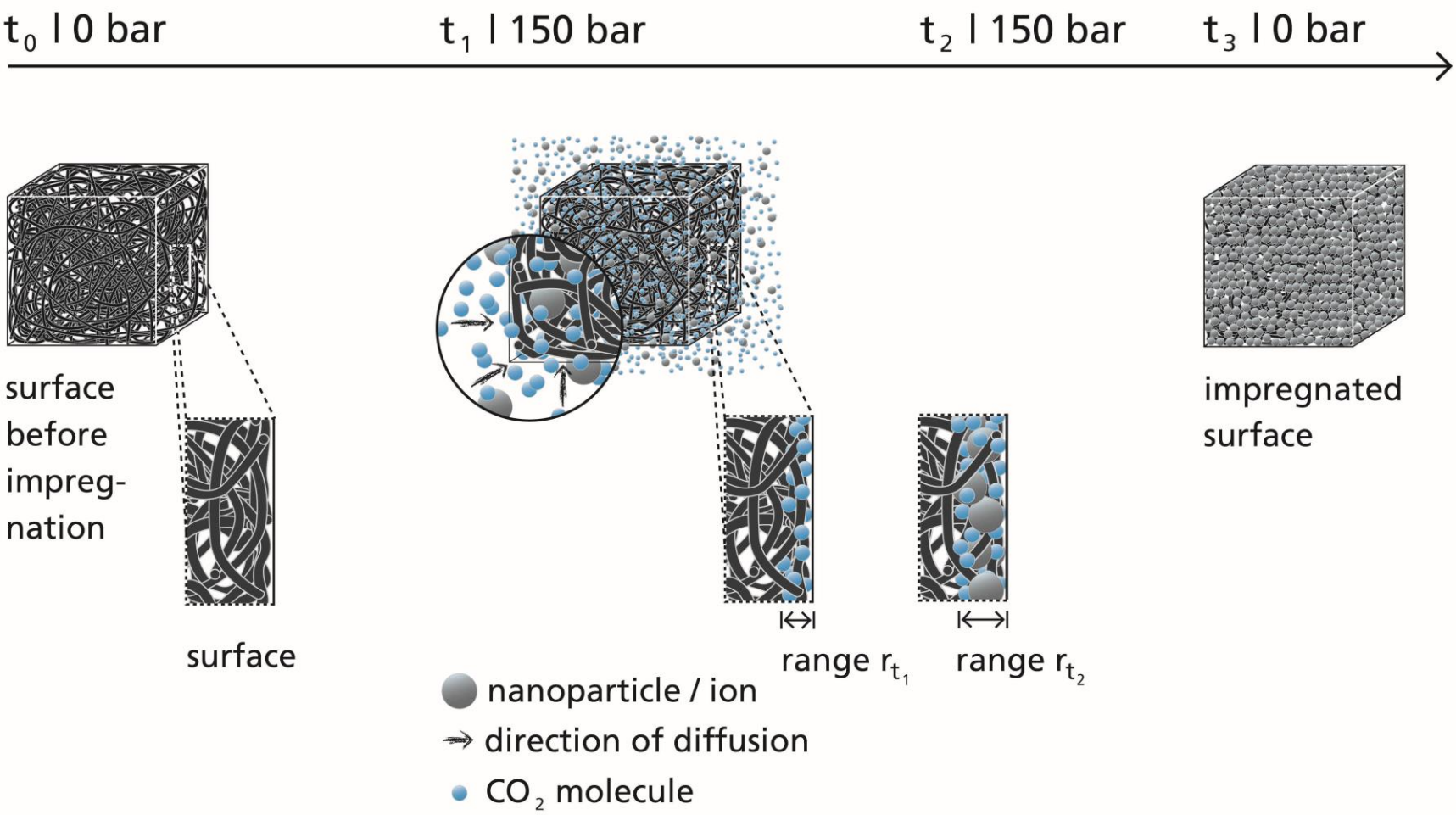
Transport phenomena | Insoluble impregnates



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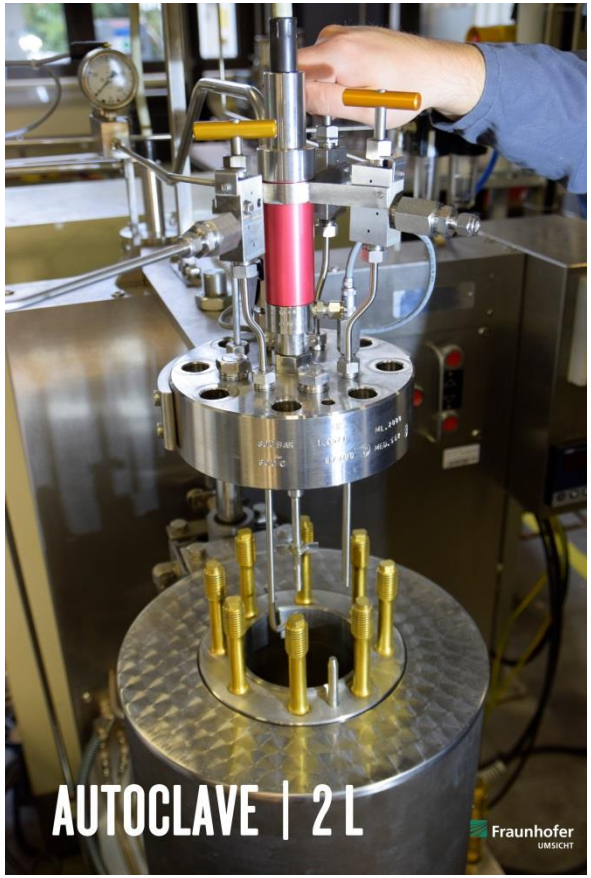
Design of experiments | Impregnation

- Hand controlled 2 L autoclave
- Impregnation of polycarbonate plates (10x15x2 mm)
- Ethanol used as cosolvent
- Process parameter 120 bar, 20 °C and 80 °C
- 2 batches with 50 plates per batch
- Pressure holding time 10 min

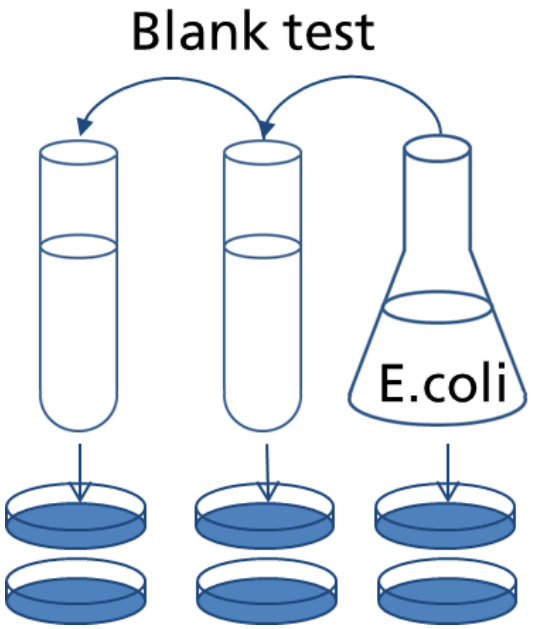


Design of experiments | Analysis

- Antimicrobial test according to ASTME 2149-01
- Determining the silver content by emission spectroscopy (ICP-OES)
- Simulating daily use by
  - Scratch test (DIN EN 60086-2-70)
  - UV-radiation test (DIN EN ISO 4892-3) according to the UV radiation in the Ruhr-area
  - Leaching test (EN 71-1)

Antimicrobial test | ASTME 2149-01

- Dynamic shake flask test
  - E. coli bacteria (living in human gut) diluted in water



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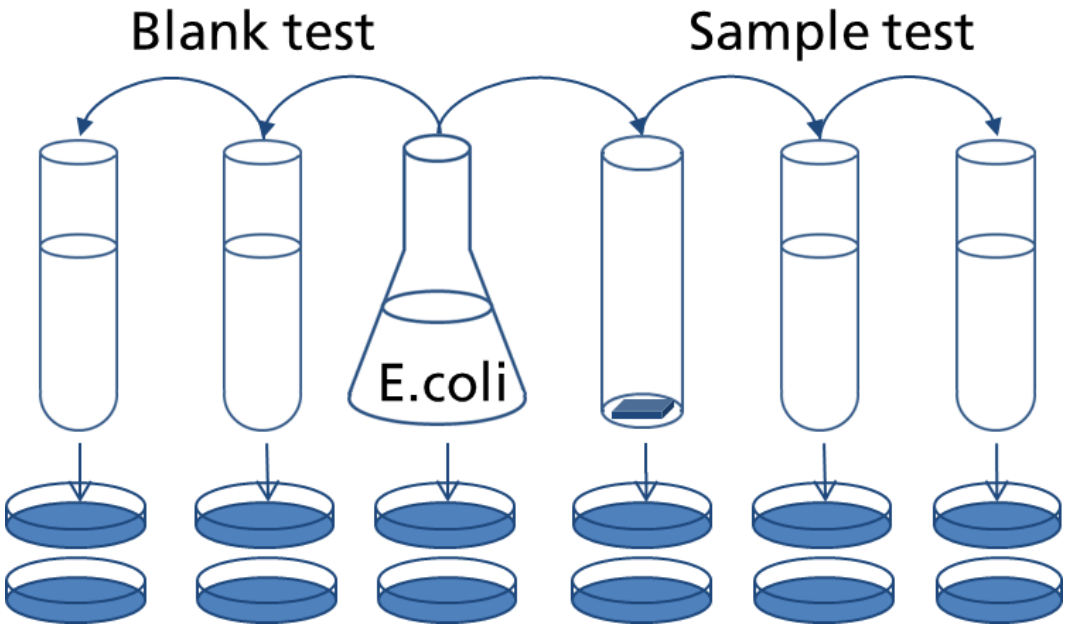
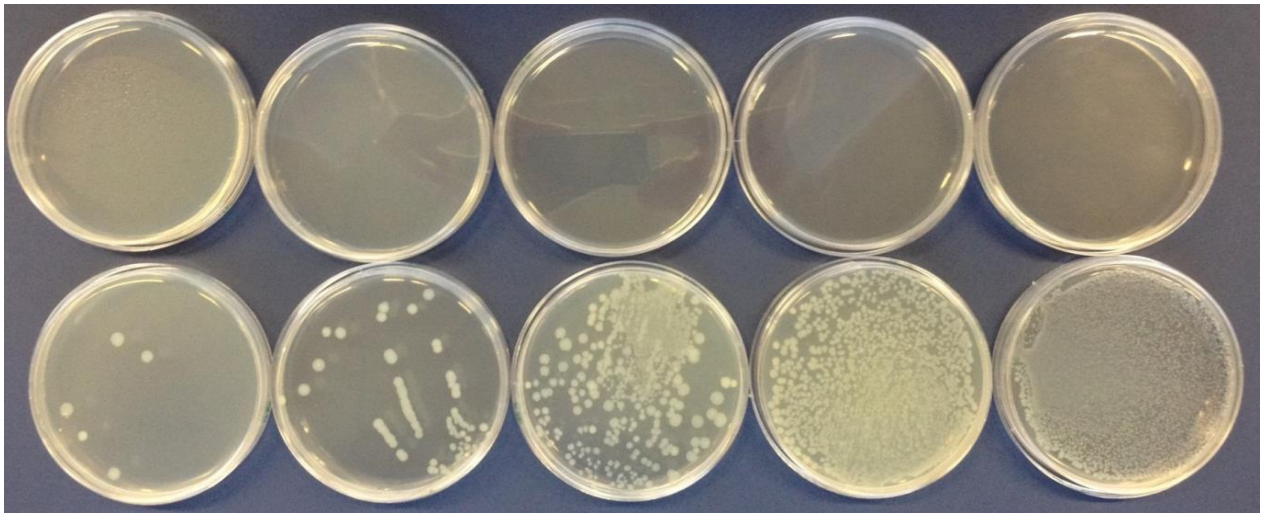
  - Dynamic contact of the sample with bacteria mixed in water for 1 h as an intensified test (standard: 24 h)



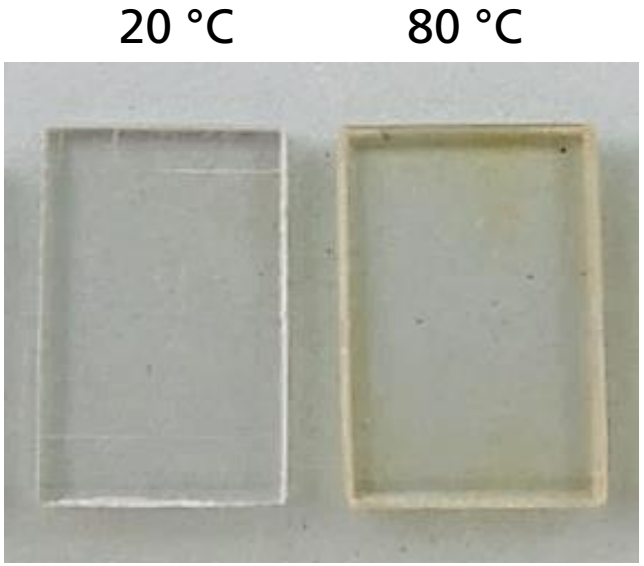
Antimicrobial test | ASTME 2149-01

- Dynamic shake flask test
  - E. coli bacteria (living in human gut) diluted in water
  - Dynamic contact of the sample with bacteria mixed in water for 1 h as an intensified test (standard: 24 h)
  - Determining the surviving bacteria, >99 % must be devitalised



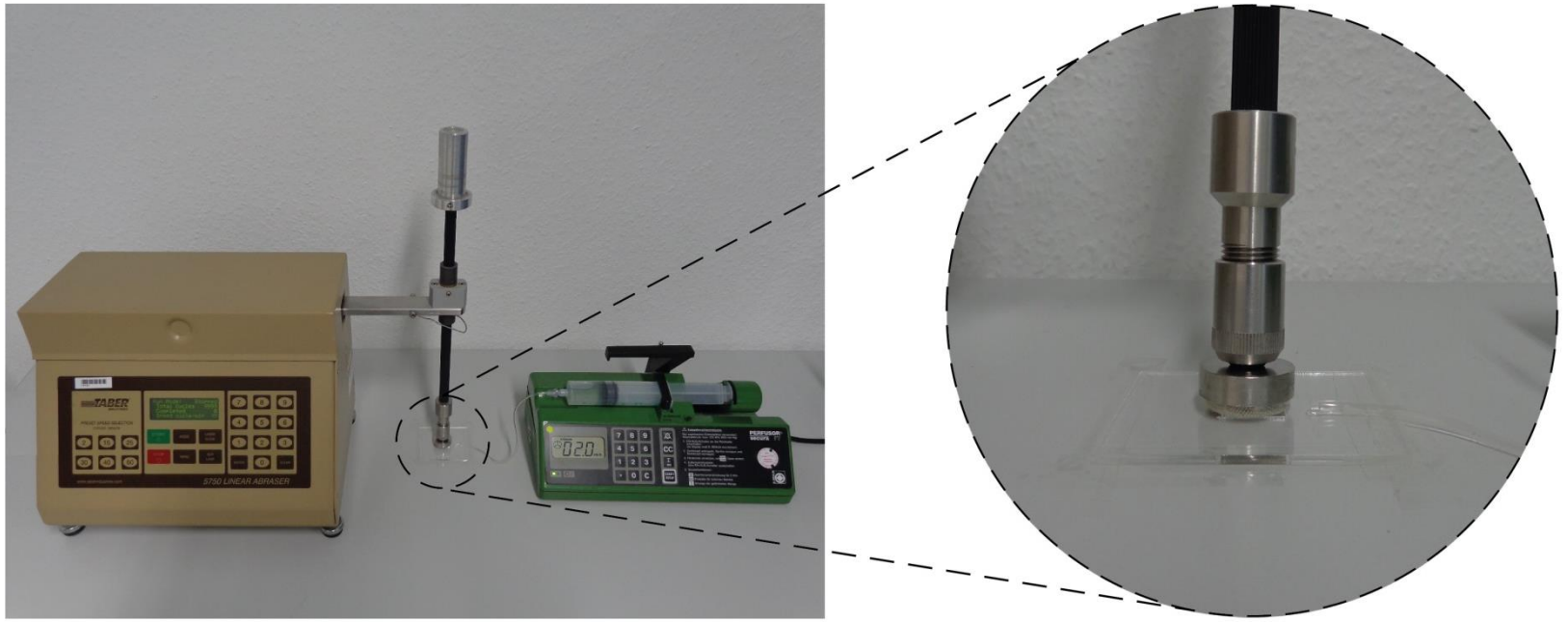
Impregnation | Results

- Average silver content
  - 120 bar, 20 °C: 2.4 [mg/kg] ± 0.3 [mg/kg]
  - 120 bar, 80 °C: 23.4 [mg/kg] ± 0.8 [mg/kg]
- Antibacterial properties
  - 99.9 % of bacteria devitalised after 1 h



Scratch test | Set-up

- Applied force 3.3 N simulating finger-type contact by textile
- 10,000 moves with 50 mm/s
  - Dry contact
  - Artificial sweat added



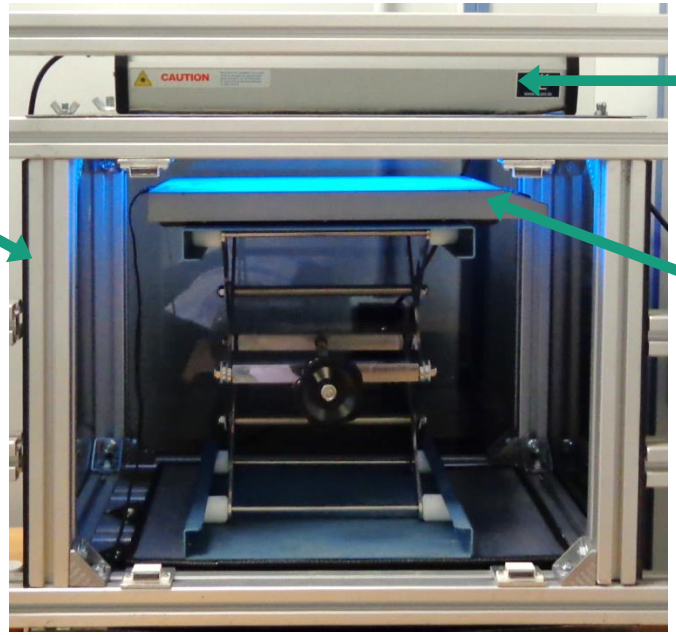
Scratch test | Results

T_{imp} [°C]	Liquid	Devitalised bacteria [%]	Average initial silver content [mg/kg]	Average silver content after scratch test [mg/kg]
20	none	59.8	2.4	2.2
	artificial sweat	21.3		
80	none	99.8	23.4	22.5
	artificial sweat	99.1		

➡ Samples impregnated at 80 °C are still active

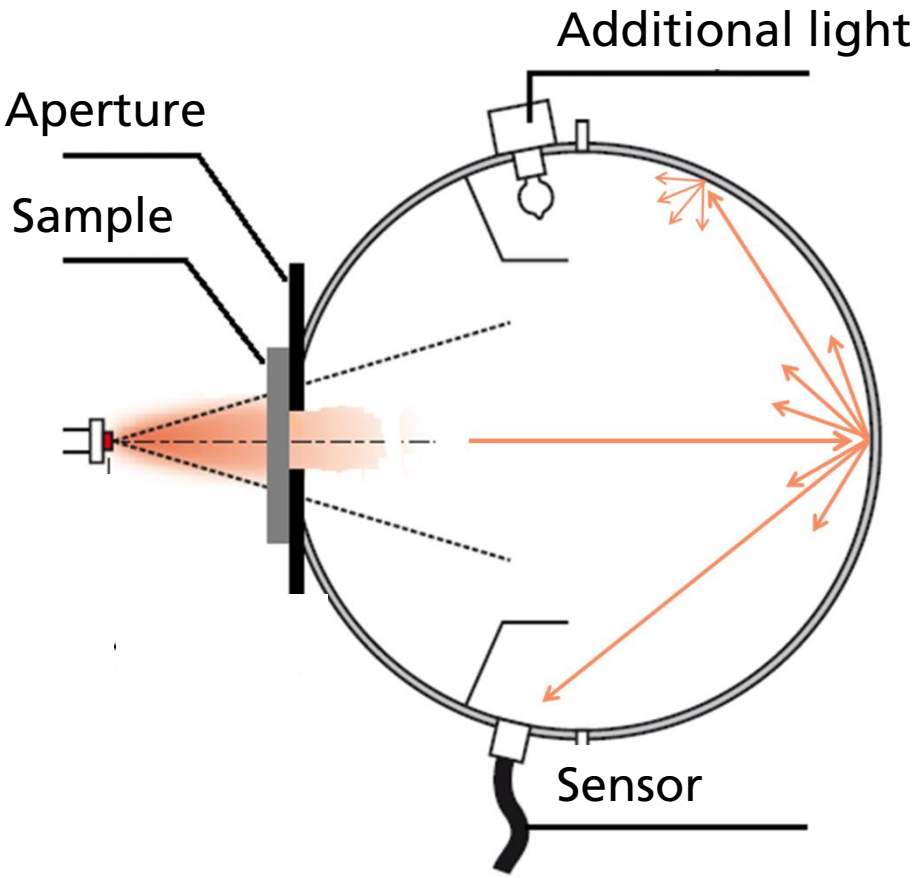
Radiation test | Set-up

- Radiation power: 67 W/m²
- Wave length: 320 to 400 nm
- Duration of radiation: 48 h (20 d), 14 days (139 d), 42 days (417 d) equal to Ruhr area

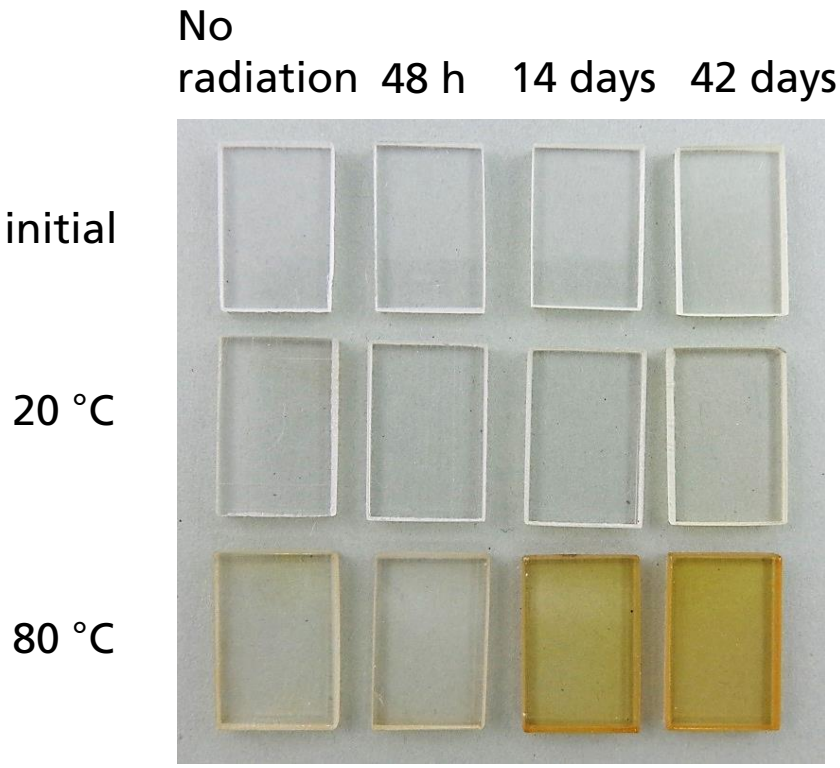


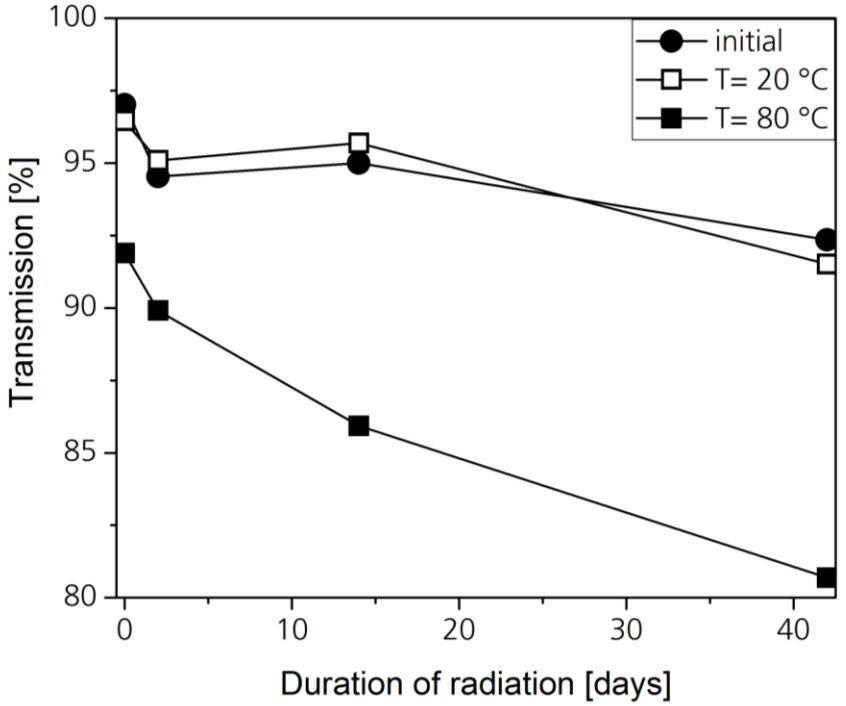
Radiation test | Set-up

- Using an Ulbricht sphere to determine the reduction of transmission



Radiation test | Results





Radiation test | Results

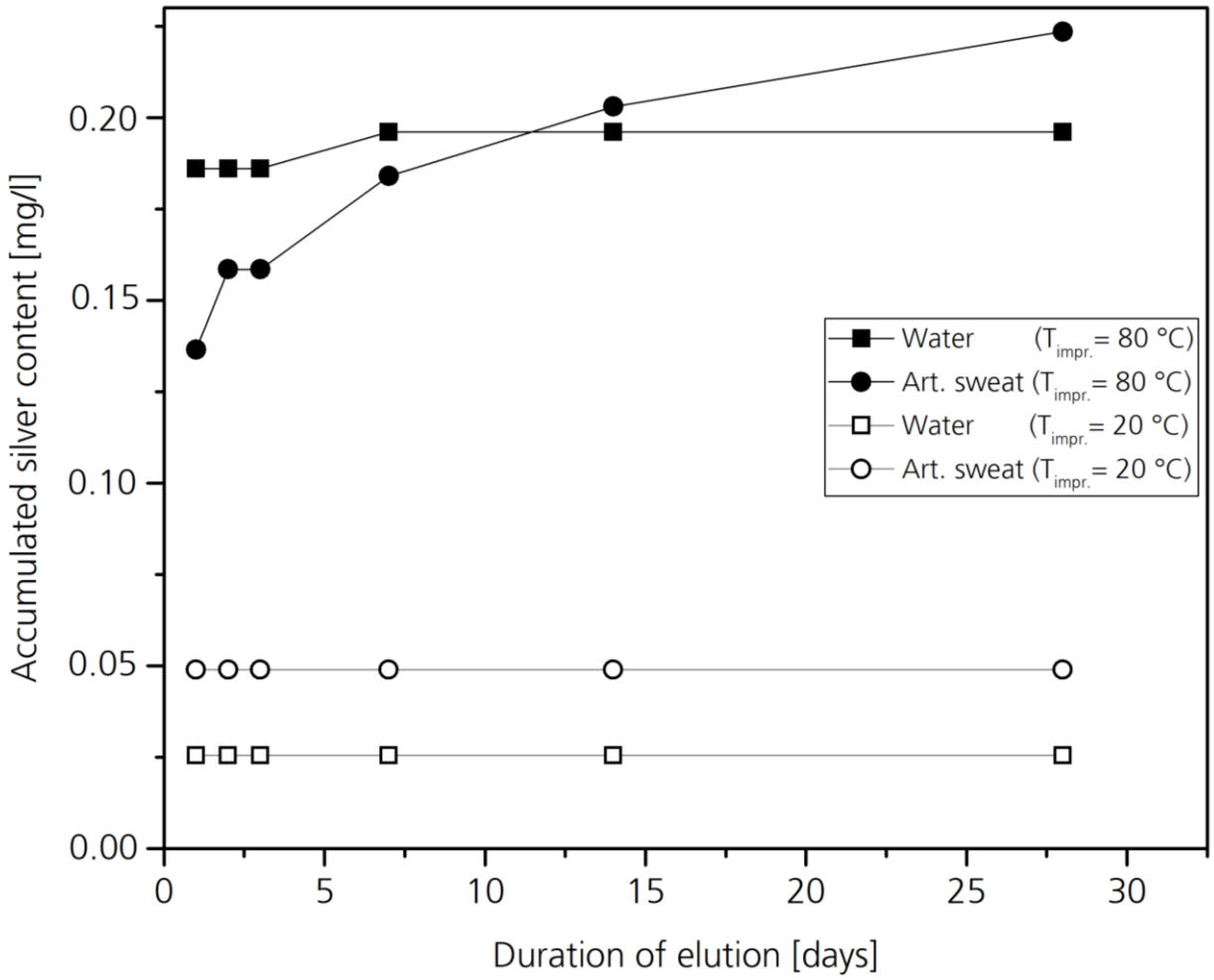
T_{imp} [°C]	Duration of radiation	Averaged devitalised bacteria [%]
20	48 h	67.3
	2 weeks	61.2
	6 weeks	57.5
80	48 h	99.9
	2 weeks	99.9
	6 weeks	99.9

➡ Samples impregnated at 80 °C are still active

Leaching test | Set-up

- According to EN 71-1 (leaching of toxic agents from toys)
- Elution time 4 weeks
  - Used liquids: distilled water, artificial sweat
  - Changing the liquids after 24 h, 48 h, 72 h, 7 days, 14 days
- Analyzing the amount of silver in the elution liquids
- Analyzing the amount of silver in the samples after elution

Leaching test | Results



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Leaching test | Results

T_{imp} [°C]	Liquid	Average initial silver content [mg/kg]	Average silver content after leaching test [mg/kg]
20	water	2.4	0.9
	artificial sweat		0.7
80	water	23.4	15.7
	artificial sweat		18.6

➡ A person of 15 kg has to swallow up to 2,280 kg impregnated polymer plates – and keep it in the stomach for 4 weeks – to get seriously damage (lethal dose of silver nitrate: 1,170 mg/kg)

Summary

- 100 samples were impregnated in 2 batches at 120 bar at 20 °C and 80 °C
- Impregnated samples at 20 °C and 80 °C are antimicrobial active
- Radiation and scratching reduce the antimicrobial activity of samples impregnated at 20 °C
- Samples impregnated at 80 °C are not harmed by radiation and scratching
- Amount of silver eluted within 4 weeks achieves standard specification for toys

Thank you for your attention

- Many thanks to my colleagues at UMSICHT

  M. Renner | C. Errenst | J. Maier | N. Nowara | E. Möhle

For further information visit us on:

www.polyimpreg-fraunhofer.de

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Oxidation of silver

- Silver ions can be oxidised by CO_2 to silver(I)oxide
  - Silver(I)oxide can be oxidised by CO_2 to silver carbonate
- Reduction of silver ions to elementary silver
  - by oxidation of the autoclave
  - by oxidation of monomers of the used polycarbonate