Sustainable Biocomposites from a Biobased Engineering Thermoplastic and Biocarbon through Additive Manufacturing

ELIZABETH DIEDERICHS[1,2], MAISYN PICARD[1,2], BOON PENG CHANG[1], MANJUSRI MISRA[1,2], DEBORAH F. MIELEWSKI[3] AND AMAR MOHANTY[1,2]

[1]Bioproducts Discovery and Development Centre, University of Guelph, Canada
[2]School of Engineering, University of Guelph, Canada
[3]Research and Innovation Center, Ford Motor Company, Dearborn, MI

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INTRODUCTION

- **3D printing or additive manufacturing** is a fast-growing field with the potential for new innovative methods of manufacturing, rapid prototyping and production

- Additive manufacturing can be used in the automotive field for **cost-effective, lightweight, and highly customizable parts** for both in-vehicle components and assembly tools

- For fused deposition modelling (FDM) to continue to succeed in industry, a **broader range of feedstock materials** need to be developed to increase the variability and use of FDM

INTRODUCTION

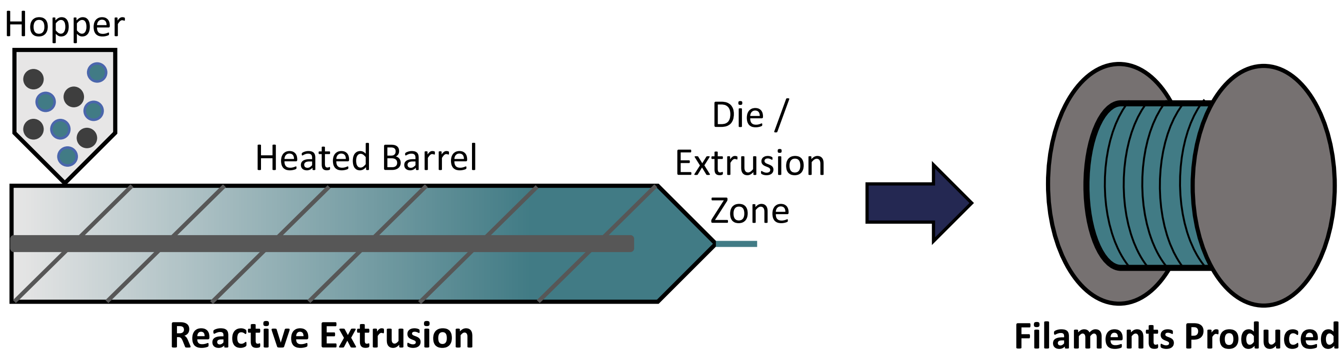
- Sorona® by DuPont is a **biobased engineering thermoplastic**
  - Brand of polymer, poly(trimethylene terephthalate) (PTT), used in this work
  - To the author's best knowledge this work represents the **first time use** of PTT for 3D printing

- It has various applications, particularly in the textile and automotive industries, such as [1]:
  - Carpets
  - Fabrics (i.e. seat covers)
  - Air conditioning vents
  - Electronic components

[1] DuPont, Renewable Sourced Automotive Interior Materials, 2019

FILAMENT FABRICATION

- Reactive extrusion was performed on a Leistritz twin screw extruder
- Processing conditions were modified to **optimize filament** (increase filament diameter and consistency):
  - Barrel temperature was slightly decreased from standard 250 °C [2]
  - Hopper feed rate was increased
  - Collector speed was decreased

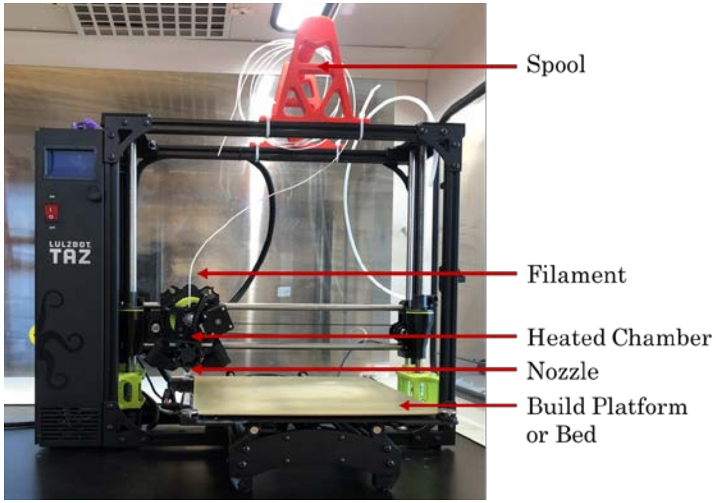


Schematic of filament fabrication via reactive extrusion *

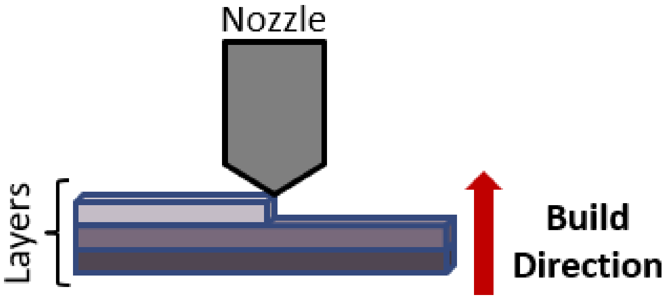
[2] Myllytie et al., *ACS Sustain. Chem. Eng.*, 2016
* Drawn by author using PowerPoint

FUSED DEPOSITION MODELLING (FDM)

- Method of **additive manufacturing** / **3D printing**
- Thermoplastic filament is extruded **layer by layer** to build parts in the Z-direction
- Beneficial for **rapid prototyping** and **complex part manufacturing** [3]
- Extensive uses in many industries, such as the automotive industries



BDDC Lulzbot Taz 6 printer



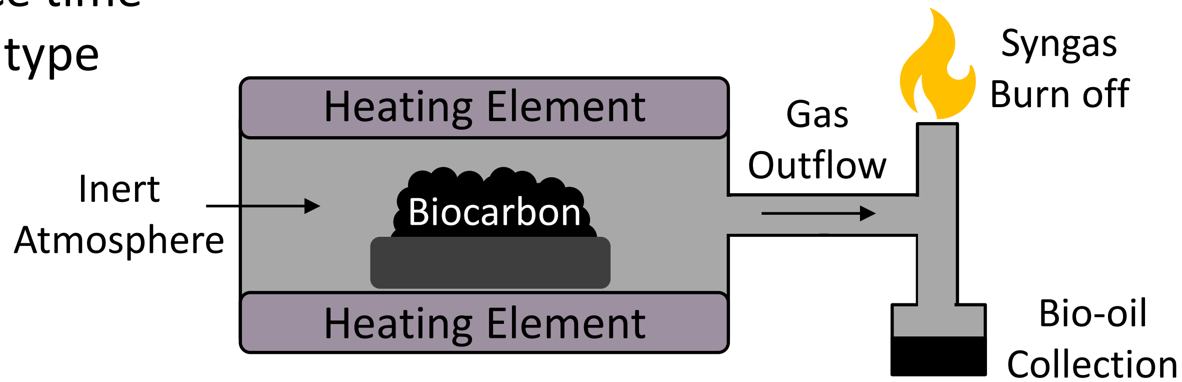
Schematic of layer deposition in FDM *

[3] Bogue, *Assem. Autom.*, 2013
* Drawn by author using PowerPoint

BIOCARBON PRODUCTION

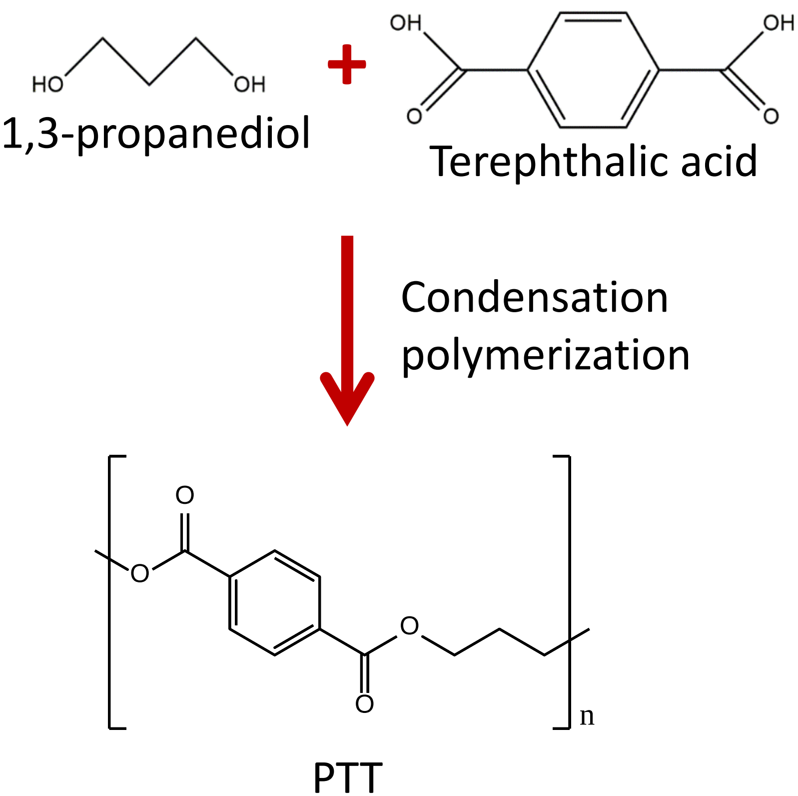
- Pyrolysis is the thermochemical conversion of biomass in an inert atmosphere to **biocarbon, syngas, and bio-oil**

- Properties of biocarbon are dependent on: [4]
  - Temperature of pyrolysis
  - Heating rate
  - Residence time
  - Biomass type



Schematic of pyrolysis *

POLY(TRIMETHYLENE TEREPHTHALATE) (PTT)



Synthesis reaction of PTT *

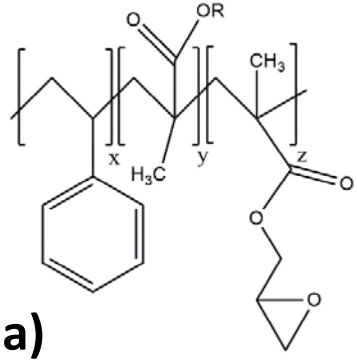
- **Engineering thermoplastic**
- Produced from 1,3-propanediol and terephthalic acid
- 1,3-propanediol can be derived from corn (Bio-PDO)
  - Sorona® PTT (DuPont) is **37 wt% biobased** [5]
- Similar mechanical properties to nylon and chemical properties to PET [5]

* Drawn by authors using ChemDraw Ultra

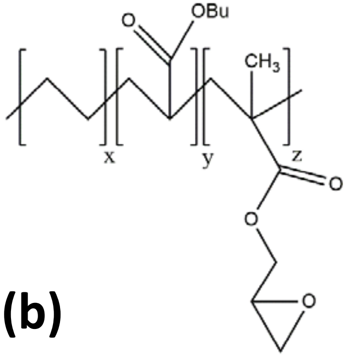
[5] Kurian, *Natural fibers, Biopolymers, and Biocomposites*, 2005

MODIFICATIONS TO IMPROVE PRINTABILITY

- Additives can be beneficial to improve materials printability and properties
- A **chain extender** was used to increase the melt stability of the filament during processing
  - Poly(styrene-acrylic-*co*-glycidyl methacrylate) **(SA-GMA)**
- An **impact modifier** was used to increase the melt strength and impact properties of the polymer
  - Poly(ethylene-n-butylene-acrylate-co-glycidyl methacrylate) **(EBA-GMA)**
- Produced **printable thick, consistent filaments**



(a)



(b)

Chemical structures of (a) SA-GMA and (b) EBA-GMA *

* Drawn by authors using ChemDraw Ultra

MISCANTHUS BIOCARBON (BC)

- *Miscanthus* biocarbon was used in this work
  - Pyrolyzed at **650 °C**
  - Ball milled for **24 hours**

Biocarbon powder

- Wang et al. investigated the properties *Miscanthus* biocarbon [6]
  - 24 h ball milled BC with a **particle size of 0.9 µm**
  - Lengthier ball milling times reduced the variability in particle sizes
  - Longer ball milling was found to increase impact strength of composites

- 24 h ball milling BC was chosen to **optimize particle distribution** and **mechanical properties**

[6] Wang et al., *BioResources*, 2018

PTT AND BIOCARBON BIOCOMPOSITES

- Myllytie et al. created biocomposites from **PTT** and lignin **BC** [2]

- With the addition of BC:
  - **Weight reduction** was found due to lower density BC
  - Dimensional stability improved
  - Heat deflection temperature **increased significantly**
  - **Tensile properties improved**
  - Impact properties decreased

  - Addition of chain extender had more pronounced effects in the neat PTT blends than in the PTT/BC composites

[2] Myllytie et al., *ACS Sustain. Chem. Eng.*, 2016

FDM WITH SEMI-AROMATIC POLYESTERS

- **Limited use** of polyesters (ex. **PET**, **PTT**, and **PBT**) for FDM due to their crystallinity, hydrophilicity, and high melting temperatures [7]

- **Recycled PET for FDM** [8]
  - Printability of recycled PET was superior to that of neat PET (likely due to influence of additives)
  - Mechanical properties of FDM samples ~ 50% the value of injection molded samples

PET = poly(ethylene terephthalate)
PTT = poly(trimethylene terephthalate)
PBT = poly(butylene terephthalate)

- **PBT and carbon nanotubes/graphene** [9]
  - Abrasive materials (such as these fillers) resulted in extreme nozzle wear and issues with clogging during printing
  - Additional work into modification of properties, such as flowability, crystallinity and shrinkage properties is needed

[7] Zander et al., *Addit. Manuf.*, 2019
[8] Zander et al., *Addit. Manuf.*, 2018
[9] K. Gnanasekaran et al., *Appl. Mater. Today*, 2017

FDM WITH BIOCARBON

- BC addition can:
  - **Increase applications** of polymers (i.e. into housing or automotive parts) [10]
  - Increase the **bio-based content and sustainability**
  - Reduce weight/density

- **PLA and wheat stem BC** [10]
  - High loadings of BC (30 wt%) caused clogging and impeded success of FDM printed parts
  - BC particles caused wear on FDM nozzles
  - FDM **increased the interaction** between the BC and PLA, as compared to injection molded composites

[10] Ertane et al., *Advances in Tribology*, 2018

FDM WITH BIOCARBON

- **Recycled PET and packaging waste BC** [11]

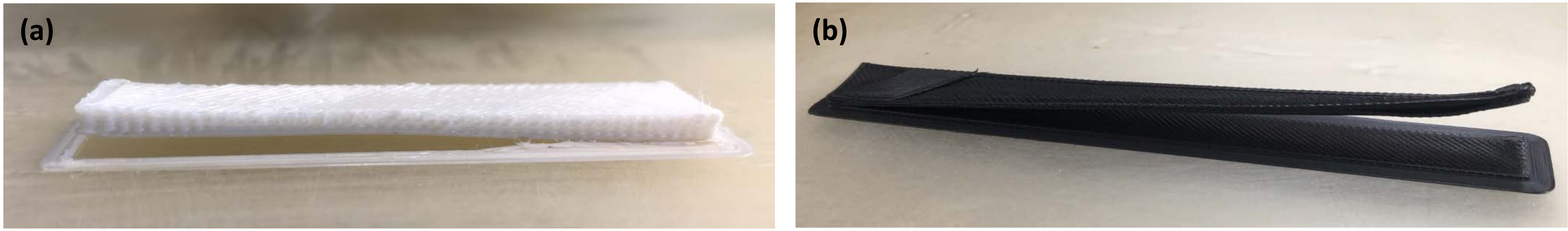
- BC addition:
  - Significantly increased tensile properties
    - 32 % increase in tensile strength with 0.5 wt% BC
    - 60 % increase in tensile modulus with 5 wt% BC
  - **Decreased coefficient of linear thermal expansion** (CLTE), therefore improving dimensional stability and **reducing internal stresses and warpage** in parts
    - 30 % reduction in CLTE with 1 wt% BC

[11] Idrees et al., *ACS Sustainable Chem. Eng.*, 2018

OPTIMIZATION FOR FDM

- It was essential to **optimize processing** and printing parameters for successful FDM

- Optimizing **processing conditions** and including **additives** were essential pre-printing modifications to create filaments suited to FDM
  - Issues with jamming and under/over-feeding were prevalent in non-ideal filaments



Challenges faced during before optimization of printing parameters: (a) warpage and (b) delamination

RESULTS (I)

- The optimal PTT/EBA-GMA/SA-GMA blend resulted in:
  - A **reduction in crystallinity** and **flowability**, and **improved filament diameter** that were crucial to successful FDM
  - Injection molded impact strength **increased significantly** from the neat PTT
  - Decreased mechanical performance in FDM samples compared to injection molded samples was seen and is a result of poor interlayer cohesion [12]
- This blend had the ability to print complex parts

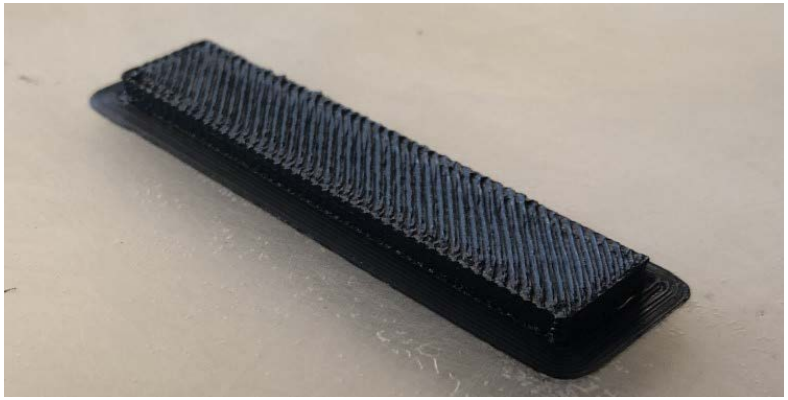
[12] Benwood et al., *ACS Omega*, 2018

RESULTS (II)

- ❖ BC composites were successfully printed at two BC loadings
- ❖ BC decreased impact properties but improved tensile properties

- ❖ Coefficient of linear thermal expansion decreased with increased BC content

- ❖ FDM samples with higher loadings of BC had poor surface finish



PTT/EBA-GMA/SA-GMA/BC FDM part

CONCLUSIONS

- Essential parameters for the success of PTT in FDM included **thick consistent filaments**, reduced crystallinity and reduced flowability

- The inclusion of EBA-GMA and SA-GMA additives permitted **printability of PTT** and BC was successfully incorporated to make printable biocomposites

- **Poor cohesion between layers** in FDM was a main contributor to reduced mechanical properties as compared to injection molded part

- This work featured a **new PTT blend** and **biocomposites** with strong potential as novel **FDM feedstocks**

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