How the Size of Silica Capsules Influences their Stability During Rubber Processing

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Motivation

Figure 1: End-of-Life tires on a landfill.

Micron- and submicron sized capsules have gained significant attention as carriers of active substances but have not yet been investigated to improve recycling/environmental degradation of rubber, in particular tires. One of the challenges is dispersing a devulcanization aid (DA), which breaks crosslinks in vulcanized rubber, due to the dense network. When using the DA shielded by a capsule, it can be better dispersed during mixing before rubber vulcanization. For this, it needs to be investigated if capsules stay intact during the mixing process.

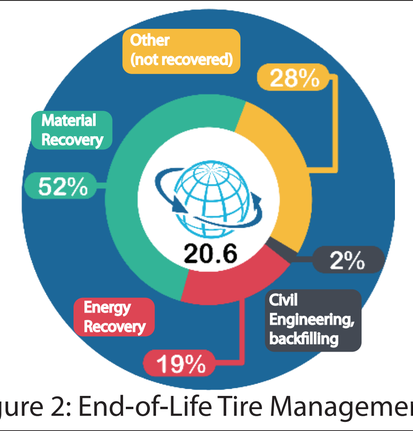


Figure 2: End-of-Life Tire Management.

Concept

- Difficulty of analyzing the chemical reaction caused by the DA during devulcanization
  → investigation of vulcanization behaviour instead
- Shielding a vulcanization accelerator and analysis of the vulcanization behaviour (Figure 3)
- Formation of rubber crosslinks can be observed during a measurement of vulcanization behavior as an increase in torque
- Accelerated vulcanization process: high maximum torque
- Not accelerated vulcanization process: low maximum torque
- Empty capsules were incorporated with and without accelerator to the compound during mixing to differentiate the effects of the capsules releasing accelerator into the compound

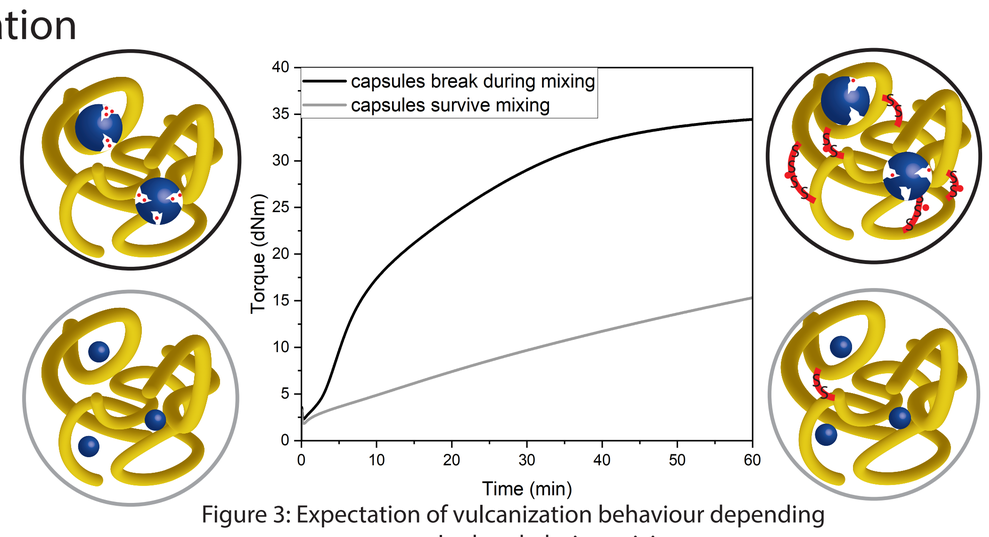


Figure 3: Expectation of vulcanization behaviour depending on capsules break during mixing.

Submicron-sized silica capsules (sSiC)

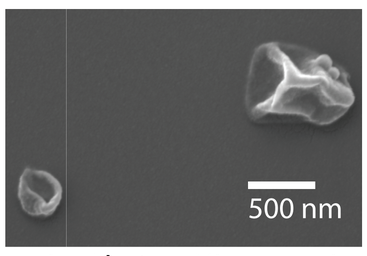


Figure 4: Scanning Electron Microscopy images of sSiCs.

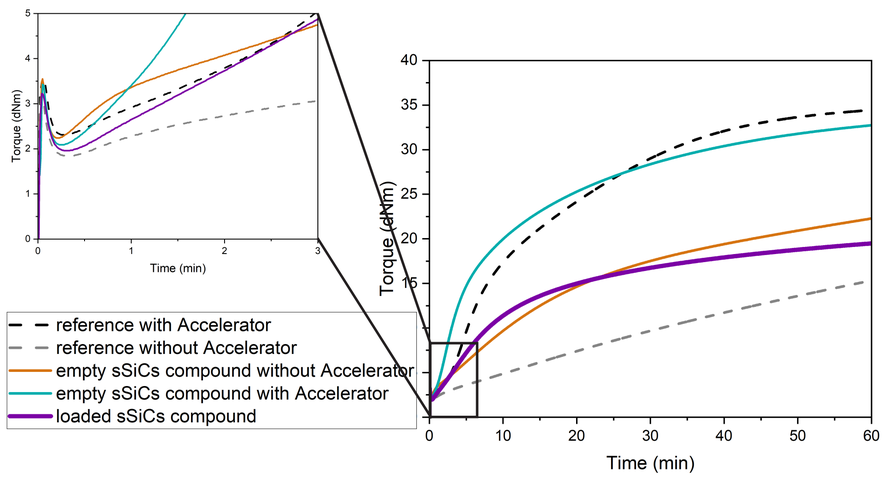


Figure 5: Vulcanization analysis of loaded and empty sSiCs and reference (without capsules) compounds.

Does the vulcanization process start during the mixing of sSiCs in rubber?

NO.

→ Similar minimum torque for all compounds (Figure 5, zoom in)

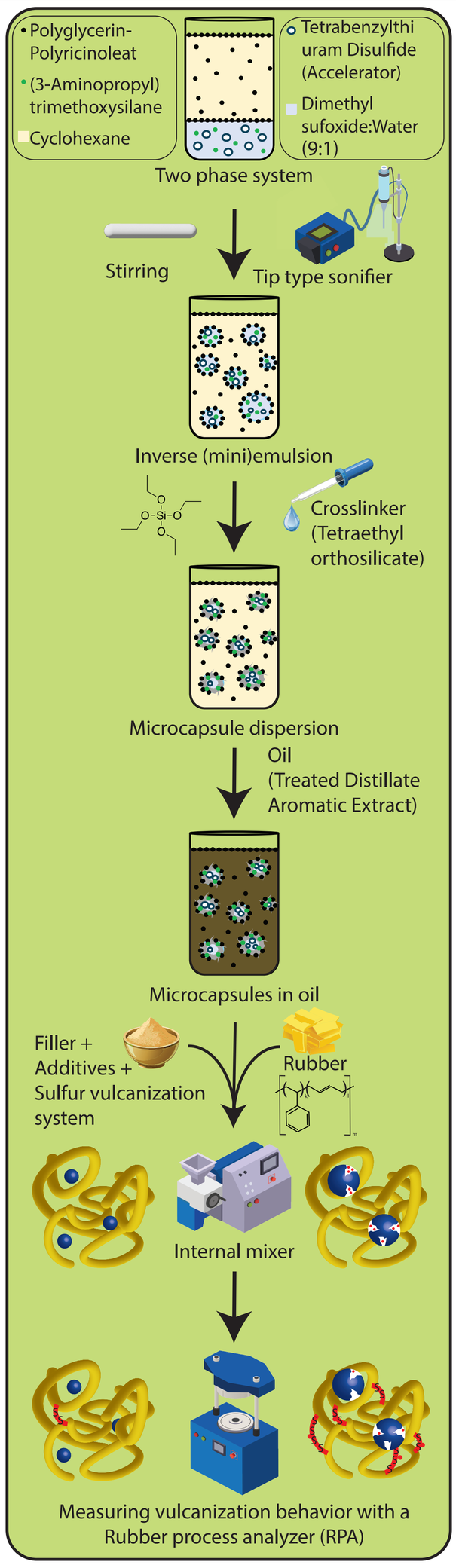
Is the vulcanization process accelerated by the loaded sSiCs compound?

NO.

→ Lower maximum torque for loaded sSiCs compound than for all compounds with accelerator added seperately during mixing (Figure 5)

→ Similar maximum torque for loaded sSiCs compound as for empty sSiCs compound without accelerator (Figure 5)

survive the mixing process



Micron-sized silica capsules (mSiC)

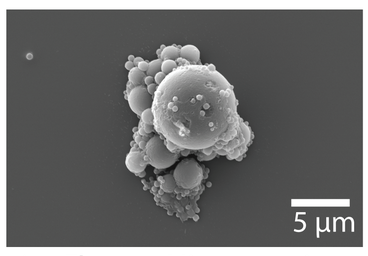


Figure 6: Scanning Electron Microscopy images of mSiCs.

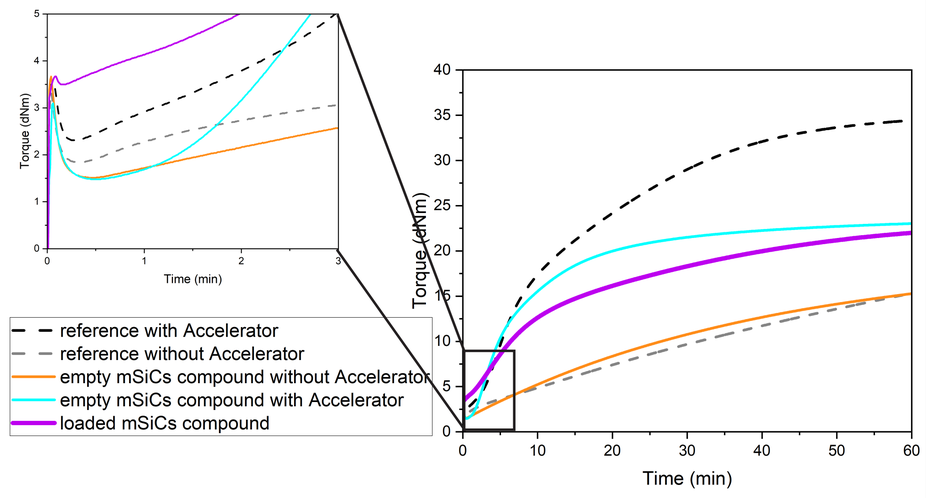


Figure 7: Vulcanization analysis of loaded and empty mSiCs and reference (without capsules) compounds.

Does the vulcanization process start during the mixing of mSiCs in rubber?

YES.

→ Higher minimum torque of loaded mSiCs compound compared to all other compounds (Figure 7, zoom in)

Is the vulcanization process accelerated by the loaded mSiCs compound?

YES.

→ Higher maximum torque for loaded mSiCs compound than for compounds without accelerator added seperately during mixing (Figure 7)

→ Similar maximum torque for loaded mSiCs compound as for empty mSiCs compound with accelerator (Figure 7)

break during the mixing process

Summary

In a vulcanization study it was shown that…

… micron-sized (average ≈ 5-7 µm) silica capsules break during mixing

… submicron-sized (average ≈ 300-700 nm) silica capsules **do not break** during mixing

→ Valuable insights for the development of a capsule-enhanced rubber system in which the shielded DA is well dispersed within the rubber matrix.

References

1 Haritha Kirla, et al., Use of Silica Nanoparticles for Drug Delivery in Cardiovascular Disease, Clinical Therapeutics, 45, 11, 2023.
2 Xiangyu Zhu, et al., Accelerated hydrolysis and degradation of polylactide nanocomposites using loaded silica nanocarriers, Chemical Engineering Journal, 491, 2024.
3 Wurm, F. R., Dierkes, W. K., Blume, A., & Filzer, K. (2026). Rubber composition comprising core-shell particles.
4 https://lh5.ggpht.com/-6trcejqF1I8/VK-NMO_dXNI/AAAAAAAA-dE/3Gae5IW4hUg/kuwait-tire-graveyard-2%25255B2%25255Dn.jpg?imgmax=800

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