Polymeric Capsules with VOCs for Controlled Emission

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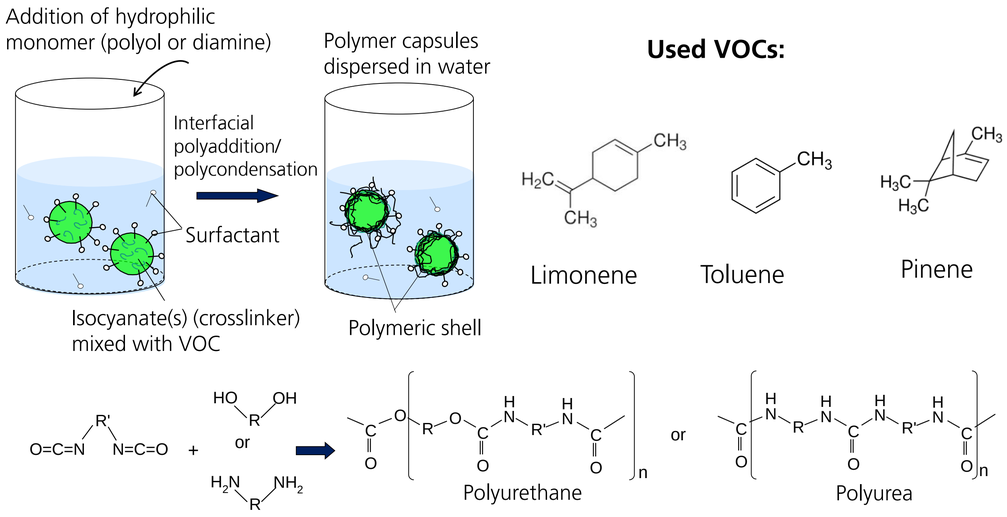
Introduction

Micro-(nano-)encapsulation technology involves building a barrier between the core and the environment and offers several benefits to preserve the functional and physicochemical properties of core material. Tremendous progress has been made in synthesizing well-defined capsules to achieve desired properties such as particle size, chemical composition, and controlled release of loaded compounds.
Encapsulation of volatile organic compounds (VOCs) that could evaporate with a defined rate is of immense interest for application in emission reference materials (ERM). These are urgently needed for quality assurance and quality control purposes (QA/QC) required by test standards for the determination of chemical emissions of construction and other materials for interior use. As such ERMs are hardly available on the market, the EU-funded EMPIR project MetrIAQ [1] was started to fill this gap by developing a material with temporally constant emission of VOCs typically found in indoor air.

Encapsulation of VOC

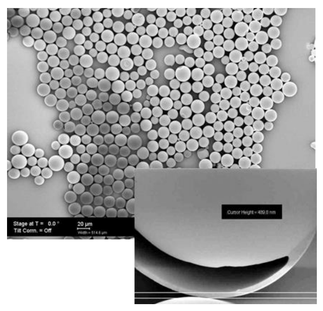
- Shirasu porous glass (SPG) membrane emulsification: formation of oil-in-water (O/W) droplets
- Polyaddition/Polycondensation crosslinking reaction at oil droplets interface



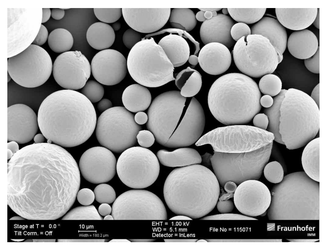
Chemical composition and average size of VOC loaded capsules

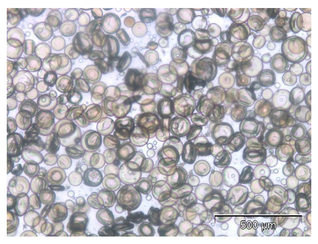
Sample Name	VOC	Crosslinker	Hydrophilic monomer	Surfactant	Capsule size
GTIL_1	Limonene, 4.7 ml	IPDI 0.92 g / Tub 0.2 g	Glycerin, 0.1 g	PVA, 0.4 wt%	16±4 µm
HDTIL_1	Limonene, 4.7 ml	IPDI 0.92 g / Tub 0.2 g	HMDA, 0.5 g	PVA, 0.4 wt%	21±10 µm
HTIT_1	Toluene, 4.7 ml	IPDI 0.92 g / Tub 0.2 g	Hexandiol, 0.12 g	PVA, 0.4 wt%	14±9 µm
HDTT_2	Toluene, 4.7 ml	Tub, 0.8 g	HMDA, 0.5 g	SDS, 0.1 wt%	43±11 µm
GTIP_1	Pinene, 4.7 ml	IPDI 0.92 g / Tub 0.2 g	Glycerin, 0.1 g	PVA, 0.4 wt%	19±5 µm
HDTIP_1	Pinene, 4.7 ml	IPDI 0.92 g / Tub 0.2 g	HMDA, 0.5 g	PVA, 0.4 wt%	23±7 µm

IPDI - Isophorone diisocyanate; Tub - TUBASSIST® FIX 157W (CHT R. BEITLICH GmbH) is a solvent-free commercial product based on hexamethylene diisocyanate oligomers; HMDA – Hexamethylene diamine; SDS – sodium dodecyl sulfate; PVA- polyvinyl alcohol, M_w = 31000 g/mol; O/W phase ratio = 1/8



Shell thickness: ~ 490 nm



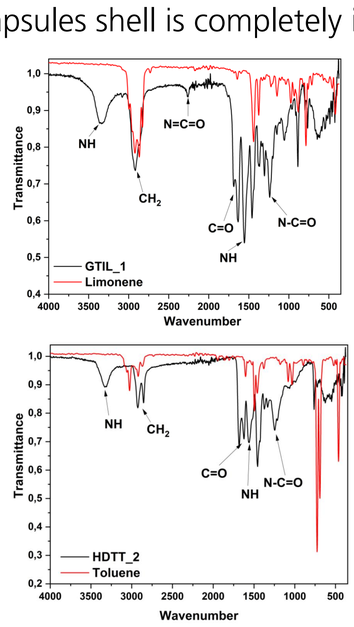


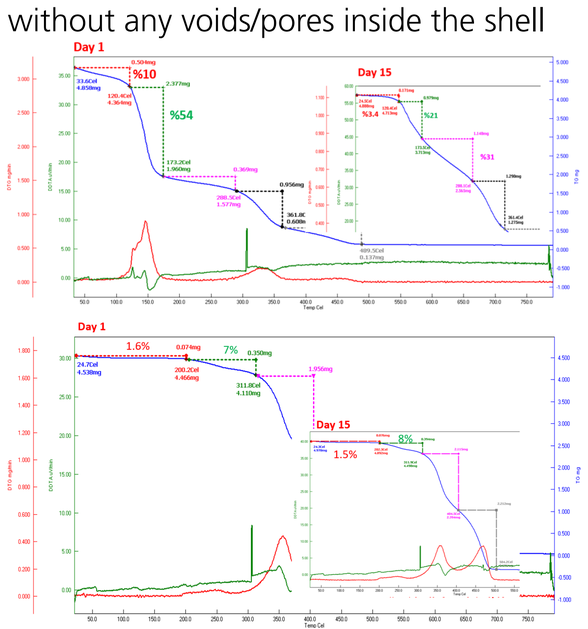
SEM image of sample GTIL_1 *SEM image of sample HDTIP_1* *LM image of sample HDTT_2*

- Encapsulation efficiency of 90 % could be reached

Characterization of VOC loaded Capsules (FTIR and TGA)

- The FTIR spectra confirmed the polyurethane/polyurea structure of the capsules with the typical characteristic bands
- The TGA curves performed on capsules before (Day 1) and after 15 days of drying at 50 °C (Day 15) revealed that more than 60 % of encapsulated limonene was emitted, whereas in HDTT_2 sample no reduction in VOC amount was observed. This indicates that in the presence of toluene capsules shell is completely intact, without any voids/pores inside the shell

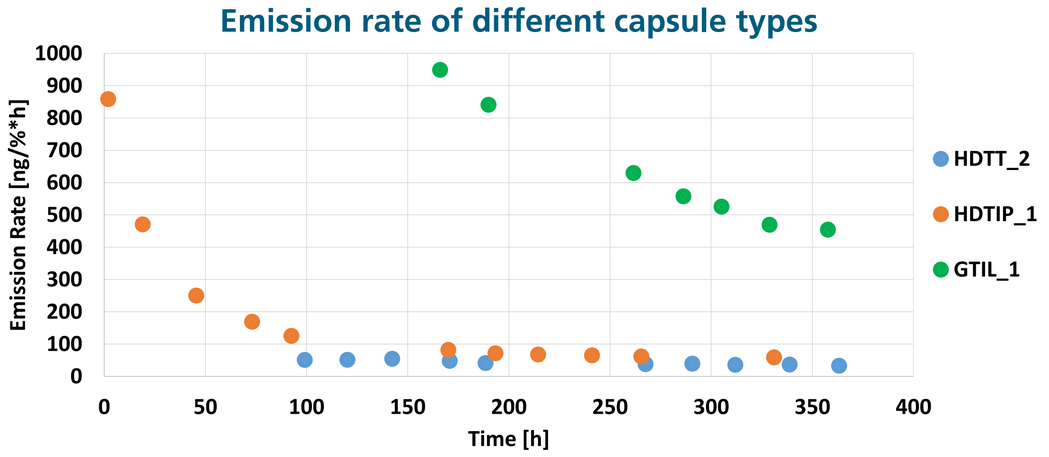




Emission experiments

- VOC emission is measured with help of emission test chambers, sampling tubes (e.g. filled with Tenax®) and TD-GC-MS
- Project goal is a stable emission with less than 10 % deviation over two weeks
- The emission behavior of different capsule types is quite divers (see below), with the lowest deviations of 44 % for HDTIP_1 and 48 % for HDTT_2

Emission rate of different capsule types



*Emission behavior of three different capsule types: HDTT_2 (average emission of 41 ng/%*h, 48 % decrease), HDTIP_1 (average emission of 76 ng/%*h, 44 % decrease) and GTIL_1 (average emission of 477 ng/%*h, 78 % decrease).[a]*
[a] Over a course of two weeks.

[1] Published Summary for 20NRM04 MetrIAQ – Metrology for the determination of emissions of dangerous substances from building materials into indoor air, 2022, https://www.bam.de/metriaq, Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany

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