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Particle Fusion via Reactive Material Jetting:

Fabricating Functional Net-Shape Polymeric Structures with Varying Mechanical Properties

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1. Introduction: *Project Overview*

A ***novel method*** is introduced capable of overcoming issues associated with ***polymer manufacturing***.

2018	Tuck *et al.* [1] granted ***patent*** for process.
2019	PhD candidate recruited for development.
2020	Novel process christened ***Reactive Powder Bed Fusion (RPBF)***.

Research focus is on **process optimisation** and **material development** of reactive constituents:

- Thermoplastic polyurethane (TPU) powders
- Isocyanate formulations (Ink A)
- Polyol formulations (Ink B)

Advantages over traditional polymeric manufacturing:

- **Low temperature** process (<100 ° C)
- **Customisable** functionality + mechanical ***properties***
- All AM benefits including no tooling costs, **design freedoms, net-shape** parts

Intrinsic **challenges** associated with process:

- **Toxic** monomers
- **Clogged printheads** due to moisture-sensitive inks

[1] Tuck, C., Begines Ruiz, B., He, Y., Wildman, R. and Hague, R., 2018. Additive manufacturing. WO 2018/083500 Al.

2. Background: *Reactive Fusion Process*

Molar Ratio: Ink A **1 : 1** Ink B   Activation Temperature: ≥ 50 ° C

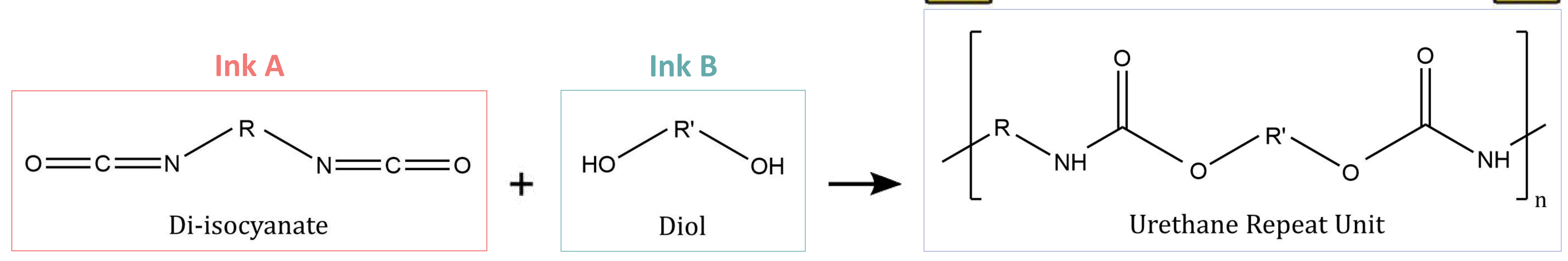

Figure 1: Reaction between Ink A (isocyanate-based) and Ink B (polyol-based) in the presence of a catalyst to form polyurethane.

Polymeric ***particles consolidate*** via ***chemical bonding*** and physical binding of highly ***reactive inks.***

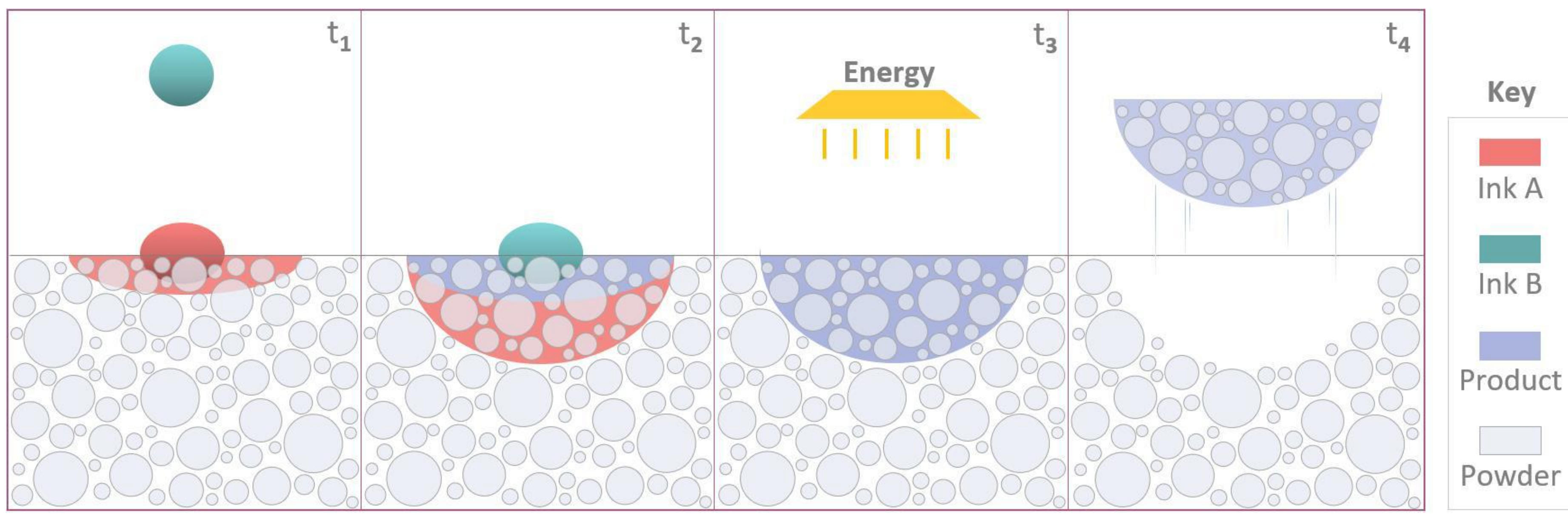

Figure 2: Two droplets of reactive ink selectively penetrate and consolidate the powder to form a three-dimensional part.

3. Methodology: *Research Process*

3.1 Print Suitability	3.2 Reactivity	3.3 Printing Trials	3.4 Optimisation
Ink Viscosity (4.1)	Reaction Time (4.2)	Ink Dynamics (4.3)	Mechanical Loading
Particle Morphology (4.1)	Conversion Level (4.2)	Particle Binding	Print Resolution

4. Results: *Material Development + Characterisation*

4.1 Reactive Ink + Powder Developments

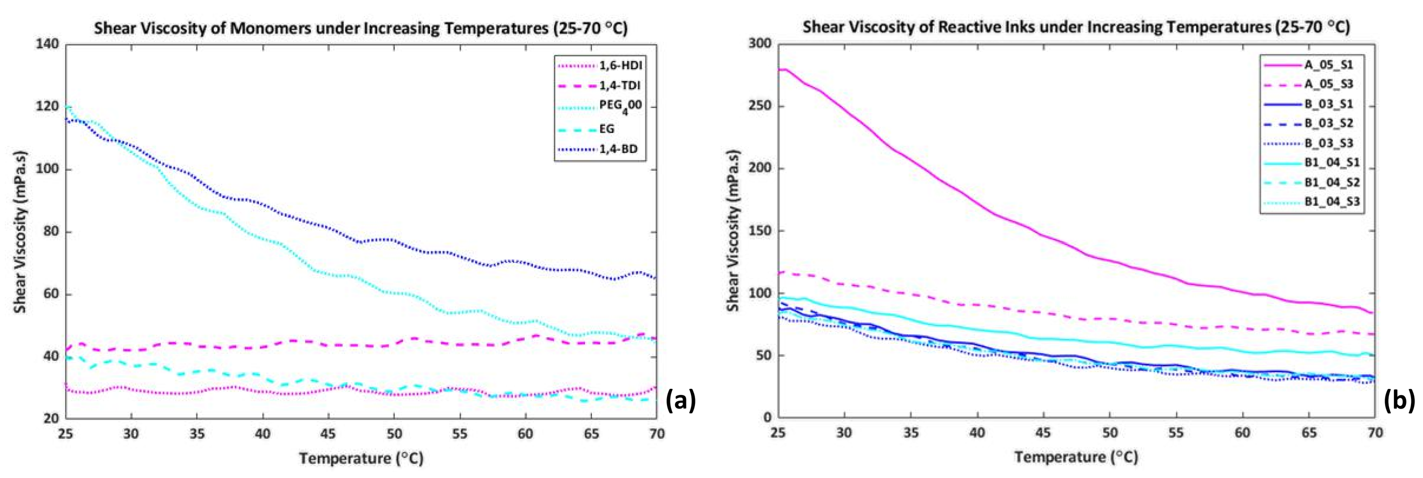

Figure 3: Shear viscosity against increasing temperature for (a) constituent monomers and (b) reactive inks.

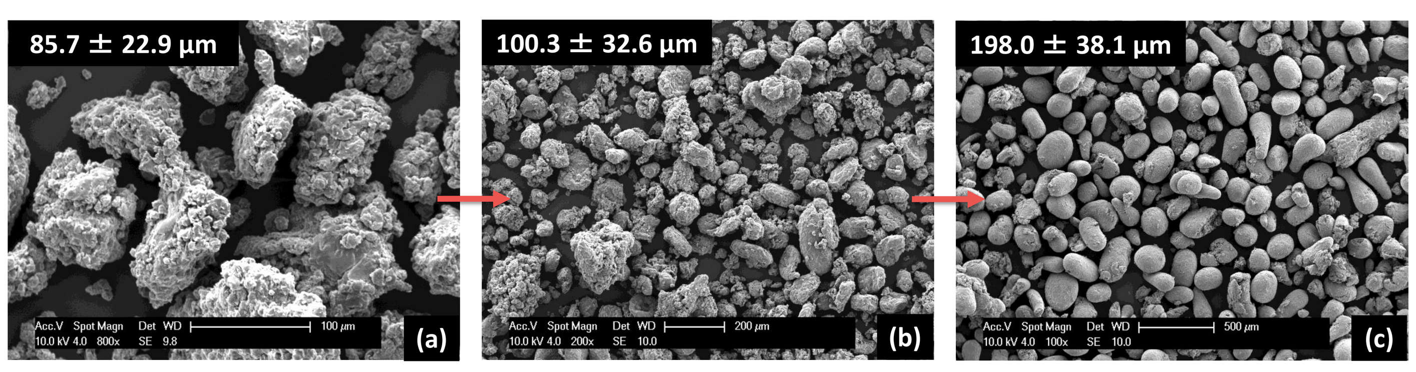

Figure 4: SEM images of TPU powder synthesised using the same process parameters and sodium dodecyl sulphate (SDS) at concentrations of (a) 0.45 wt% (*DP16*), (b) 0.30 wt% (*DP17*) and (c) 0.25 wt% (*DP18*).

4.2 Ink Reactivity Analysis

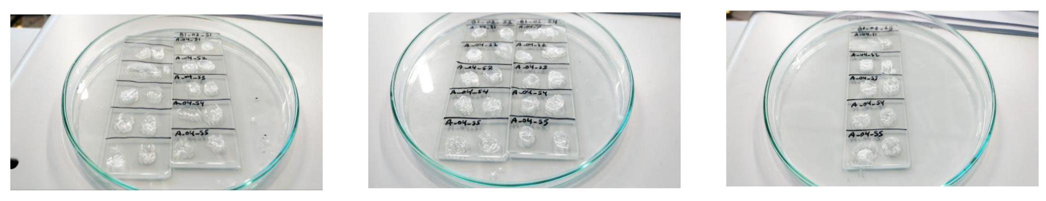

Figure 5: Droplet reaction tests for 5x samples of *B1_02* onto 5x samples of *A_04*.

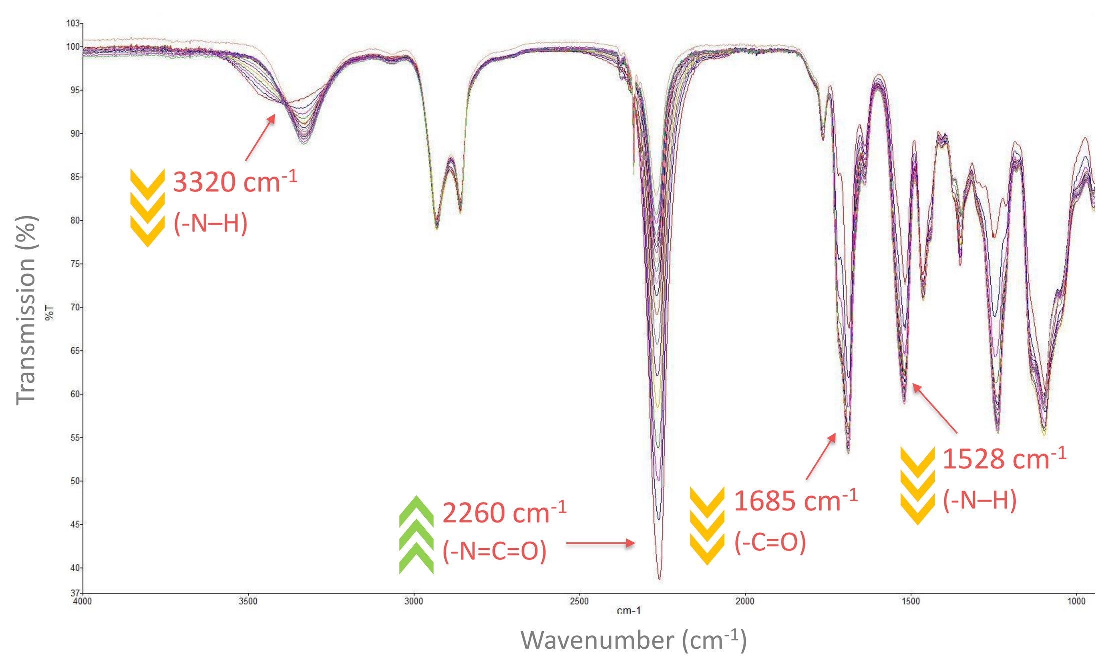

Figure 6: ATR FT-IR spectra of inks *A_05_S3* (pHDI/HDI) and *B1_04_S2* (PEG/EG/DBTDL) at time intervals of 0-2-4-6-9-12-15 mins (same sample throughout).

4.3 Sample Printing

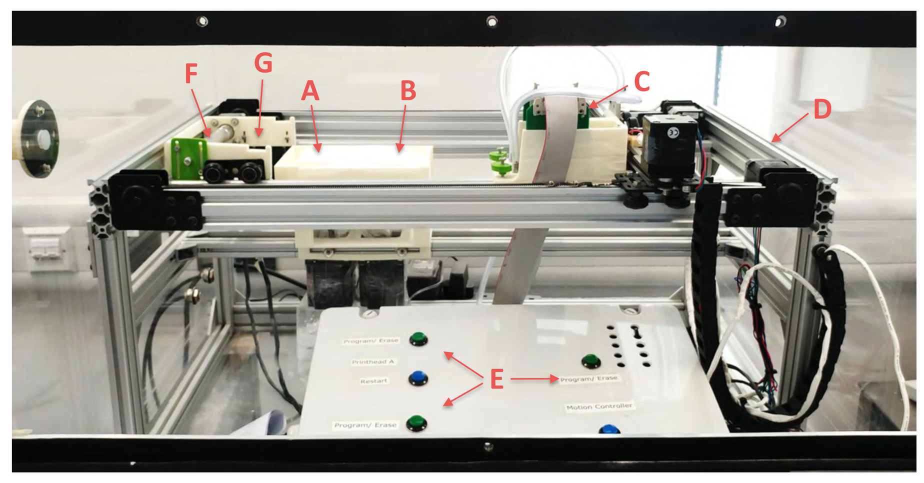

Figure 7: Dual-printhead 3D printer composed of (A) powder refill, (B) build platform, (C) dual-printheads, (D) frame, (E) controls box, (F) roller and (G) IR lamp.

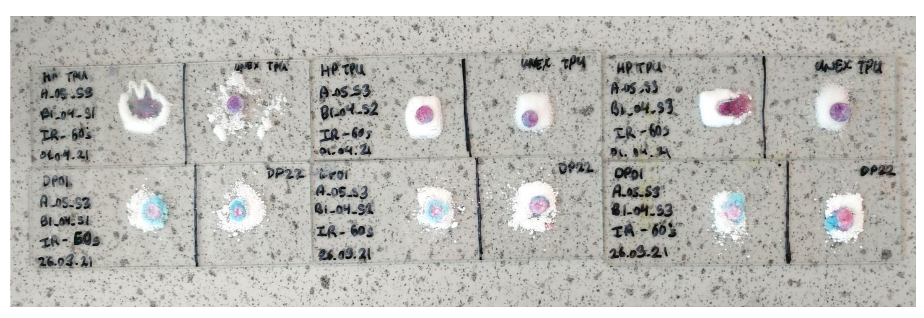

Figure 8: Printed samples of 3 ink combinations onto 4 TPU powders.

5. Discussion: *Critical Analyses*

5.1 Materials

Inks can be heated to 70 ° C so if viscosity is ≤ 50 mPa·s the ink is chosen for printing.

Surfactants help to form particles during synthesis, thus the critical micelle concentration (CMC) effects powder size.

5.2 Ink Reactivity + Polymerisation

Intermittent **FT-IR scans** of materials reacting in ambient conditions provides:

- Comparable **reaction times**
- Degree of **polymerisation**

Functional group transitions occur at:

- 2260 cm^{-1} (-N=C=O), indicating a **decrease in isocyanates** present
- 1685 cm^{-1} (-C=O), indicating the **formation of urethane linkages**.

5.3 Ink-to-Powder Interactions

Powders have unique packing densities and particle size distributions which create pores or channels that directly influence ink penetration.

6. Conclusions + Future Work: *Take Away*

Powder	Particle **size increases** and **roughness decreases** as surfactant concentration approaches CMC of SDS in water. (SDS_{CMC} = 0.26 wt %).
Inks	Reaction **time decreases** with ink **miscibility** and higher **catalytic concentrations** (1.3 wt%).
Product	**Poor mixing** of ink in reactive powder leads to **poor consolidation**. **Slow penetration** of ink at surface of commercial powder.

Next stages of work will focus on:

i. Broadening printable reactive ***inks portfolio***

ii. Printing complex, three-dimensional (3D) ***structures***

iii. Optimisating printing ***process parameters***

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