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World Packaging Conference 2024
Valencia, Spain
CAL POLY
UHASSELT
Encapsulation of hexanal in calcium-squarate metal organic frameworks UTSA-280 for active packaging applications
Bollen Tuur
19/06/2024
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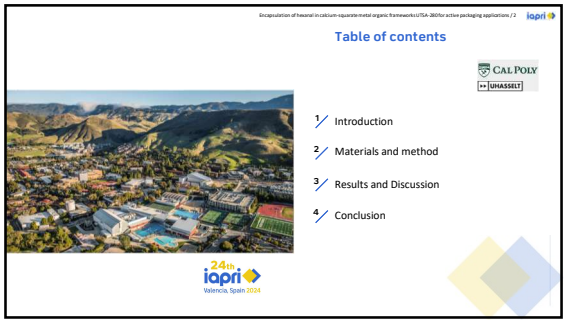
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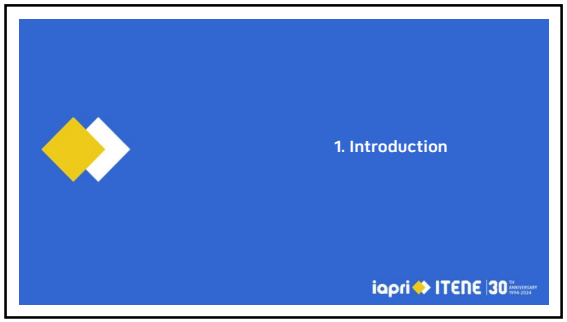
1. Introduction
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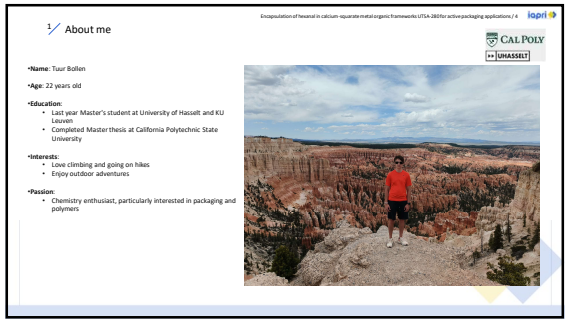
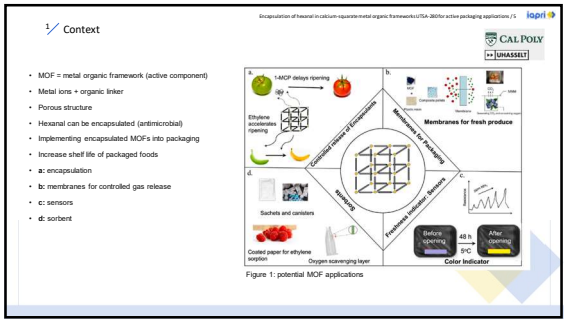
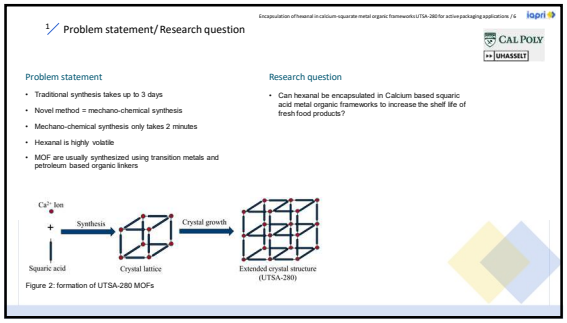

About me
CAL POLY
UHASSELT
•Name: Tuur Bollen
•Age: 22 years old
•Education:
Last year Master's student at University of Hasselt and KU Leuven
Completed Master thesis at California Polytechnic State University
•Interests:
Love climbing and going on hikes
Enjoy outdoor adventures
•Passion:
Chemistry enthusiast, particularly interested in packaging and polymers


Context
CAL POLY
UHASSELT
MOF = metal organic framework (active component)
Metal ions + organic linker
Porous structure
Hexanal can be encapsulated (antimicrobial)
Implementing encapsulated MOFs into packaging
Increase shelf life of packaged foods
a: encapsulation
b: membranes for controlled gas release
c: sensors
d: sorbent
1-MCP delays ripening
Ethylene accelerates ripening
Sachets and canisters
Coated paper for ethylene sorption
Oxygen scavenging layer
Membranes for fresh produce
Before opening
48 h 9°C
After opening
Color Indicator
Figure 1: potential MOF applications


Problem statement/ Research question
CAL POLY
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Problem statement
Traditional synthesis takes up to 3 days
Novel method = mechano-chemical synthesis
Mechano-chemical synthesis only takes 2 minutes
Hexanal is highly volatile
MOF are usually synthesized using transition metals and petroleum based organic linkers
Research question
Can hexanal be encapsulated in Calcium based squaric acid metal organic frameworks to increase the shelf life of fresh food products?
Synthesis
Crystal growth
Squaric acid
Crystal lattice
Extended crystal structure (UTSA-280)
Figure 2: formation of UTSA-280 MOFs

1 Research objectives

1.Synthesize Calcium-Based MOFs: Achieve the rapid synthesis of calcium-based squared acid metal-organic frameworks (UTSA-280) within a matter of minutes

2. Activate UTSA-280: Develop and implement a method for the effective activation of UTSA-280 MOFs.

3. Characterize Pre-Encapsulation: Conduct a comprehensive characterization of UTSA-280 MOFs prior to encapsulation to assess their initial properties.

4. Characterize Post-Encapsulation: Perform detailed characterization of UTSA-280 MOFs after encapsulation to evaluate changes in their properties.

5. Quantify Hexanal Encapsulation: Accurately determine the quantity of hexanal encapsulated within the UTSA-280 MOFs.

Figure 3: MOF powder after synthesis and during washing

2. Materials and method

2 Synthesis, activation and encapsulation

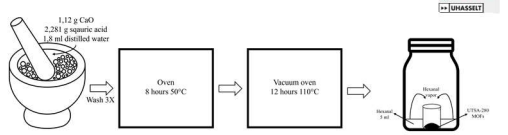


Figure 4: synthesis and activation of UTSA-280 MOFs followed by encapsulation of hexanal

2 X-ray diffraction

- **Definition**: Non-destructive technique for determining the structure of solid materials.
- **Capabilities**:
  - Identifies amorphous or crystalline structures.
  - Analyse phase composition, structure, and texture.
- **Comparison**: XRD patterns compared to reference samples, akin to identifying a fingerprint.
- **Principle**:
  - Atoms' regular arrangement causes X-rays to scatter and constructively interfere at specific angles.
  - Bragg's law explains diffraction and interference as reflections at the crystal lattice's atomic planes.

Figure 5: RIGAKU XRD machine

2 Fourier transform infrared spectroscopy

- **Definition**: Measures absorption and emission spectra in the infrared region.
- **Purpose**: Determines how effectively a sample absorbs light at different wavelengths.
- **Molecular Identification**:
  - Unique spectra for different molecular structures.
  - Identifies specific bond types (e.g., N-H, C-H, O-H) by their infrared absorption.
- **Application**: Distinguishes substances and provides molecular structural information.

Figure 6: Miracle 10 FTIR machine

2 Thermogravimetric analysis

- **Definition**: Analyses materials by monitoring mass changes under controlled temperature changes.
- **Process**: Measures weight changes of a sample as it is heated or cooled in a furnace.
- **Application**:
  - Determine thermal stability
  - Measure decomposition T
  - Evaluate temperature-dependent properties

Figure 7: TGA Q50

Synthesis, activation and encapsulation

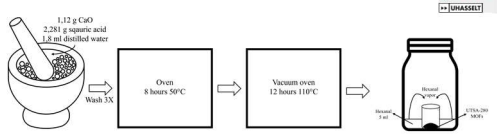


Figure 4: synthesis and activation of UTSA-280 MOFs followed by encapsulation of hexanal

Differential scanning calorimetry

- **Definition**: Measures thermal properties by monitoring heat flow into or out of a sample.
- **Function**: Detects guest molecules, like hydrocarbon gases, in pores.
- **Capability**: Determines thermal properties, such as the melting point (Tm) of impurities.
- **Application**: Conducted after encapsulating hexanal to analyse the thermal properties in UTSA-280 pores

Figure 8: DSC Q1000

Scanning electron microscopy

- **Definition**: Uses an electron beam within a high-energy range (100-30,000 electron volts) to produce detailed images of a specimen.
- **Process**:
  - Electron beam emitted from a thermal source.
  - SEM lenses focus the beam onto the specimen.
  - Electron beam scans the specimen in a raster pattern.
  - Electron detector collects emitted signals, including secondary electrons (S.E.) and backscattered electrons (BSE).
- **High Voltage Mode**:
  - Higher voltages penetrate deeper into the sample.
- **Magnification**:
  - Achieves magnification beyond 10,000x for detailed examination.

Figure 9: Miracle 10 SEM

3. Results and discussion

Synthesis

- Light grey powder
- UTSA-280 MOF crystals
- Molecular structure:

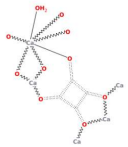


Figure 10: UTSA-280 MOF powder after activation

XRD - crystal analysis

- Strong XRD patterns indicate high crystallinity
- Similar peaks in simulated and synthesized structures confirm success
- Crystal structure remains unchanged post-encapsulation
- Comparison with reference data confirms similarity
- Peak ratios match, indicating preserved integrity and composition

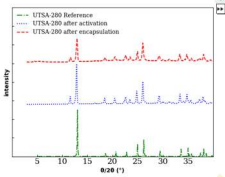


Figure 11: XRD results

FTIR - confirming reaction

- Peak around 3500-3000 cm^{-1}
  - O-H bonds (from excess water)
- Peak around 1660 cm^{-1}
  - C=O bonds
- Peak around 1400 cm^{-1}
  - C=C bonds
- UTSA-280:

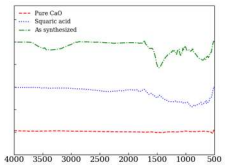


Figure 11: FTIR results before activation

FTIR - confirming encapsulation

- Peak around 3500-3000 cm^{-1}
  - O-H bonds (from excess water)
- Peak around 1660 cm^{-1}
  - C=O bonds
- Peak around 1400 cm^{-1}
  - C=C bonds
- Squaric acid
- Hexanal

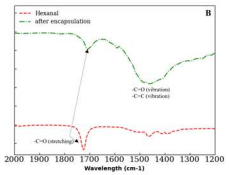


Figure 12: FTIR data of pure hexanal and UTSA-280 MOFs before and after encapsulation

TGA - Validating acvtivation

- Weight drop at 100°C
  - Water evaporation
- Weight drop at 250°C
  - H2O coordinated with Ca2+ ions
- Weight drop above 392°C
  - Framework breakdown
- Comparable with literature
  - Thermal stable crystals are formed

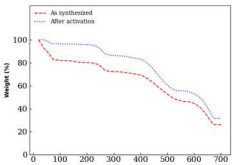


Figure 13: TGA results before and after activation

TGA - Validating encapsulation

- Encapsulated MOF
  - Weight drop at 100°C
- Pure hexanal
  - Weight drop at 70°C
- Hexanal successfully encapsulated
  - 30°C difference
  - ~20% successfully encapsulated
- Weight drop above 392°C
  - Framework breakdown

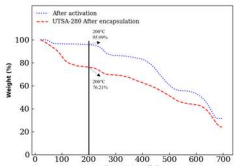


Figure 14: TGA results before and after encapsulation

DSC - Comfirming encapsulation

- Pure hexanal evaporation
  - Peak at 40°C
- After encapsulation
  - Peak between 100-150°C
- Encapsulation successful
  - Big temperature difference
- After encapsulation
  - Peak at ± 200°C
  - Hexanal coordinated with Ca2+ ions
- After activation
  - Peak between 100-170°C
  - Strong secondary bound

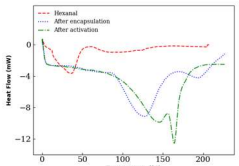


Figure 15: DSC results of pure hexanal and UTSA-280 before and after encapsulation

SEM - Comfirming crystal formation

- SEM pictures of UTSA-280 post-encapsulation confirmed XRD findings
- SEM images validated crystal presence and morphology.
- High-resolution SEM images matched XRD data, confirming crystal integrity.

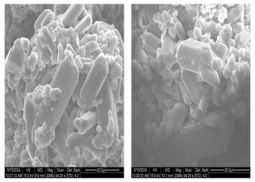
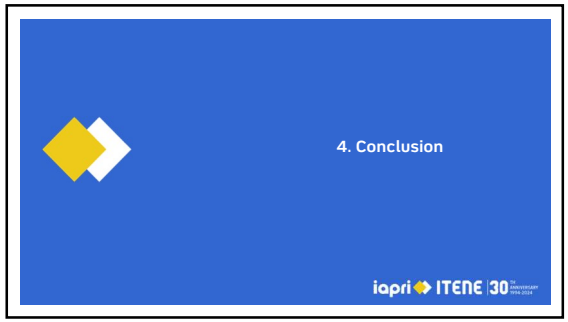
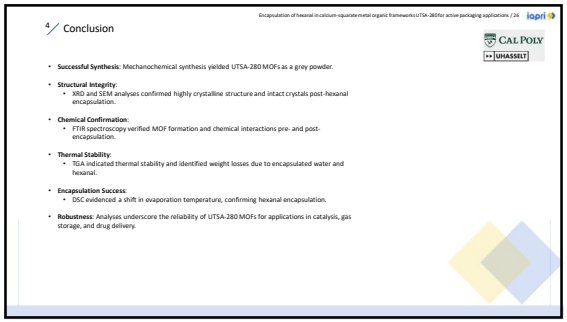


Figure 16: SEM images after encapsulation


4. Conclusion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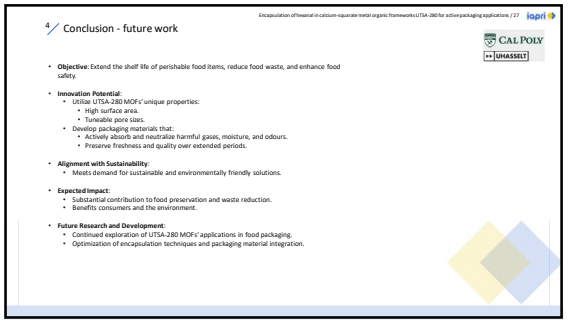
4 Conclusion
Successful Synthesis: Mechanochemical synthesis yielded UTSA-280 MOFs as a grey powder.
Structural Integrity:
XRD and SEM analyses confirmed highly crystalline structure and intact crystals post-hexanal encapsulation.
Chemical Confirmation:
FTIR spectroscopy verified MOF formation and chemical interactions pre- and post-encapsulation.
Thermal Stability:
TGA indicated thermal stability and identified weight losses due to encapsulated water and hexanal.
Encapsulation Success:
DSC evidenced a shift in evaporation temperature, confirming hexanal encapsulation.
Robustness: Analyses underscore the reliability of UTSA-280 MOFs for applications in catalysis, gas storage, and drug delivery.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4 Conclusion - future work
Objective: Extend the shelf life of perishable food items, reduce food waste, and enhance food safety.
Innovation Potential:
Utilize UTSA-280 MOFs' unique properties:
High surface area.
Tuneable pore sizes.
Develop packaging materials that:
Actively absorb and neutralize harmful gases, moisture, and odours.
Preserve freshness and quality over extended periods.
Alignment with Sustainability:
Meets demand for sustainable and environmentally friendly solutions.
Expected Impact:
Substantial contribution to food preservation and waste reduction.
Benefits consumers and the environment.
Future Research and Development:
Continued exploration of UTSA-280 MOFs' applications in food packaging.
Optimization of encapsulation techniques and packaging material integration.


Questions?
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