Master's Thesis Engineering Technology

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Textile Transformations: Upcycling Waste rPET-Textiles with Elongated, Bio-based Soft Blocks into High-Value TPC Materials

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1. INTRODUCTION

Problem statement

Plastics are essential for many applications, but traditional waste management is inadequate, leading to environmental pollution and resource loss. Polyethylene terephthalate (**PET**) is widely used in textiles and packaging, highlighting this issue. It is important to develop **innovative recycling technologies** and **biobased alternatives** for addressing these challenges. One solution involves upcycling PET waste into thermoplastic elastomers (**TPEs**) using a biobased fatty acid. [1] The addition of the **soft segment** is **limited** to 60 wt% due to its viscosity and properties [1], but **increasing the length** of the soft blocks could potentially allow for a higher wt% of soft block by extending the hard blocks.

Research goals

Research aim: synthesize longer soft blocks to create extended hard blocks in final polymer. This is done by:

- **Optimizing the synthesis** of FADD-SA oligomers
- Incorporating PET upcycling methods to **produce TPCs**
- **Characterization** of the resulting polymers to asses their properties and potential applications

2. MATERIALS & METHODS

Oligomer synthesis

- Oligomer synthesis via one-pot reaction (setup: Fig. 1)
- Reaction mechanism followed (Fig. 2).
- **Analysis**: Gel permeation chromatography (GPC) and Nuclear Magnetic Resonance (NMR) spectroscopy.

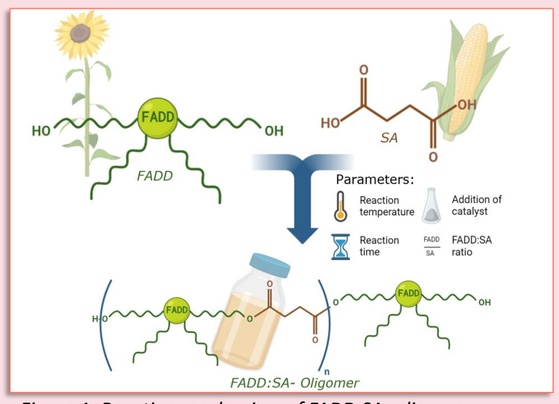

Figure 1: Reaction mechanism of FADD:SA- oligomer synthesis with varied parameters [2]

Polymer synthesis

- Polymer synthesis via one-pot condensation (setup: Fig. 2).
- Followed by precipitation and drying.
- Reaction mechanism shown (Fig. 3)
- Characterization: GPC and NMR spectroscopy

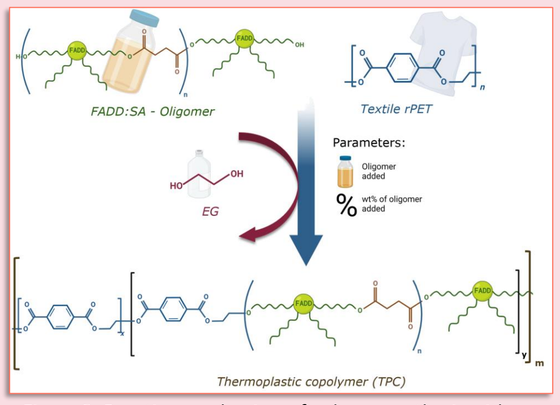

Figure 2: Reaction mechanism of polymer synthesis with varied parameters [2]

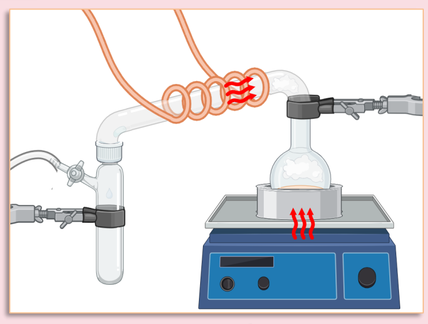

Figure 3: Reaction set up for one-pot condensation polymerization [2]

Mechanical and thermal properties

- **Tensile testing** for strength and elasticity
- **Thermal properties** analyzed using Differential Scanning Calorimetry (DSC): melting and glass transition temperatures

3. RESULTS OLIGOMER SYNTHESIS

Structural Analysis

- **^{1}H-NMR** (Fig. 4, left) confirms expected oligomer structure (top right).
- **Without catalyst:** Longer reaction time and moderately higher temperature improve oligomer ratio.
- **With catalyst:** Enhances oligomer elongation; more FADD reacts
- **Optimal conditions:** 2 hours Argon at 190°C, then 3 hours Vacuum at 220°C
- **Effective ratios:** Both 3:2 and 2:1 FADD

Molecular weight distribution

- **1H-NMR support:** Catalyst improves reaction efficiency
- **Oligomer formation:** Various FADD:SA ratios, mostly 2:1 and 3:2; some higher ratios like 5:4 observed.
- **GPC results:** Shown in Fig. 4 (bottom right).

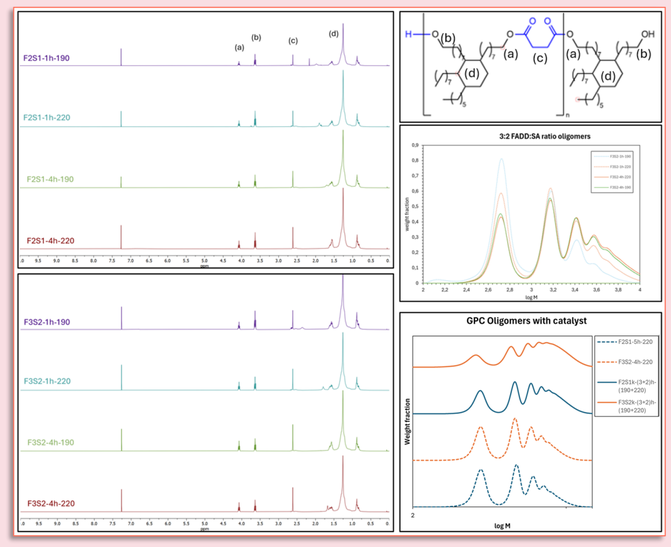

Figure 4: Results ^{1}H-NMR analysis (left), Structural formule with corresponding peaks (top right), GPC analysis results (bottom right)

4. RESULTS POLYMER SYNTHESIS

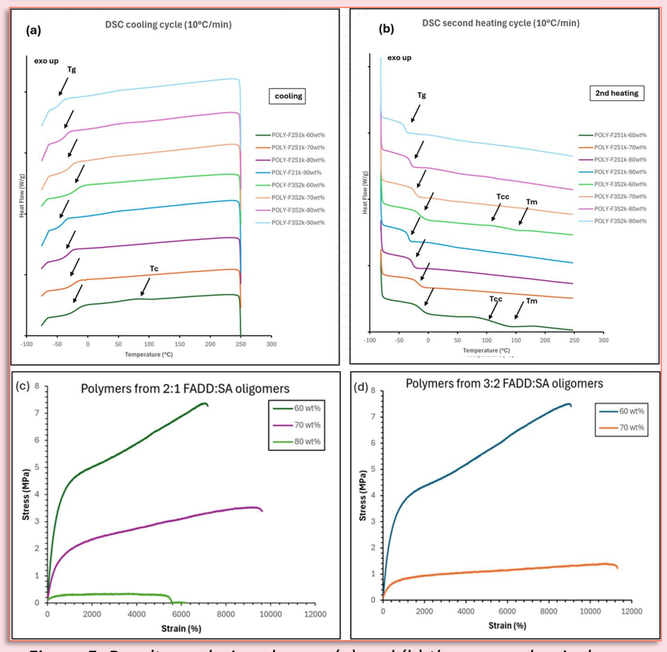

Figure 5: Results analysis polymers (a) and (b) thermomechanical properties (c) and (d) mechanical properties

Mechanical properties

- **Soft block elongation:** Reduces strain at break and maximum stress (Fig. 5 (c) and (d)).
- **Cause:** Transesterification increases material randomness.

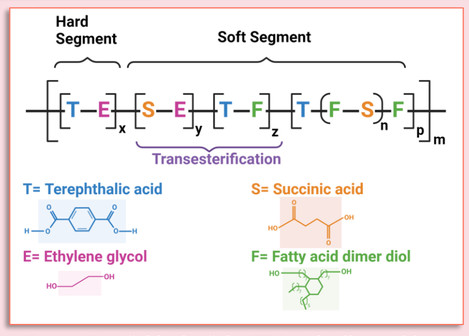

Figure 6: Soft block of the TPC with all possible sequences shown in one figure all together

Thermal properties

- **Increased soft block wt%:** Prevents crystallization, enhances transparency (Fig.5(a)-(b)).
- **Transesterification:** Disrupts regular structure, forms new structures.

Adhesion properties

- **Adhesion tests:** Polymer adhesion comparable to scotch tape, better than sticky note. (Fig. 8)
- **Consideration:** Unknown glue layer thickness in commercial products may affect results.
- **Conclusion:** Good adhesive for light use, no residue upon removal.

Structural analysis

- **^{1}H-NMR and ^{13}C-NMR** (Fig. 5): Confirm expected material formation
- **Calculations:** Show higher soft block wt% than initially added.
- **Transesterification:** Leads to additional polymer chain formations (Fig. 6 and 7).

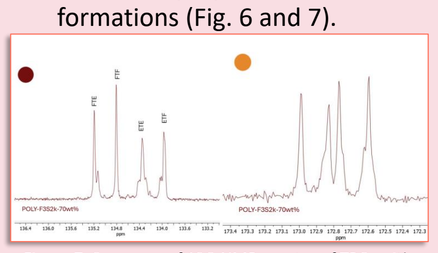

Figure 7: Summary of 13C-NMR spectra of TPCs with magnifications of the key areas for sequence analysis. (left) represents the sequences FTE, FTF, ETE, and ETF, which can be used for hard block length calculations. (right) represents the sequences FSE, FSF, ESE, and ESF, which proves the presence of transesterification.

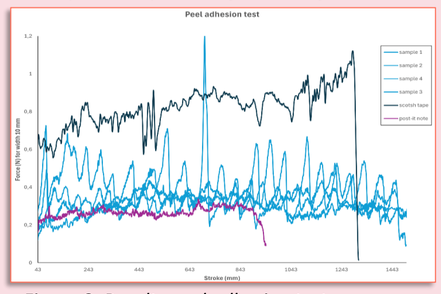

Figure 8: Results peel adhesion test

5. CONCLUSION

- **^{1}H-NMR and GPC:** Confirmed expected oligomer structures.
- **Optimal conditions with catalyst:** 2 hours at 190°C (argon) and 3 hours at 220°C (vacuum)
- **Without catalyst:** required longer times and higher temperatures
- **rPET upcycling and transesterification:** Confirmed by 1H-NMR and 13 C-NMR, led to additional polymer structures.
- **High soft block wt% (>70%):** Material becomes amorphous; decreases strain at break and maximum stress.
- **Adhesion behavior high SB wt%:** Tacky, glue-like useful for flexiple, sticky applications.

Figure 9: (left) synthesized oligomer, (right) synthesized TPC Material with 60 SB wt% and 80 SB wt%

Figure 10: (left) tensile test of a sample (right) TPC materials of high (left to right: 70-80-90) SB wt% before drying in a vacuum oven overnight

REFERENCES

[1] Karanastasis, A. A., Safin, V., Damodaran, S., & Pitet, L. M. (2022). Utility of chemical upcycling in transforming postconsumer PET to PBT-Based thermoplastic copolyesters containing a renewable Fatty-Acid-Derived soft block. *ACS Polymers Au*, *2*(5), 351–360. https://doi.org/10.1021/acspolymersau.2c00019
[2] *Scientific image and illustration software | BioRender*. (n.d.). https://biorender.com/

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De opleiding industrieel ingenieur is een gezamenlijke opleiding van UHasselt en KU Leuven