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Three dimensional ink-jet printing of biomaterials using ionic liquids and co-solvents

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1-ethyl-3-methylimidazolium acetate ([C_2C_1Im][OAc]) and 1-butyl-3-methylimidazolium acetate ([C_4C_1Im][OAc]) have been used as solvents for the dissolution and ink-jet printing of cellulose from 1.0 to 4.8 wt %, mixed with the co-solvents 1-butanol and DMSO. 1-Butanol and DMSO were used as rheological modifiers to ensure consistent printing, with DMSO in the range of 41-47 wt % producing samples within the printable range of a DIMATIX print-head used (printability parameter <10) at 55 °C, whilst maintaining cellulose solubility. Regeneration of cellulose from printed samples using water was demonstrated, with the resulting structural changes to the cellulose sample assessed by scanning electron microscopy (SEM) and white light interferometry (WLI). These results indicate the potential of biorenewable materials to be used in the 3D additive manufacture process to generate single-component and composite materials.

Introduction

Additive manufacturing (3D printing)[1] is able to produce objects for a wide variety of applications in a material-efficient fashion with little or no waste, and has shown particular benefit in areas of high-value and bespoke manufacture, such as for medical devices.[2] Further enhancements to the manufacturing process can be achieved by sourcing the base materials from biorenewable sources. Biopolymers such as cellulose, lignin, wood etc. are particularly promising materials to be used in additive manufacturing, as they are biodegradable, biocompatible, can be sourced from waste streams, and offer interesting physical and chemical properties.[3, 4] However, the low solubility of many biopolymers in water and other common solvents has limited their application to the additive manufacture process.[3, 5] Ionic liquids have recently been introduced as an effective class of solvent for the dissolution of these biopolymers.[3-6]

Cellulose is the most abundant component of lignocellulose.[7, 8] It is a linear syndiotactic polymer with D-glucopyranose (glucose) as the repeating unit attached by β-1,4-glycosidic bonds. Glucose, cellobiose and short oligomers of glucose (degree of polymerisation < 10 units) are soluble in water.[9] However, due to the presence of the strong glycosidic bonds and intra- and inter molecular hydrogen bonds, cellulose does not dissolve in water.[5]

Ionic liquids are defined as liquids that consist entirely of ions and have a melting/glass transition temperature less than 100 °C. An important characteristic of ionic liquids is the ability to vary the cation and anion to produce a wide variety of ionic liquids with different chemical and physical properties. Ionic liquids possess some unique combinations of properties such as negligible vapour pressure, high thermal stability, ionic conductivity, low surface tension and non-flammability, which can be exploited to generate enhanced manufacturing processes. These properties make them suitable to replace traditional solvents.[10] Several reviews have summarised the factors that affect the dissolution of cellulose in different ionic liquids.[3, 4, 6] These can be used as an initial guideline when selecting ionic liquids for cellulose dissolution.

Different additive manufacturing technologies have been introduced over the past few decades that use a variety of materials, i.e. polymers, metals, ceramics and composites to produce parts layer by layer.[2] Materials jetting utilising piezo-based ink-jet technology is one of the most promising techniques that can be used to deposit drops continuously (continuous ink-jet printing) or when needed (drop-on-demand ink-jet printing).[11-13] Material jetting can use a variety of materials,[14] is versatile, and printed patterns can be easily changed.[15] These advantages make it a suitable technology to produce three-dimensional objects. Ink-jet printed biomaterials can be used in biomedical applications (tissues and organs)[16] and in smart materials (actuators and sensing system).[17]

Markstedt *et al.*,[18] demonstrated the first use of extrusion printing with cellulose and ionic liquid ([C_2C_1Im][OAc]) to form

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Electronic Supplementary Information (ESI) available: [sample calculations, apparatus used to fill the DIMATIX materials print cartridge, scanning electron microscopy images, white light interferometry images and data can be found in Electronic Supplementary Information]. See DOI: 10.1039/x0xx00000x three-dimensional objects. Cylinders reaching a maximum height of 25 mm were printed on a vertical agar support (made from agar and water).[18] Haverhals *et al*.,[17] reported simple ink-jet printing a mixture of [C_2C_1Im][OAc] and acetonitrile on to a cellulosic paper and exposed samples to varying conditions of heat and rinsing protocols. They concluded that it was possible to obtain printed materials with exceptional properties that could be used in a wide variety of applications.[17] Recently, similar work conducted by Sweely *et al*.,[19] showed the results of ink-jet printing a mixture of [C_2C_1Im][OAc], carbon black and microcrystalline cellulose on to a paper substrate (100% cotton). They suggested that adding a co-solvent (like acetonitrile, ethanol or DMSO) can both increase the amount of cellulose dissolved in an ionic liquid containing solution and reduce the overall viscosity.[19] This opens up the possibility of utilising such solutions in conventional 3D ink-jet printers, which generally require low (<20 mPa.s) viscosities.

This paper describes the identification of mixtures of ionic liquids and organic co-solvents (DMSO and 1-butanol) for formulating materials for ink-jet based 3D printing of cellulose, with a view to identify solutions that could be exploited for other ionic liquid-soluble biopolymers. Rheological properties of the ionic liquid-co-solvent mixtures have been measured and assessed to inform the characteristics required for effective printing. Methods for subsequent removal of the ionic liquid from the final 3D-printed structure have also been evaluated.

Experimental

Chemicals

Ionic liquids: 1-ethyl-3-methylimidazolium acetate ([C_2C_1Im][OAc]) (purity ≥95%) and 1-butyl-3-methylimidazolium acetate ([C_4C_1Im][OAc]) (purity ≥95%) were purchased from Sigma Aldrich (United Kingdom) and used as received. Co-solvents: 1-butanol and dimethyl sulfoxide (DMSO) were purchased from Thermo Fisher Scientific (United Kingdom). Microgranular cellulose was purchased from Sigma Aldrich (United Kingdom) and dried at 60 °C in an oven (Lenton) for 3 hours before use. Deionised water was used in all the experiments.

Sample Preparation

The mass of cellulose used was calculated by taking 2 and 5% of the ionic liquid mass (outlined in Table 1). The required quantity of cellulose was weighed using a four figure digital balance (Denver Instruments) and placed into a glass vial. The ionic liquid was measured out using a 1 mL ink-jet syringe and was added to the cellulose. To investigate the effect of adding a co-solvent on cellulose dissolution and the physical properties of the resultant solution, two different percentages of cellulose (calculated as above) and three different percentages for co-solvent (50, 70 and 90% of ionic liquid mass) were then added to samples containing cellulose and [C_4C_1Im][OAc] (Table 2). The amount of cellulose, ionic liquid and co-solvent in all the samples were also calculated as a wt % (Tables 1 and 2), alongside mole fraction of ionic liquid relative to co-solvent (χ_{IL}) for the mixtures (Table 2). To create the final formulation, the mixtures were stirred using a magnetic stirrer at 800 rpm whilst heating in an oil bath at 100 °C (samples 1 to 4) and 80 °C (samples 5 to 10), and visually observed until no particulate matter remained (refer to ESI for example calculations).

Viscosity and Surface Tension Measurements

Viscosity measurements were carried out using a Malvern Kinexus pro$^+$ rheometer, using a cone-plate geometry (angle 4°, diameter 40 mm, gap size 0.15 mm) and a cup and bob (cup size C14 (DIN), bob diameter 14 mm). Cone-plate geometry was used to measure the viscosities of [C_2C_1Im][OAc], [C_4C_1Im][OAc], deionised water and for all the samples in Tables 1 and 2, and cup and bob was used to measure the viscosities of DMSO and 1-butanol. Viscosities of the pure chemicals were measured with shear rates of 10 to 1000 s^{-1} at 25 °C, and the viscosities of mixtures (as identified in Tables 1 and 2) were measured with shear rates of 1 to 1000 s^{-1} at 60 °C. This was because the maximum working temperature for the DIMATIX print head was 70 °C. Viscosity was measured in triplicate and the average viscosity at shear rate 1000 s^{-1} was used, except for sample 2 where the average viscosity was calculated at a shear rate of 631 s^{-1}.

Surface tension of pure chemicals and mixtures were measured at room temperature using a KRUSS DSA100 drop shape analyser. Measurements were taken six times and the average value was recorded.

Ink-jet Printing

Filling the DIMATIX Materials Print Cartridge

Ink-jet printing was performed using a FUJIFILM DIMATIX DMP-2831 printer. The cartridge used (10 pL) was purchased from FUJIFILM DIMATIX. It consists of 16 nozzles, has a nozzle diameter of 21 μm, and a built in heater that can heat the cartridge up to 70 °C. Jetting is driven by a piezo element with amplitudes that can be varied between 0 and 40 V.

Table 1. Formulations containing cellulose and ionic liquid.

Sample	Cellulose (g)	[C_4C_1Im][OAc] (g)	[C_2C_1Im][OAc] (g)	Cellulose (%)	Cellulose (wt %)	Ionic Liquid (wt %)
1	0.1688	8.4		2.0	2.0	98
2	0.4220	8.4		5.0	4.8	95
3	0.1643		8.2	2.0	2.0	98
4	0.4108		8.2	5.0	4.8	95

Table 2. Formulations containing cellulose, ionic liquid and co-solvent.

Sample	Cellulose (g)	[C$_4$C$_1$Im][OAc] (g)	DMSO (g)	1-butanol (g)	Cellulose (%)	Co-solvent (%, χ_{IL})	Cellulose (wt %)	[C$_4$C$_1$Im][OAc] (wt %)	Co-solvent (wt %)
5	0.1266	6.3	3.2		2.0	50, 0.44	1.3	66	33
6	0.1266	6.3	4.4		2.0	70, 0.36	1.2	58	41
7	0.1055	5.3	4.7		2.0	90, 0.30	1.0	52	47
8	0.1266	6.3		3.2	2.0	50, 0.43	1.3	66	33
9	0.1846	3.7	1.8		5.0	50, 0.44	3.2	65	32
10	0.3165	6.3		3.2	5.0	50, 0.43	3.2	65	32

The apparatus used to fill the DIMATIX cartridge are shown in the ESI (Figure S1). The required volume of sample was initially measured using a 1mL ink-jet syringe and transferred to the DIMATIX fluid module using a 5 μm nylon syringe filter (Cole-Parmer) and the fill needle (supplied with the cartridge). The nylon syringe filter was used to prevent any particles from agglomerating in the nozzle. When filling the DIMATIX fluid module, care was taken to reduce the formation of air bubbles by tapping into the fluid module when filling it. The fluid module was filled with 2 mL of sample. Finally, the DIMATIX jetting module was attached to the fluid module and installed into the DIMATIX printer. A cleaning pad (supplied with the cartridge) was also inserted into the DIMATIX printer.

Printing

DIMATIX Drop Manager Software was used to control the printing process. After installing the cartridge, a cleaning cycle was performed to prime the nozzles. This cycle ensures that additional air trapped inside the fluid module and cartridge is removed. Polyethylene Terephthalate (PET) and glass were used as the substrates. Printing was carried out with the print head temperature set at 55 °C and droplet spacing of 150 μm (sabre angle 36.2°). Voltage, frequency and the waveform were adjusted to achieve stable drop formation. During printing, when the cleaning cycles were unable to unblock the nozzles, the print head was manually cleaned using a polyester wipe. Ink-jet printed samples were dried for approximately 18 hours under different conditions, one under room temperature and the other in the oven at 50 °C.

Cellulose Regeneration

Cellulose was regenerated by adding 0.1 mL of deionised water at room temperature. Deionised water was left on ink-jet printed samples for different time intervals (30 minutes, 1 hour, 1 hour 30 minutes or 2 hours) before drying for approximately 18 hours at 50 °C.

Optical Characterisation

Optical characterisation of the ink-jet printed samples was performed using a Nikon ECLIPSE LV100ND. Scanning electron microscope (SEM) images of untreated cellulose were obtained using a Hitachi TM3000 Table Top SEM and for ink-jet printed and regenerated samples a Philips XL30 SEM was used. Surface profile analysis of the ink-jet printed samples was performed using a white light interferometry (WLI) Bruker Contour CT. All ink-jet printed samples analysed using the SEM and WLI were coated with platinum to ensure reduced charging during SEM and provide reflectivity for white light interferometry.

Results and Discussion

Rheological Properties

Viscosities of [C$_2$C$_1$Im][OAc], [C$_4$C$_1$Im][OAc] and deionised water were measured using a cone-plate geometry and the viscosities of DMSO and 1-butanol were measured using cup and bob to avoid DMSO and 1-butanol evaporation.

The printability parameter, Z, which is a combination of physical properties of the fluid including density (ρ), viscosity (η) and surface tension (σ) and the characteristic length of the nozzle (d), (21 μm in this case) was calculated using Equation 1. To obtain stable drops during printing, it is recommended to have the printability parameter between 1 and 10.[13]

$$Z = \frac{\sqrt{\sigma \rho d}}{\eta} \qquad (1)$$

Both [C$_2$C$_1$Im][OAc] and [C$_4$C$_1$Im][OAc] have very high viscosities that exceed the printing range for the DIMATIX ink-jet printer (12-18 mPa.s). The surface tension of [C$_4$C$_1$Im][OAc] is within the DIMATIX ink-jet printing range (28-32 mN/m). However, [C$_2$C$_1$Im][OAc] has a higher value than the recommended range. Overall, these values result in the printability parameters for the two ionic liquids being much less than the acceptable range of 1 to 10 (Table 3).

Dissolution and Rheological Properties of Samples

The rheological properties of samples containing cellulose and ionic liquids ([C$_4$C$_1$Im][OAc] and [C$_2$C$_1$Im][OAc]) are shown in Table 4. The viscosity of sample 2 was measured at a lower shear rate of 631 s^{-1} due to a limitation in the rheometer when measuring samples with high viscosity. Sample density was calculated by dividing the total sample mass by the total sample volume (refer to ESI for example calculations).

Table 3. Rheological properties and printability parameter of pure chemicals.

Chemical	Density (g/cm^3)	Viscosity (mPa.s)	Viscosity SD (±)	Surface Tension (mN/m)	Surface Tension SD (±)	Printability Parameter, Z
[C_4C_1Im][OAc]	1.1	278.00	15.74	30.30	0.78	0.093
[C_2C_1Im][OAc]	1.0	85.47	5.03	39.94	0.54	0.34
Deionised water	1.0	2.99	0.31	71.64	0.51	13
DMSO	1.1	4.11	1.03	29.99	1.01	6.4
1-butanol	0.81	4.31	0.01	30.12	0.91	5.2

Table 4. Rheological properties of samples containing ionic liquid and cellulose.

Sample	Density (g/cm^3)	Viscosity (mPa.s)	Viscosity SD (±)
1	1.0	163.90	7.58
2	1.0	723.13	49.53
3	1.0	87.30	2.56
4	0.99	290.70	22.21

The viscosity of the ionic liquid and cellulose solutions were higher than the printing range (12-18 mPa.s), even at 60 °C. Whilst increasing the temperature is known to decrease the viscosity,[20, 21] temperature modulation in this printing system was limited by the maximum working temperature for the DIMATIX cartridge (70 °C). To decrease the viscosity, different concentrations of co-solvents were added, following the recommendations by Sweely *et al*.[19] As the amount of cellulose is increased, from 2.0 to 4.8 wt % sample viscosity increased (Table 4). A similar trend was seen in a study conducted by Kosan *et al*.[22]

Cellulose dissolution in [C_4C_1Im][OAc] was further studied in the presence of different co-solvents (DMSO and 1-butanol). Samples containing DMSO dissolved easily compared to samples containing 1-butanol, where a cloudy solution formed, which resulted in a precipitate at room temperature. Therefore, the printability parameter for samples containing 1-butanol (samples 8 and 10) was not calculated.

Initially 33 wt % of DMSO was added and the viscosity was measured, then DMSO concentration was increased from 41 to 47 wt % to bring the sample viscosity within the ink-jet printing range (12-18 mPa.s). It can be seen from the rheological properties summarised in Table 5, increasing the concentration of DMSO reduces the viscosity of the samples. For sample 9, viscosity was more than 90 mPa.s at 60 °C, which was much higher than the printing range (12-18 mPa.s) required.

Comparing the surface tension and viscosity of the as-received chemicals recorded in Table 3 with the samples in Table 5, it can be seen that when mixed to create the formulations given in Table 2, surface tension increases and the viscosity decreases. Surface tension and density recorded in Table 5 remain approximately the same and, the characteristic length of the nozzle being a constant, results in the printability parameter (Z) being mainly affected by the sample viscosity.

Based on Z, samples 6 and 7 (Table 5) were chosen for ink-jet printing. This was because their Z values were within the acceptable range (between 1 and 10) for stable drop formation.

Both the samples showed non-Newtonian behaviour. To further study the rheological behaviour exhibited by these fluids, viscosities of samples 6 and 7 were measured against time at fixed shear rate (1000 s^{-1}) and temperature (60 °C). From the results (Figure 1) it can be seen that samples 6 and 7 show thixotropic behaviour, exhibiting shear thinning.[23]

Table 5. Rheological properties and printability parameter of samples containing [C_4C_1Im][OAc], cellulose and DMSO.

Sample	Density (g/cm^3)	Viscosity (mPa.s)	Viscosity SD (±)	Surface Tension (mN/m)	Surface Tension SD (±)	Printability Parameter, Z
5	1.1	28.49	2.12	36.71	0.18	1.0
6	1.1	19.64	1.13	35.58	0.64	1.4
7	1.1	15.66	1.32	36.06	0.41	1.8
9	1.0	91.27	2.21	37.15	0.43	0.31

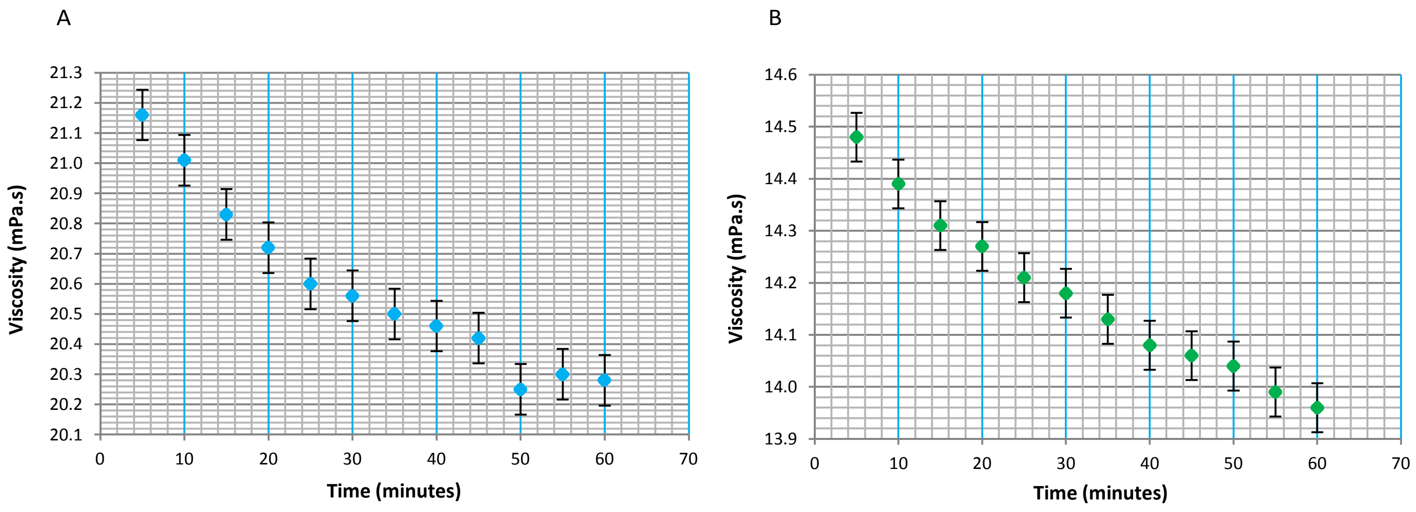

Figure 1. Viscosity *vs* time at fixed shear rate and temperature for A) sample 6 (58 wt % [C_4C_1Im][OAc] + 1.2 wt % cellulose + 41 wt % DMSO) and B) sample 7 (52 wt % [C_4C_1Im][OAc] + 1.0 wt % cellulose + 47 wt % DMSO).

When the viscosity decreases under shearing it becomes easier for the ink to pass through the nozzle.[24] When shear is removed, viscosity increases[25] and the printed pattern is able to retain its shape.[24] This is a useful property of the formulated ink that can be used in ink-jet printing to eject droplets at a viscosity lower than that recorded in Table 5.

Ink-Jet Printing

When printing sample 6, the nozzles were blocked more easily than for sample 7, possibly due to sample 6 possessing a viscosity higher than the manufacturer's acceptable viscosity range of 12-18 mPa.s. During printing, the drop leaves the nozzle as a jet with a long extended tail/ligament attached to the leading drop. The tail/ligament breaks after some time where part of the ink returns to the nozzle and the remaining joins the leading large drop, but on occasion it is possible that smaller satellite drops can form.[12, 13] When observing the drops using the Drop watcher in the DIMATIX Drop Manager Software, frequency, waveform and voltage were adjusted until acceptable drops that merge with the leading drop were formed. Jetting parameters for sample 7 are summarised in Table 6 and a schematic diagram of the waveform is shown in Figure 2.

The pattern printed on the PET and glass was a 3 mm × 3 mm square having an array of single drops with a droplet spacing of 150 μm (sabre angle 36.2°) and printed with the print head temperature at 55 °C. Printing was achieved using a single nozzle. Figure 3 shows the array of drops printed using samples 6 and 7. From the microscopic images obtained, it can be seen that some drops were missing (Figure 3A), which may be due to a blockage in the nozzle. Small drops were also deposited next to the large drop (Figure 3B) indicating the formation of smaller ligaments alongside the primary drop.

Table 6. Jetting parameters for sample 7 (52 wt % [C_4C_1Im][OAc] +1.0 wt % cellulose + 47 wt % DMSO).

Segment	Level (%)	Slew Rate	Duration (μs)
1	0	0.65	3.584
2	100	0.93	3.712
3	27	0.60	3.392
4	40	0.80	0.832
Duration Scalar			1
Width			11.520 μs
Maximum Jetting Frequency			1.5k Hz
Jetting Voltage			35 V

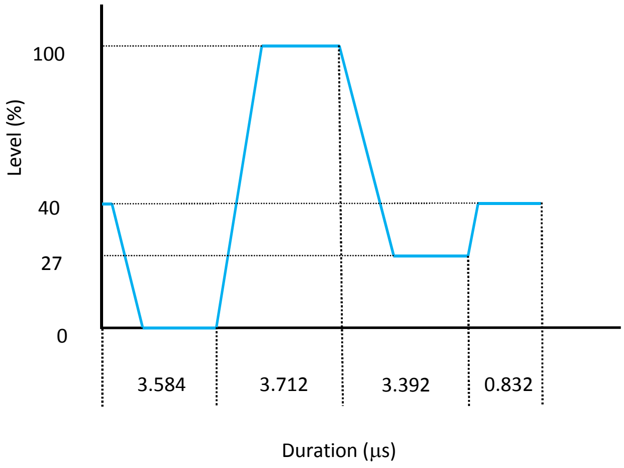

Figure 2. Schematic diagram of the waveform described in Table 6.

Scanning electron microscopy images obtained by ink-jet printing samples 6 and 7 and drying approximately for 18 hours at 50 °C are shown in Figure 4 (other SEM images can be found in ESI Figure S2). From the SEM images, it can be seen that there was more material deposited for ink-printed samples using formulation 6 compared to formulation 7. The principle difference between these two samples is the amount of DMSO. DMSO composition in sample 7 was higher (47 wt %) than in sample 6 (41 wt %).

To further study the distribution of materials on the droplet, surface profile analysis was performed using a white light interferometry. The surface profile images indicate that the height of the surface, corresponding to the amount of material deposited, differs (Figure 5). This was further investigated by calculating the average height of the ink-jet printed droplet obtained from the surface profile data (Table 7). All WLI images and data can be found in ESI.

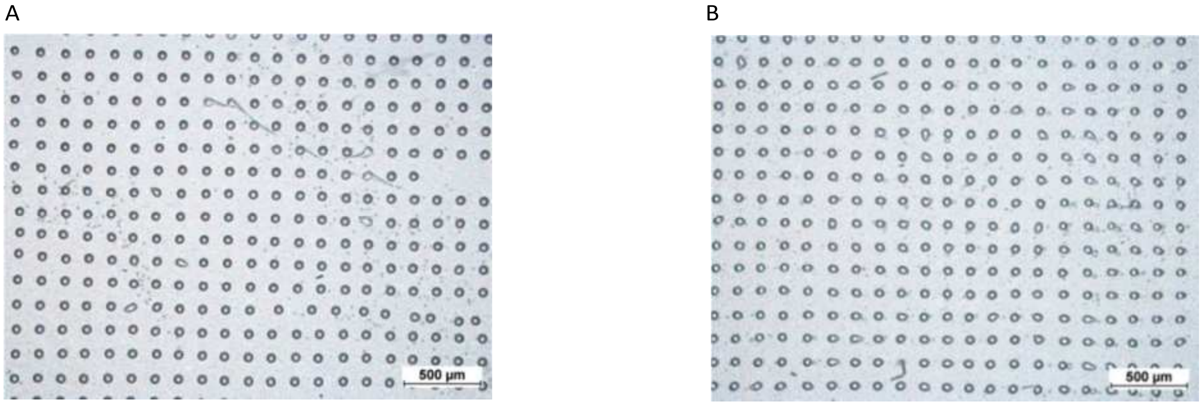

Figure 3. Microscopic images obtained using a Nikon ECLIPSE LV100ND. A) sample 6 ink-jet printed on PET and B) sample 7 ink-jet printed on PET

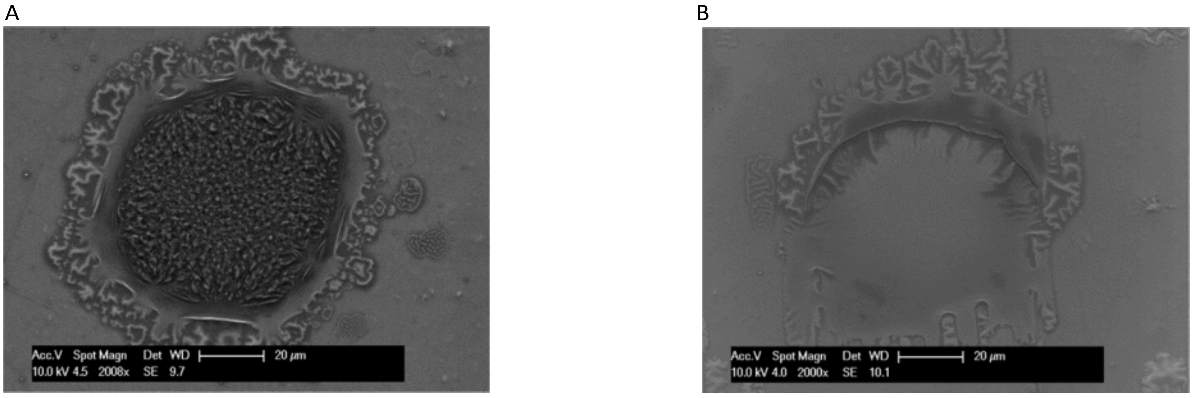

Figure 4. SEM images obtained from Philips XL30 scanning electron microscope. A) sample 6 printed on PET and dried approximately for 18 hours at 50 °C B) sample 7 printed on PET and dried approximately for 18 hours at 50 °C .

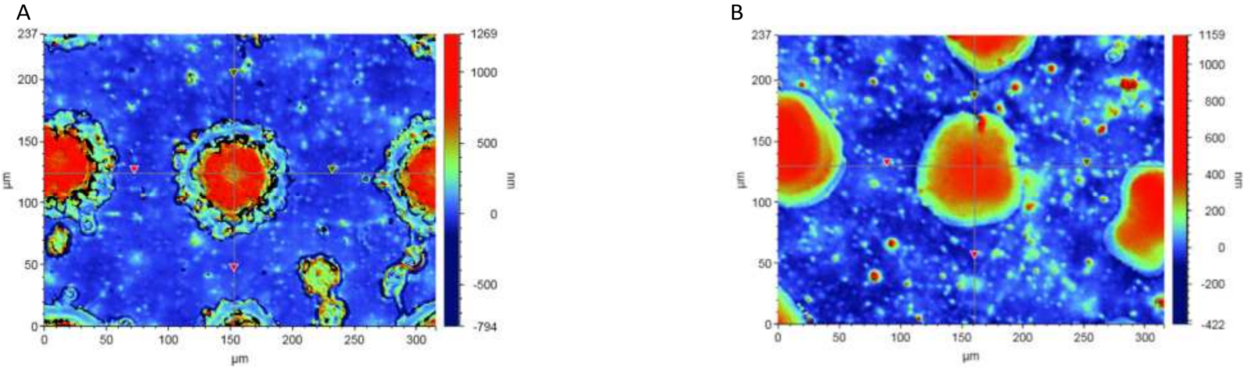

Figure 5. White light interferometry results obtained from Bruker Contour CT interferometer. A) sample 6 printed on PET and dried approximately for 18 hours at 50 °C B) sample 7 printed on PET and dried approximately for 18 hours at 50 °C.

Table 7. Average height of a droplet for ink-jet printed samples.

Remarks	Average height in X direction (nm)	Average height in Y direction (nm)
Sample 6, dried approximately for 18 hours at room temperature	510	530
Sample 6, dried approximately for 18 hours at 50 °C	680	680
Sample 7, dried approximately for 18 hours at room temperature	180	84
Sample 7, dried approximately for 18 hours at 50 °C	340	380

From Table 7, it can be seen that samples printed using formulation 6 showed a higher height over both X and Y axis, compared to samples printed using formulation 7. This is consistent with the results obtained from the scanning electron microscope.

Cellulose Regeneration

Cellulose has previously been regenerated by adding an anti-solvent such as either water,[26-28] ethanol, or acetone.[26] Zavrel *et al*.,[28] explained this phenomenon as a solute-displacement, where the water forms a hydrodynamic shell around the ions present in the ionic liquid, preventing it interacting with cellulose. This leads to a reformation of the hydrogen bonds in cellulose causing it to precipitate and forming a disordered structure.[28] The observed regeneration of cellulose points towards a mechanism to generate 3D structures through an ink-jet based deposition-regeneration process.[17, 19]

The regeneration experiments were conducted by adding deionised water and leaving the ink-jet printed samples for different time intervals. It was assumed that leaving deionised water for a longer time interval (2 hours) would remove more ionic liquid than leaving for a short time interval (30 minutes). Untreated microgranular cellulose was used as a benchmark for a qualitative comparison of morphology (Figure 6).

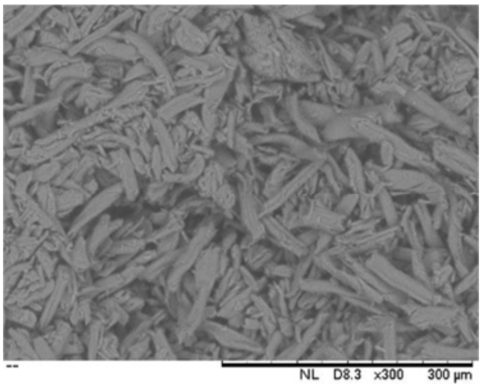

Figure 6. SEM image obtained from Hitachi TM3000 Scanning electron microscope of untreated cellulose.

Figure 7 shows the scanning electron microscopy image obtained from a regenerated ink-jet printed sample. As seen from the images, characterisation of the morphology of the regenerated cellulose was challenging, due to the presence of debris on and around the printed droplet. Further experiments must be carried out to distinguish the composition of the droplets.

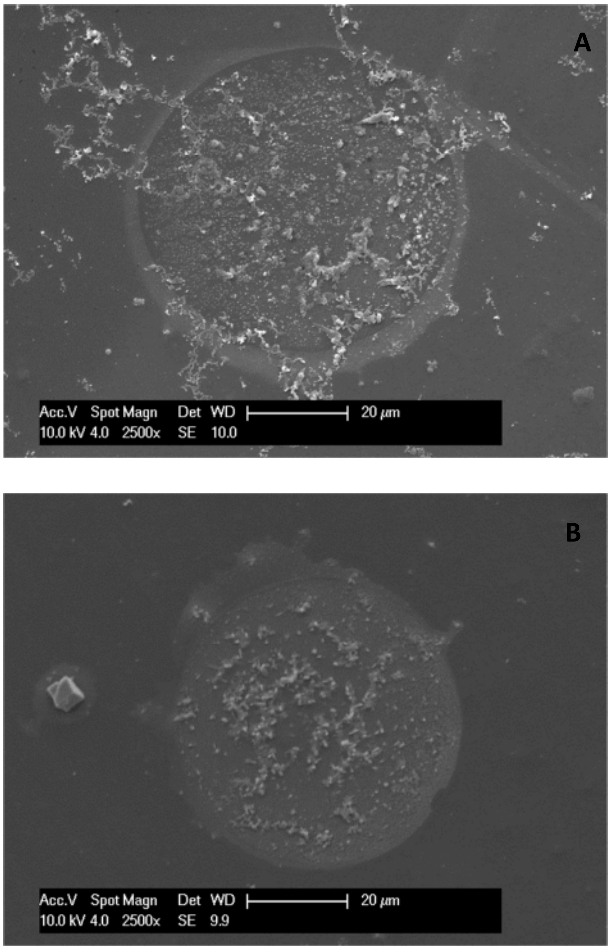

Figure 7. SEM image obtained from Philips XL30 scanning electron microscope. The samples were ink-jet printed on PET and regenerated by leaving deionised water for 1 hour and 30 minutes before drying approximately for 18 hours at 50 °C. A) Sample 6 and B) Sample 7.

Surface profile images obtained from the regenerated samples indicate the central region of the drop has sunken, creating a concave residue (Figure 8). A study conducted by Wang *et al*.,[29] found that $[C_4C_1Im][OAc]$ was responsible for PET degradation. In their work, 3.4 wt % of PET dissolved in $[C_4C_1Im][OAc]$ at 150 °C. Even though the ink-jet printed samples were treated at a maximum temperature of 55 °C in this study, the surface profile images in Figure 8 suggest some degree of PET degradation.

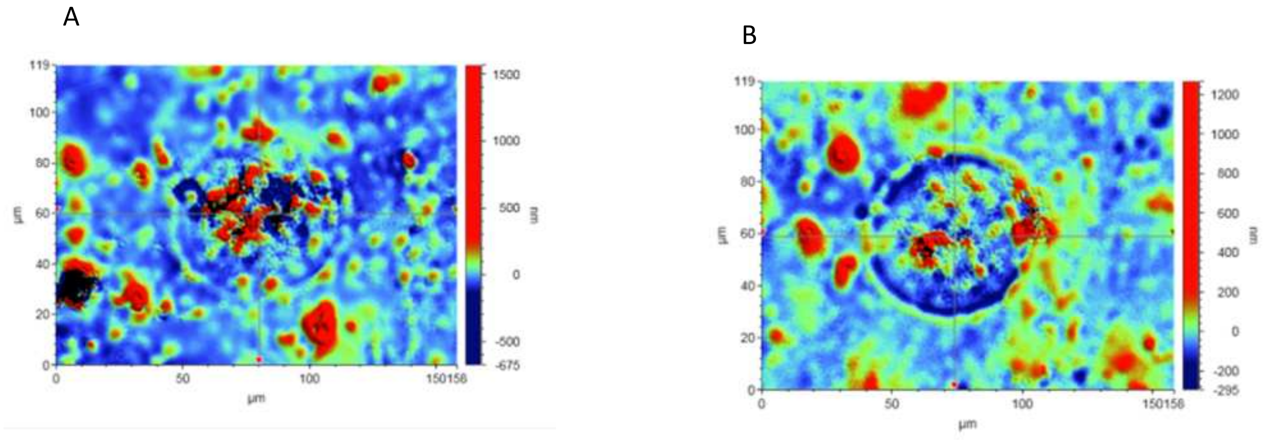

Figure 8. White light interferometry results obtained from Bruker Contour CT interferometer. The samples were ink-jet printed on PET. A) sample 6 ink-jet printed and regenerated by leaving deionised water for 1 hour and 30 minutes before drying approximately for 18 hours at 50 °C and B) sample 7 ink-jet printed and regenerated by leaving deionised water for 30 minutes before drying approximately for 18 hours at 50 °C.

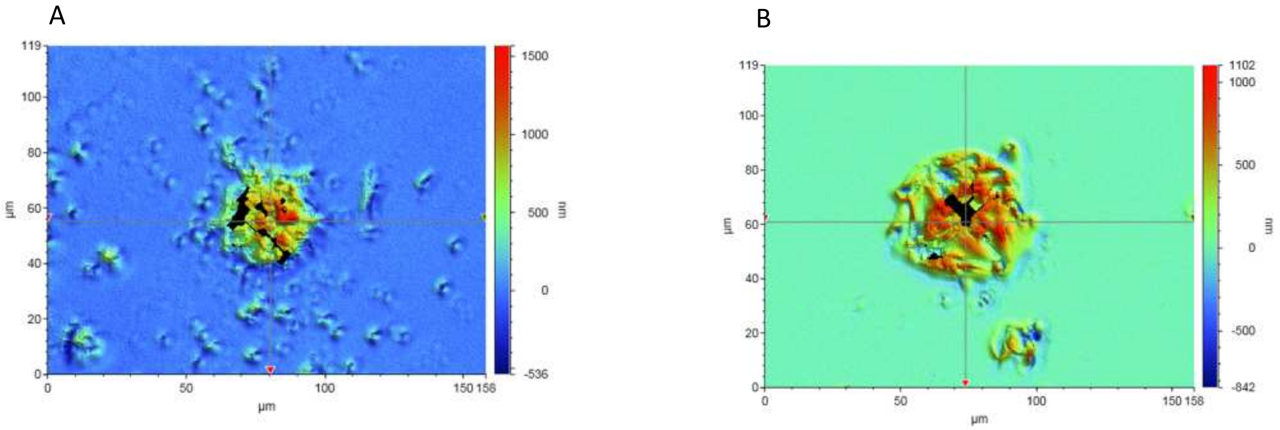

Figure 9. White light interferometry results obtained from Bruker Contour CT interferometer. The samples were ink-jet printed on glass. A) sample 6 ink-jet printed and regenerated by leaving deionised water for 1 hour and 30 minutes before drying approximately for 18 hours at 50 °C and B) sample 7 ink-jet printed and regenerated by leaving deionised water for 30 minutes before drying approximately for 18 hours at 50 °C.

Further ink-jet printing was carried out using glass as the substrate and the surface profile images, as shown in Figure 9, reveal no evidence of a sunken central region in the drop. This shows the possibility of forming 3D structures on glass as an improved printing substrate, relative to PET.

Conclusions

In this study, cellulose dissolved in the ionic liquids [C_4C_1Im][OAc] and [C_2C_1Im][OAc] resulted in high viscosity solutions (> 80 mPa.s) that are not suitable for 3-D printing. Different concentrations of the co-solvent DMSO were able to bring these solutions into the DIMATIX ink-jet printing range, whilst maintaining cellulose solubility. Use of alternative co-solvents, such as 1-butanol, resulted instead in precipitation in the solutions studied here. The ink-jet printed samples indicated that some drops were missing and small ligaments were formed. This implies a blockage in the nozzle and formation of small ligaments that did not return to the nozzle or merge with the leading drop, but demonstrates that printing using such equipment is possible. Modifying the ink formulation and waveform would help to overcome this problem in future. The non-solvent deionised water was added to regenerate the ink-jet printed samples on both PET and glass. Data obtained from WLI studies exhibited structural distortion for regenerated samples printed on PET, potentially related to the dissolution of the substrate by either the ionic liquid or co-solvent. Glass substrates exhibited no such issues, and as such are recommended to be used instead of PET for future characterisation and applications. The preliminary work presented herein provides the basis for 3-D printing of biopolymeric materials, by demonstrating that utilisation of a co-solvent with an ionic liquid is able to modulate liquid printability to a suitable range, whilst maintaining the biopolymer solubility effected by the ionic liquid and affording materials that can be regenerated. Further characterisation must be conducted to distinguish the composition of the regenerated samples in more detail in order to apply this methodology to suitable end-applications.

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