Enzymatic degradation of PET plastic

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Motivation

- Polyethylene terephthalate (PET) is one of the most common plastics produced worldwide; it is found in increasing amounts in the environment
- Environmental factors controlling enzymatic plastics degradation are incompletely understood
- Additives in commercial plastics impart large, but mostly poorly characterized, variability in enzymatic degradation kinetics

Research questions:

- What are the effects of temperature and pretreatment on the enzymatic degradation of PET?
- Does degradation change the spectral fingerprint of PET?
- How different are the degradation kinetics of commercial PET compared to lab-grade PET?

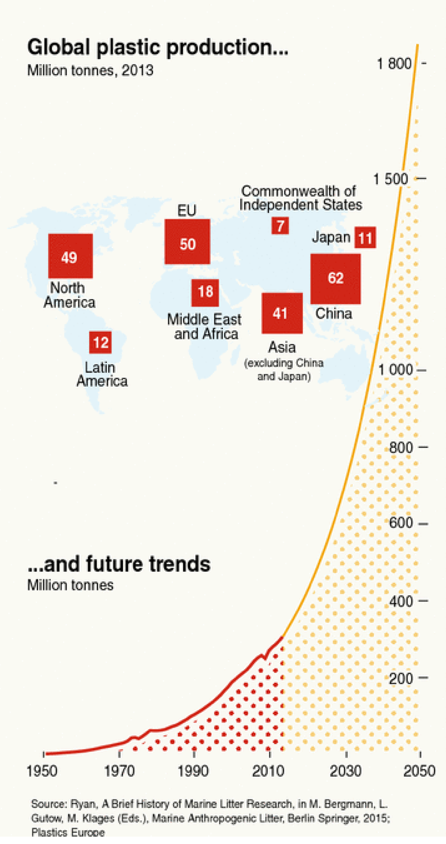

Figure 1. Global Plastic production trends.

Experimental design

Humicola insolens cutinase (HiC), a commercially available enzyme, is known to hydrolyze PET [1]. Enzyme activity is optimal at temperatures in the range 50-65°C and pH of 8.

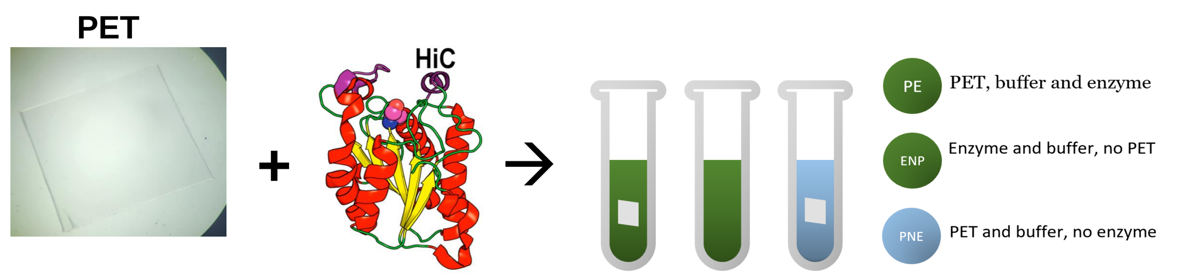

Figure 2. Schematic of experimental design and conditions.

- A phosphate buffer kept pH at 8 in all experimental tubes;
- PET sheets were cut into squares (1 x 1 cm) for incubation in the buffer solution with or without the HiC
- HiC top-ups occurred every 2 days to maintain enzyme activity, except in the control incubations without HiC
- Tubes were sacrificed at prescribed times and centrifuged at a G value of 1388 for 1 hour at 7°C, for experiments lasting more than 4 weeks long
- Plastic pieces were cleaned with Tween detergent solution and water, then air dried before weighing

Analyses:

- Mass loss
- Fourier Transform Infrared Spectroscopy (FTIR)
- Scanning electron microscopy (SEM)
- Differential Scanning Calorimetry (DSC)
- Tensile strength
- Thermogravimetric Analysis (TGA)

Experimental series

Baseline incubation
PET + HiC at 40°C for 16 weeks; sampling every 2 weeks

Temperature
PET + HiC at 25°C for 16 weeks; sampling every 2 weeks;
PET + HiC at 55°C for 10 days; sampling every 2 days

Pretreatments
Pre-incubation freeze-thaw cycles (FTCs) from -12°C to +40°C for 6, 16, and 26 consecutive FTCs; then incubation with HiC for 4 weeks at 40°C and sampling every 2 weeks

Pre-incubation exposure to extreme temperatures of -70°C and +55°C for 1 week; then incubation with HiC for 4 weeks at 40°C and sampling every 2 weeks

Consumer-grade PET
Square PET plastic pieces cut from consumer-grade water bottles: blue transparent 100% recycled PET (BL WB) and clear transparent PET (CL WB); incubation with HiC at 55°C for 10 weeks and sampling every 2 weeks

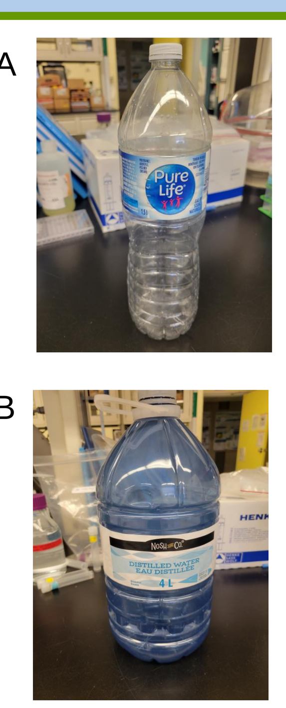

Figure 3. Consumer-grade PET: A) clear water bottle (CL WB), B) blue water bottle (BL WB).

Temperature

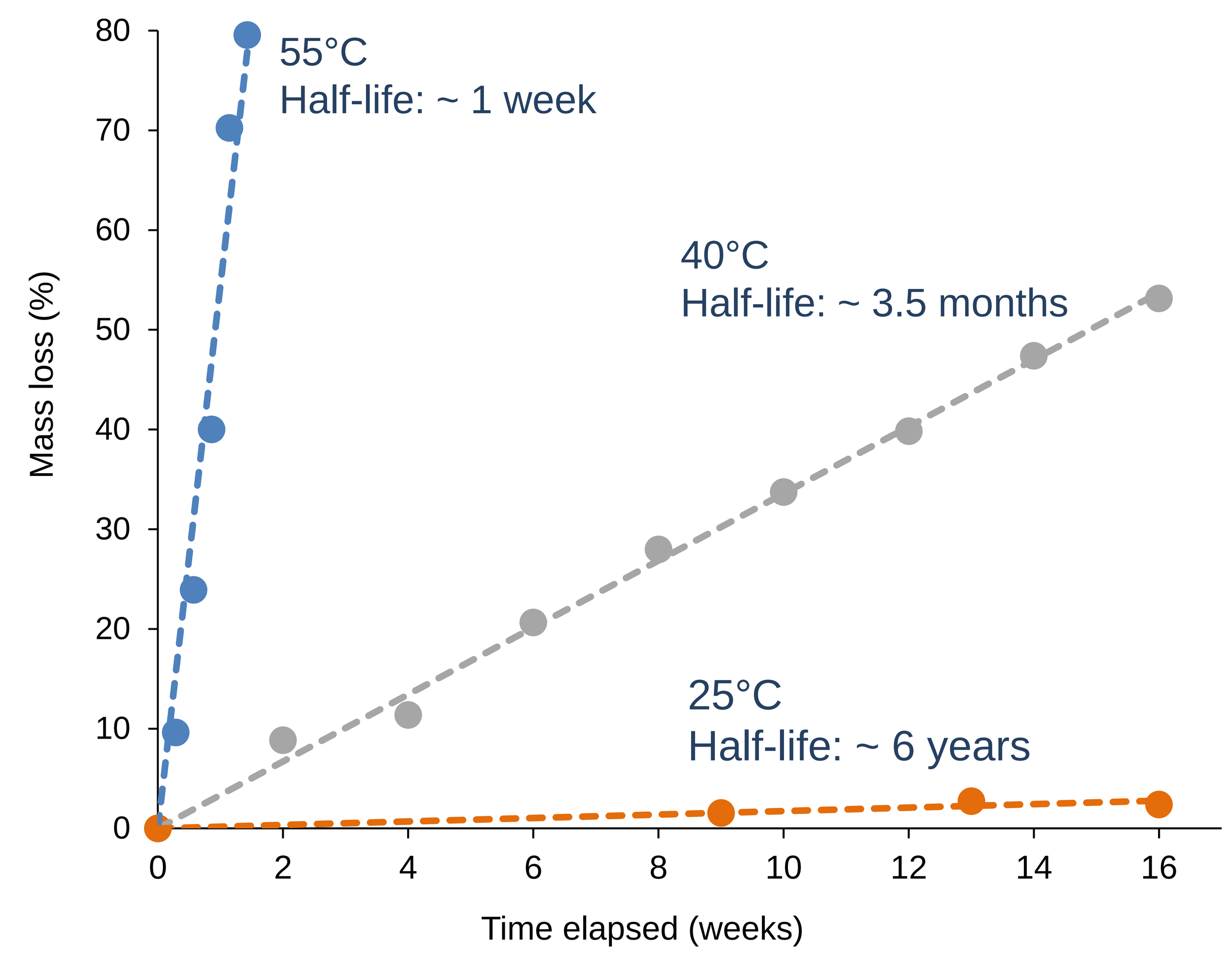

Figure 4. PET mass loss versus time at 25°C, 40°C and 55°C. Half-life values are derived from the linear regressions.

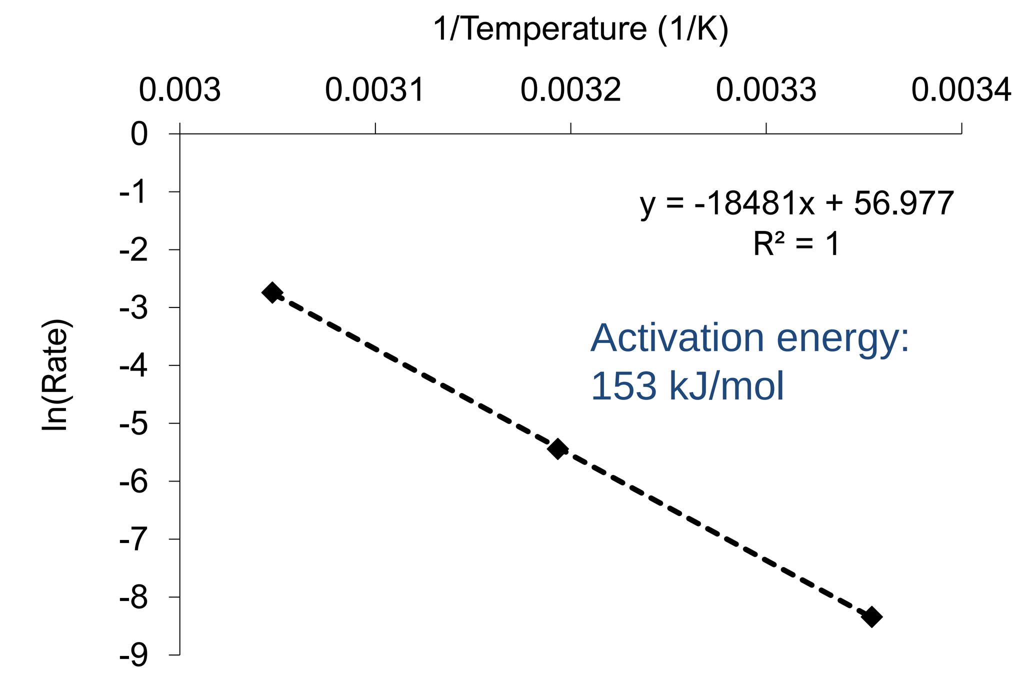

Figure 5. Arrhenius plot for PET degradation by HiC (data from Figure 4).

➢ Literature-reported enzymatic hydrolysis rates range from 20 to 150 kJ/mol → the 153 kJ/mol activation energy is on the upper end for hydrolysis

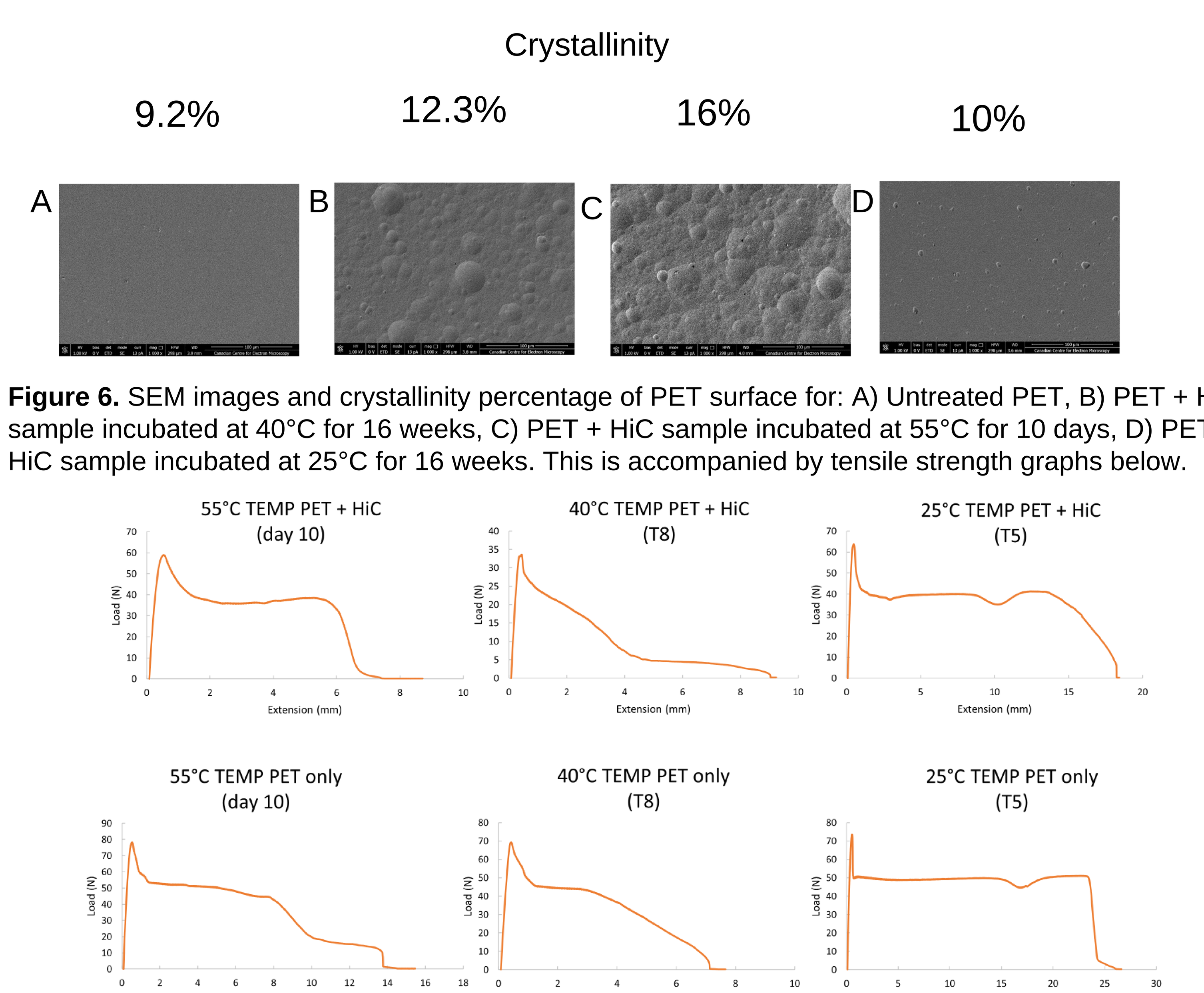

Figure 6. SEM images and crystallinity percentage of PET surface for: A) Untreated PET, B) PET + HiC sample incubated at 40°C for 16 weeks, C) PET + HiC sample incubated at 55°C for 10 days, D) PET + HiC sample incubated at 25°C for 16 weeks. This is accompanied by tensile strength graphs below.

Pretreatments

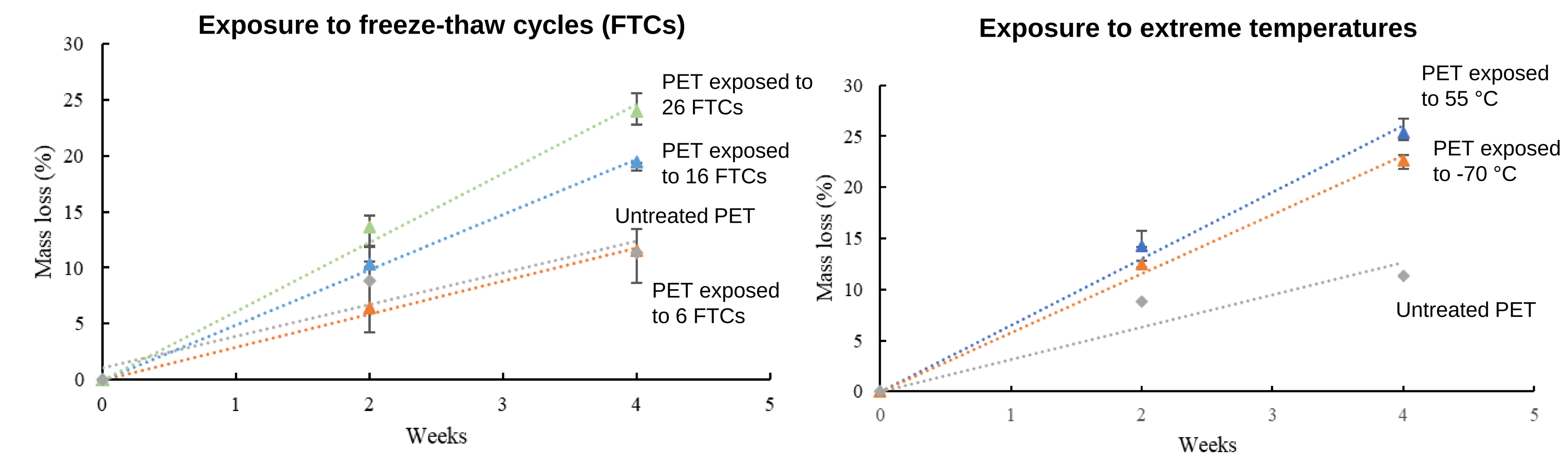

Figure 7. Effect of pretreatments on PET mass loss observed versus time during incubation with HiC at 40 °C: A) Effect of number of freeze-thaw cycles (FTCs). B) Effect of exposure to extreme temperatures.

➢ Exposure to freeze-thaw cycles and extreme temperatures enhance the degradation rate relative to untreated PET
➢ Interpretation: pretreatments are inducing structural defects, supported by decreases in tensile strength and changes to crystallinity

FTIR

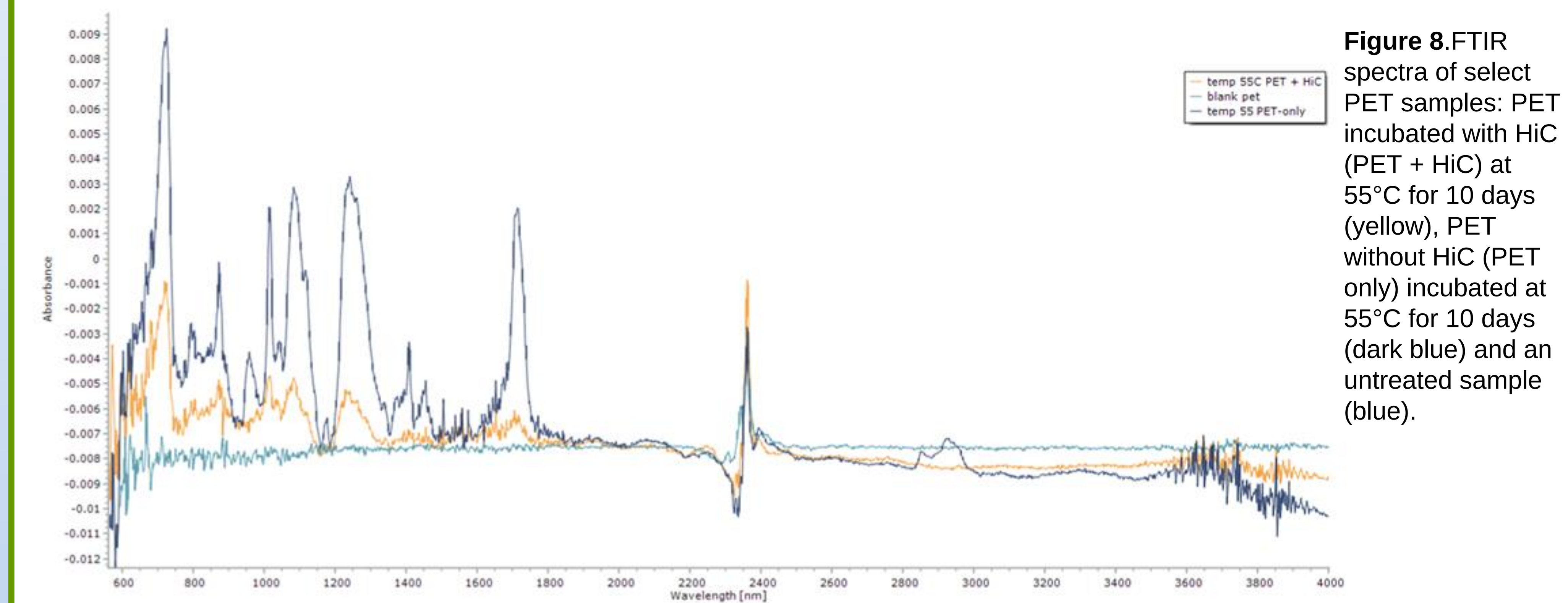

Figure 8. FTIR spectra of select PET samples: PET incubated with HiC (PET + HiC) at 55°C for 10 days (yellow), PET without HiC (PET only) incubated at 55°C for 10 days (dark blue) and an untreated sample (blue).

Conclusions

- Activation energy of lab-grade PET degradation by HiC is 153 kJ/mol:
  → very strong temperature dependence
- FTIR spectra of PET change during enzymatic and thermal exposure
- Freeze-thaw cycles and exposure to extreme temperatures accelerate PET degradation:
  → highly variable degradation kinetics in environmental systems
- Consumer-grade PET degrades much slower than lab-grade PET:
  → plastic additives (and other fabrication processes) alter degradation kinetics, making consumer-grade PET in-comparable to laboratory grade PET
  → PET should be classified by crystallinity and source to improve comparability within the field

Commercial PET

No measurable mass loss was observed for incubations of commercial-grade PET (both CL WB and BL WB) after 10 weeks at 55°C

➢ Implication: high variability in degradability of (micro)plastics expected even for the same polymer due to additives (and manufacturing methods).

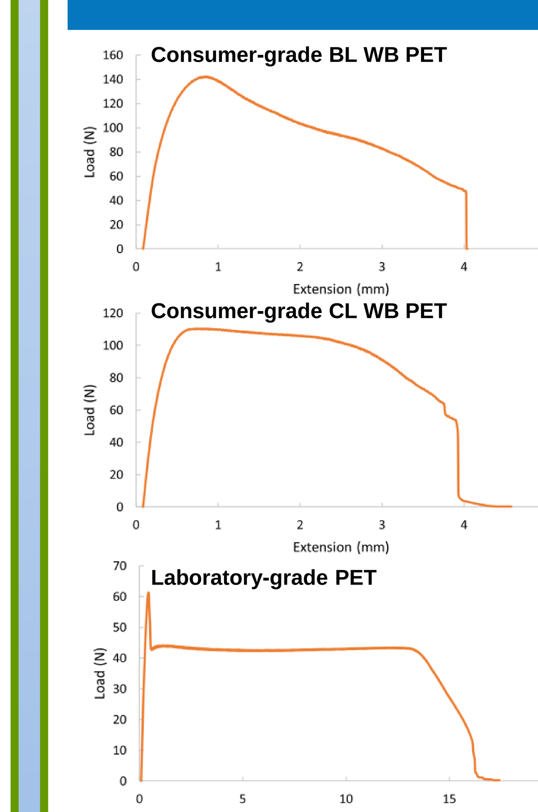

Figure 9. Tensile strength graphs of consumer-grade BL WB (top), consumer-grade CL WB (middle) and laboratory-grade PET (bottom).

Acknowledgments

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