

1.0 Introduction/Aims

Plastic Waste Issue

- Experts predict that by 2050 there will be more plastic in the planet's water than fish, thus it is necessary to recycle materials using the circular economy model to increase its overall lifespan. This essentially means that, in practice, it implies reducing the plastic waste to a minimum.^[1]

Proposed Solution

- Use plastic waste from coffee cups and transform it into 3D printing filament. The new 3D printing filament will be compared to traditional materials and studied the mechanical and physical characteristics.
- Use the new 3D printing filament to develop novel sensors that can be used for the detection of several compounds that can pollute the environment, such as traces of antibiotics & pesticides.

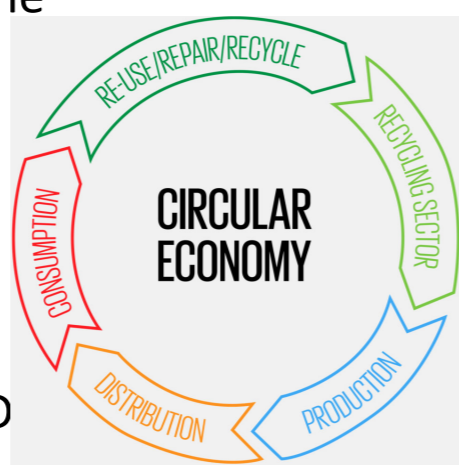


Figure 1. Diagram showing aspects of circular economy

2.0 Materials

Non-MIP particles and dopamine MIP

- Non-MIP consists of a mixture of methacrylic acid (MAA), ethylene glycol dimethacrylate (EGMA), 4-4'-azobis (4-cyanovaleric acid), water and methanol. In this case, 4-4'-azobis (4-cyanovaleric acid) is the initiator for this reaction whereby it breaks down and releases nitrogen, which is a huge thermodynamic driving force to break down and produce two free radicals which contains a nitrile group. The free radicals are both tertiary and delocalized.^[2]
- For the dopamine MIP, the mixture is the exact same as described above for non-MIP, however, there is an extra addition of dopamine in the mixture.

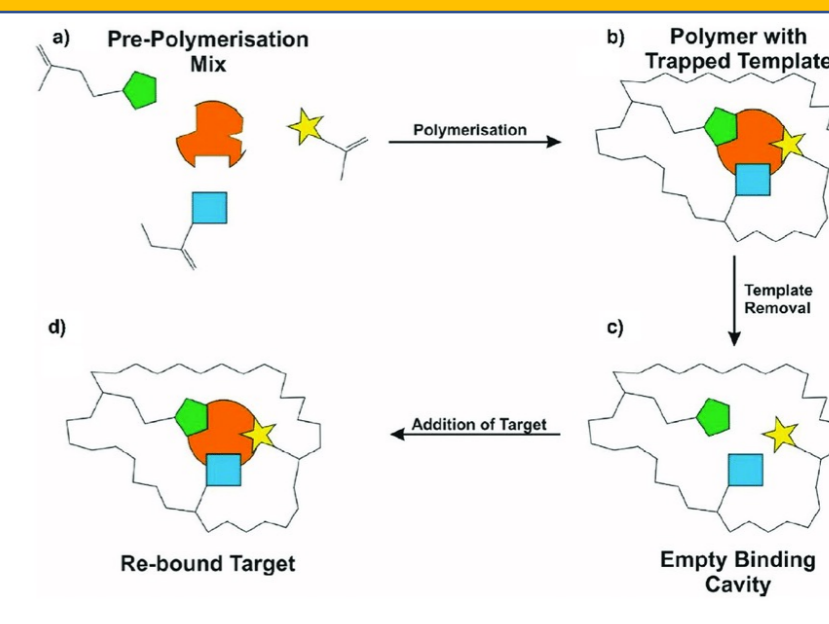


Figure 2. General diagram of MIPs

3D printing filament

A range of different materials were experimented with to discover the best material to produce sensors. These included PLA, recycled PLA, combination of pre constructed non-MIP and pre-bought ABS pellets.

3.0 Methods

Production of non-MIP (reference polymer) and dopamine MIP^[3]

- Mixture of MAA, EDGMA, 4,4'-azobis(4-cyanovaleric acid) is dissolved in methanol and water together (An addition of template molecule dopamine at this stage for the synthesis of dopamine MIP).
- Mixture was degassed with N₂ for 5 minutes and heated up to 65°C for 12 hours to initiate the polymerization process.
- After polymerization, the polymer is ground using a pestle and mortar to obtain microparticles and dried in the oven at around 65°C.
- An addition step is required for the synthesis of dopamine MIP, dopamine needs to be removed from the obtained MIP powder by continuous extraction with a 1:1 ratio mixture of methanol and water. The extracted filtrate can be tested using UV-spectroscopy to determine the concentration of dopamine within. The more extractions performed, the concentration of dopamine decreases. However, some MIP powder is lost through every extraction so a compromise must be made upon the number of extractions performed.

TGA, DSC and FT-IR analysis

The samples: dopamine MIP, non-MIP, ABS pellets + non-MIP, recycled PLA and normal PLA underwent the TGA, DSC and FT-IR analysis to determine mechanical and physical characteristics, such as point of degradation, glass transition, crystallization, melting point etc., In addition, quality control of the proposed specimens.

3D printing filament extruder

- Plug the extruder into mains power
- Switch on the heater element and adjust the temperature to desired. For the ABS pellets that was used, the desired temperature is around 180°C – 200°C and PLA is around 165°C – 175°C.
- Once the temperature has been reached, the pellets can be placed into the hopper and the screw motor and fan can be turned on.
- After a few minutes, plastic filament starts to extrude through the nozzle.
- The tolerance of the filament can be changed by adjusting the temperature. Whereby, higher the temperature, the thinner the filament and the lower the temperature, the thicker the filament.



Figure 3. Image of 3D printing filament extruder

4.0 Results

TGA analysis results

- A comparison of the normal PLA, recycled PLA, non-MIP and dopamine results are shown below respectively.
- Normal PLA is more stable than the recycled PLA with the highest point of degradation around 360°C circled in green in figure number 4. TGA measures weight changes as a function of temperature and time and the weight change that we can witness from the TGA graphs can be caused by decomposition and oxidation reactions as well as physical processes such as sublimation, vaporization and desorption.
- UV-Vis absorbance graph to show that majority of the dopamine was removed from the MIP over the course of around 4/5 extractions

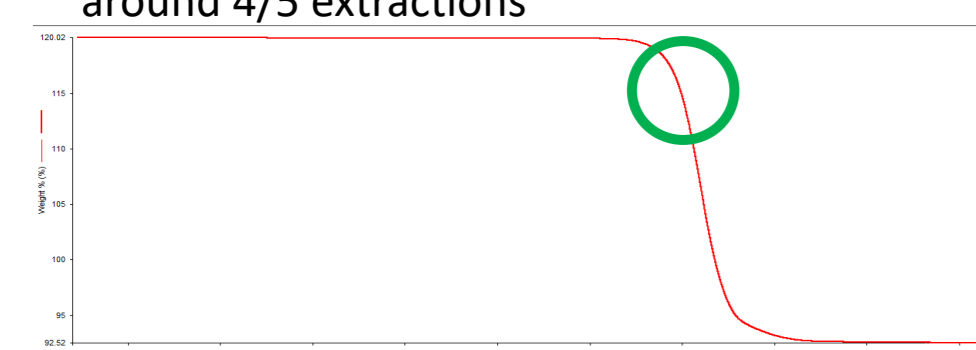


Figure 4. TGA data analysis for normal PLA.

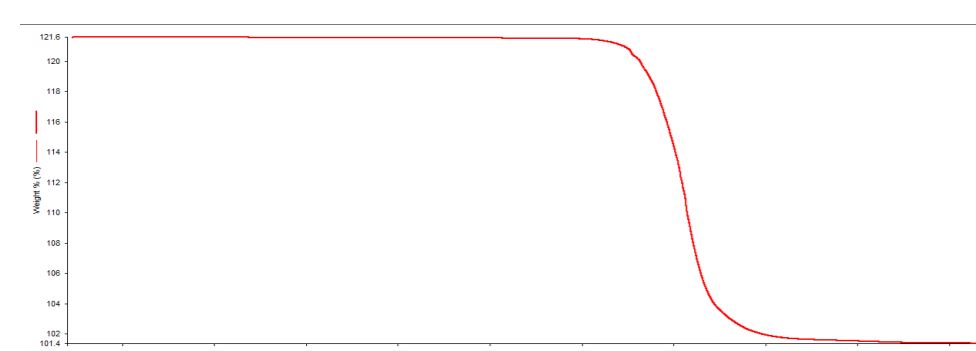


Figure 5. TGA data analysis for recycled PLA.

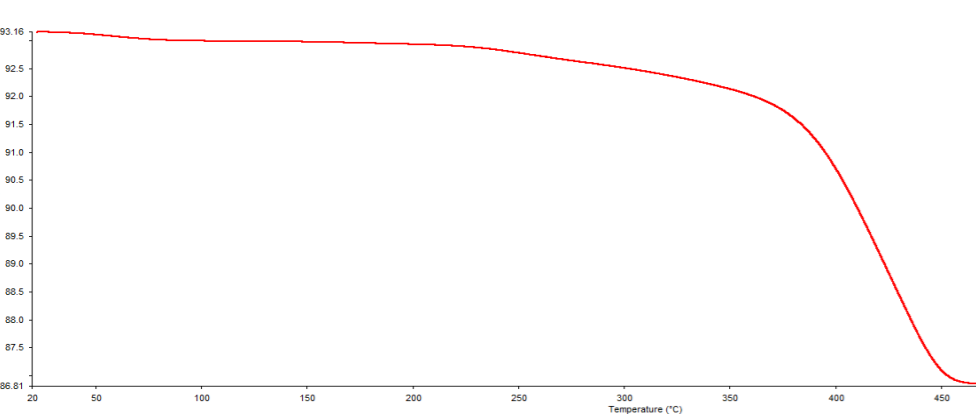


Figure 6. TGA data analysis for non-MIP.

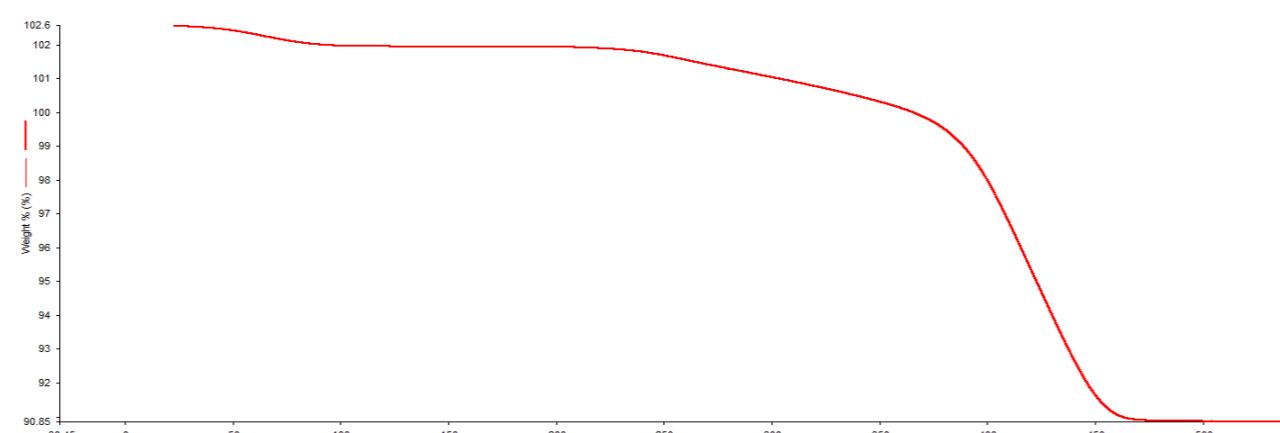


Figure 7. TGA data analysis for dopamine MIP.

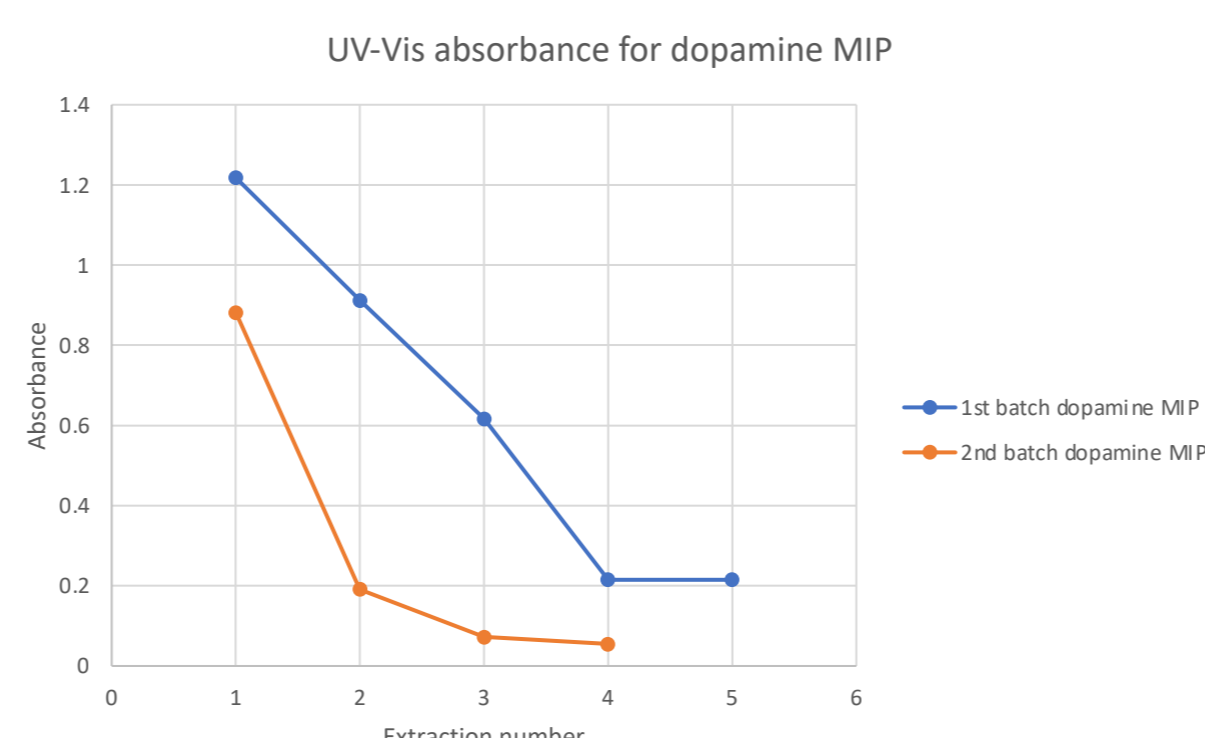


Figure 8. UV-Vis absorbance graph for dopamine MIP.

DSC analysis results

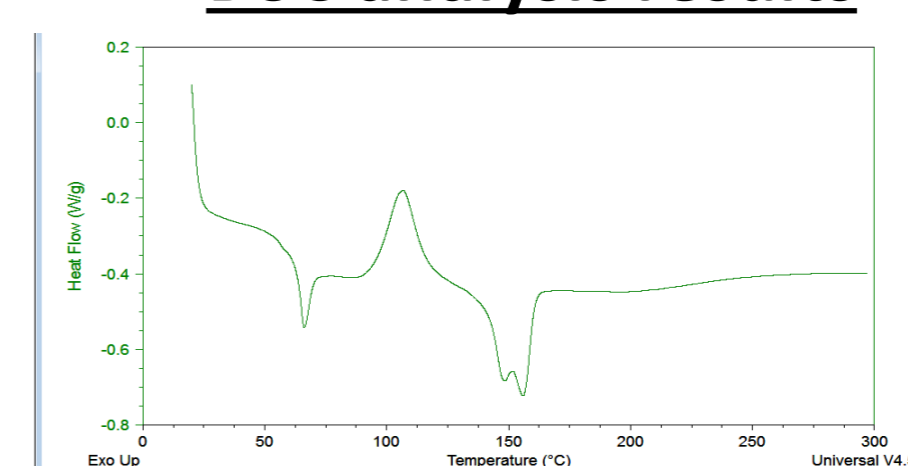


Figure 9. DSC data analysis for normal PLA.

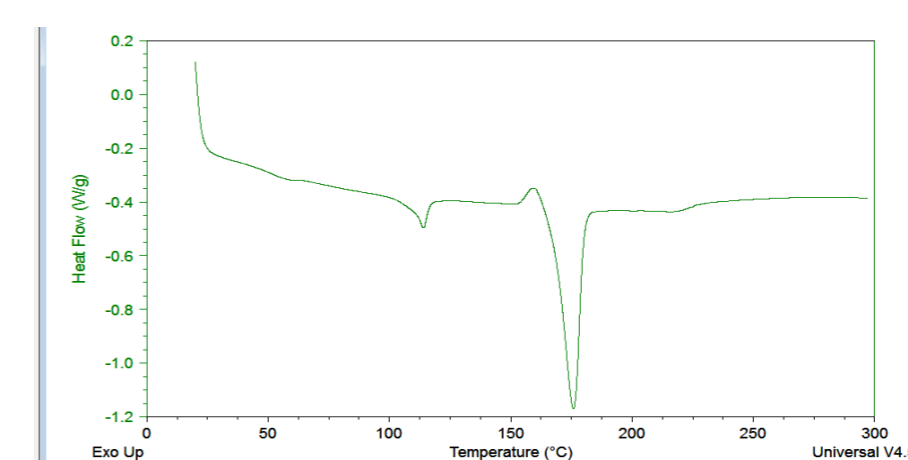


Figure 10. DSC data analysis for recycled PLA.

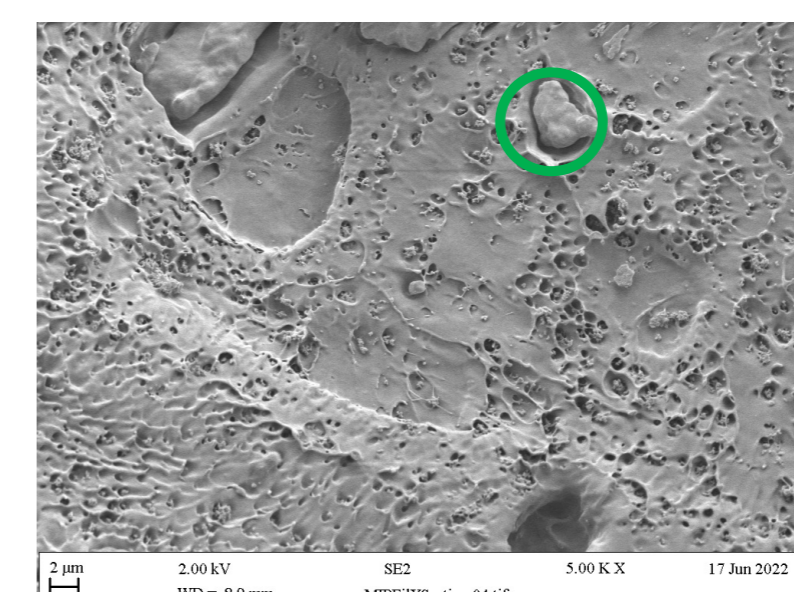


Figure 11. Cross section of MIP polymer incorporated into 3D printing filament

- A comparison of the normal PLA, recycled PLA and non-MIP&ABS pellets results are shown below respectively.
- DSC shows heat flow into or out of a sample and is measured as a function of temperature or time. This analysis can evaluate material properties such as melting point, purity, thermal stability, crystallization and many more
- Each peak/trough indicates a feature whereby the first initial section is the glass transition, crystallization, melting point, cross-linking and finally oxidation respectively.

5.0 Conclusion and future outlooks

- Ultimately this is what the MIP particles look like in figure 11 circled in green and eventually we would want the MIP powders to be incorporated into 3D printing filament to look like figure 11.
- Overall aim is to reduce the amount of plastic waste so this proposed solution can be advanced further to support the UN sustainable goals whereby it is a blueprint to achieve a better and more sustainable future for people and the planet.

1. <https://www.theguardian.com/business/2016/jan/19/more-plastic-than-fish-in-the-sea-by-2050-warns-ellen-macarthur>
 2. [https://www.wikiwand.com/en/4,4%27-Azobis\(4-cyanopentanoic_acid\)](https://www.wikiwand.com/en/4,4%27-Azobis(4-cyanopentanoic_acid))
 3. Introducing Thermal Wave Transport Analysis (TWTa): A Thermal Technique for Dopamine Detection by Screen-Printed Electrodes Functionalized with Molecularly Imprinted Polymer (MIP) Particles Marloes M. Peeters 1, Bart van Grinsven 2, Christopher W. Foster 1, Thomas J. Cleij 2 and Craig E. Banks 1

I would like to thank Newcastle University for the Climate Leadership Scholarship for the bursary for this internship. Furthermore, I would like to thank Dr Marloes Peeters for the assistance and direction for this project.