Processing Biodegradable Polycaprolactone through 3D Printing

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Abstract: An initial study of processing biodegradable Polycaprolactone (PCL) through 3D printing technology was conducted using Fujifilm Dimatix DMP-2800 material printer. The aim of this work was to investigate a potential method of preparing and processing biodegradable polycaprolactone through 3D printing. PCL inks with a concentration of 5wt% and 10wt% were prepared to investigate their processability. The influences of waveform peak height, time gap, printing voltage, droplet velocity, substrate temperature and droplet spacing on PCL ink droplet formation as well as final deposition quality were investigated. Multi-layer PCL structures were printed and characterized with the geometric quality of deposited PCL measured using a Talysurf 2000 and Bruker ContourGT-I. It was found that PCL solvent ink can reach relative stable droplet formation and deposition when plate temperature was 30 ℃ and droplet velocity was 6m/s. Printed PCL solvent ink showed 'coffee ring' effect after solidification. When deposition droplet spacing equals to 40 μm, printed PCL film showed the lowest surface roughness.

1. INTRODUCTION

Currently, there is a growing interest in producing biodegradable or bioresorbable biomedical products such as implants and stents via additive manufacturing. The stents or implants are normally very complex to achieve special biological requirements, such as controlled pore size distribution or porosity for better cell adhesion and growth [1-3]. Moreover, the sizes of stents or implants are always different for various human vessels or bones and require custom design. This makes traditional processing methods such as casting or injection moulding hard to compete with additive manufacturing due to their long production cycles and high tooling costs in moulding developing for custom product.

Polycaprolactone (PCL), semi-crystalline biodegradable polymer, is being widely investigated to develop biomedical applications with additive manufacturing such as producing scaffold or bone implant [4]. Most studies on producing bioresorbable polycaprolactone implants focus on two additive manufacturing methods: Selective Laser Sintering (SLS) and Fused Deposition Modelling (FDM) [4-7]. Due to strict printing viscosity and solidification requirements, little work was been carried out in developing bioresorbable polycaprolactone products through Jetting. Jetting is a fabrication method to produce geometrically complex products directly, by print material on a layer-by-layer basis. It is especially suitable for complex and customized low volume products. The biggest advantage comparing with other additive manufacturing methods is Jetting gives the potential possibility of producing multi-material products within a single process cycle.

This work has studied a potential method of preparing and processing biodegradable polycaprolactone ink for 3D inkjet printing. The aim of this work was to exam the processability of PCL solvent based ink and study the effects of different processing parameter on printing. In order to achieve best processing stability, printing parameters such as voltage waveform, substrate temperature, droplet spacing needs to be decided. Pyungho et al [8] studied a new double peak waveform to print low viscosity ink including water and water mixing with Ethylene glycol. Anke et al [9] and Jae Kwan et al [10] studied parameters influence of printing solvent based semi-conducting polymer.

The influence of waveform peak height, time gap, printing voltage, droplet velocity, substrate temperature and droplet spacing on printing quality were discussed.

2. EXPERIMENTAL

Materials

Polycaprolactone (Mn~10000g/mol) and 1, 4-dioxane (Anhydrous 99.8%) were purchased from Sigma-Aldrich. 2-propanol (99.9% min) was purchased from Fisher Scientific. Glass slides (Pre-cleaned Microscope Slides 75*25*1.0mm) and syringe filters (Nylon, 5.0μm, 30mm dia) were purchased from Cole-Parmer.

Instrumentation

Inkjet printing experiments of PCL solvent inks were carried out using Dimatix material printer DMP-2800 (piezo jetting technology based) and Dimatix materials cartridge with 16 nozzles， 21μm nozzle diameter and 10pl droplet volume were used. A Branson Ultrasonic Bath Model 1210 was used to clean glass slides. The PCL solutions were mixed by using IKA RCT Basic IKAMAG Magnetic Stirrer with Temperature Controller. The viscosity of PCL solvents were measured by using Malvern Kinexus Pro. The surface tension of PCL solvents were measured by a Kruss DSA100S. Optical microscopy pictures were taken by Reichert-Jung MEF3. Printed PCL film quality was characterized by Bruker ContourGT-I and Talysurf 2000.

Methods

Polycaprolactone (PCL) solvent inks（5wt% and 10wt%）were prepared by dissolving PCL flakes into 1,4-dioxane. After adding PCL flakes, the ink samples were settled for 24h at room temperature to allow them fully dissolved. Inks were stirred at 800rpm at room temperature for 5mins to improve dispersion of dissolved PCL. Microscopy glass slides were used as a printing substrate. Before printing, the slides were soaked into 2-propanol and ultrasonicated for 5mins. Then they were rinsed by 2-propanol and dried in air.

The viscosity and surface tension of the PCL solvent ink with differing concentrations were measured to make sure they were in the suggested printing range. The PCL ink was injected into printing cartridge respectively. The inks were purged through syringe filter (pore size: 5μm) during injection to prevent nozzle blocking by any particle contaminants. About 2ml solvent ink was filled into a Dimatix materials cartridge. The droplet formation of both PCL solvent inks was checked and a double pulse waveform was chosen as the printing waveform and the effects of different printing parameters including printing voltage, waveform structure, droplet velocity, substrate temperature and droplet spacing were investigated to study their influence on the printing quality.

3. RESULTS AND DISCUSSION

Printability Assessment

The viscosity of each PCL solvent was characterized by shear rate sweep between 1 to 1000 s^{-1} at 20 ℃ and 25 ℃. The results are shown in Figure 1 which approved that the viscosity of PCL solvent with 5wt% and 10wt% PCL were all within the suggested printing range which is between 0.001 to 0.027 Pa.s. PCL solvent with higher concentration had higher viscosity under the same environment temperature. Also as the temperature increased, PCL solvent viscosity decreased. The viscosity of PCL solvent gradually increased as the increment of shear rate.

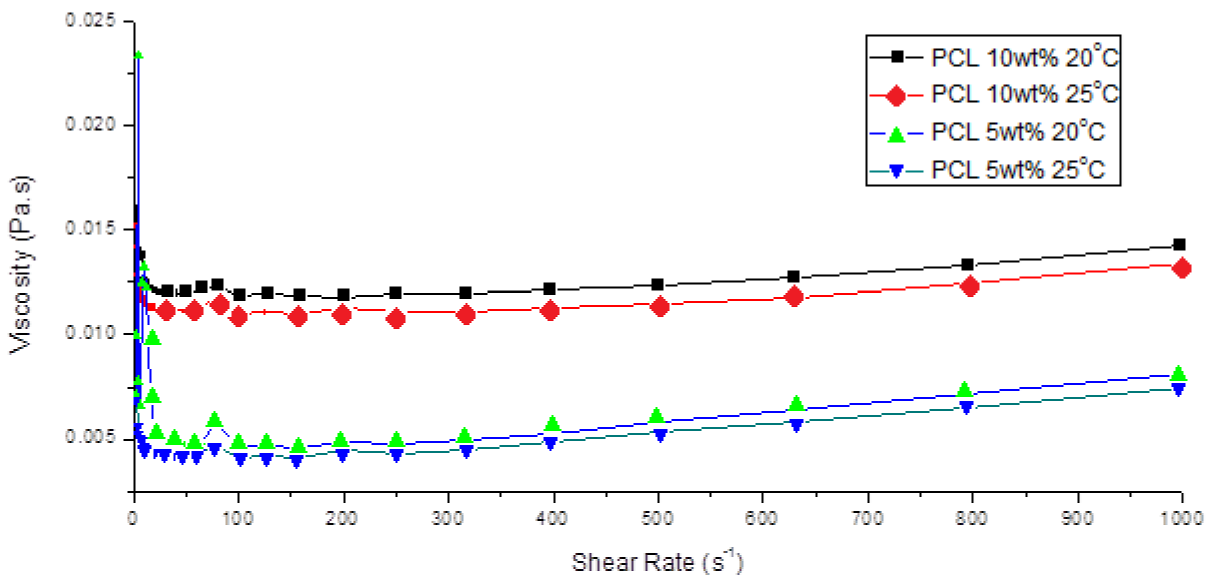


Fig 1: Viscosity of 5wt% and 10wt% PCL solvent ink tested under 20 ℃ and 25 ℃ with shear rate range between 1 to 1000 s^{-1}.

Table 1 shows the physical properties of 5wt% and 10wt% PCL solvents. It shows that the surface tension tends to increase when more PCL was added into the solvent. The printing indicators (Oh^{-1}) for each PCL solvent were then calculated based on Eq 1 and shown in Table 1.

$$Printing\ Indicator(PI) = \frac{Re}{We^{\frac{1}{2}}} = \frac{\sqrt{\rho r \gamma}}{\mu} \qquad \text{Eq.1 [11]}$$

Table 1: Physical properties and printing indicator value of PCL solvent ink at temperature of 25 ℃

Sample	Nozzle Diameter (μm)	Density (g/cm^3)	Viscosity (at $1000s^{-1}$) (mPa s)	Surface Tension (mN/m)	PI (Oh^{-1})
PCL 5wt%	21	1.03	7.5	31.9	3.51
PCL 10wt%	21	1.05	13	33.6	2.09

Ainsley et al [11] suggested that normally when the value of the printing indicator is between 1 and 10, the ink will be printable. From table 1, it can be noticed that based on the theoretical calculation, the printing indicator values of both PCL 5wt% and 10wt% were within the printing range.

Droplet Formation

During test printing, it was found that only the 5wt% solvent ink samples were printable. For the 10wt% sample, due to fast evaporation occurring at the nozzle, PCL precipitated on the nozzle plate and blocked the nozzle. Therefore, all the following experiments were based on 5wt% PCL solvent sample.

The aim of this stage was to optimize the printing parameters for droplet formation and achieve single regular ink droplet formation. The main side effect which happens at this stage is the 'satellite effect', where small droplets formed from the breaking up tail of the main droplet.

A double pulse waveform suggested by Pyungho et al [8], which was suitable for low viscosity ink printing was chosen as a printing waveform in this experiment (Figure 2).The unit of the time gap is μs which represents the time delay to apply the second pulse peak within a single droplet formation cycle. Percentage (%) was used as the unit for the peak height in the waveform. This was because printing voltages varies within droplet formation experiments. Therefore the actual peak height was different with different printing voltage and equals to current printing voltage times Peak Height (%). The droplet formation within a printing voltage range between 21V and 23V was investigated. At each printing voltage, the influences of various Peak 1 and Peak 2 height (including 20%, 40% 60% 80% and 100%) and time gap (including 1μs, 2μs, 3μs, 4μs, 5μs, 6μs, 7μs and 8μs) were recorded respectively.

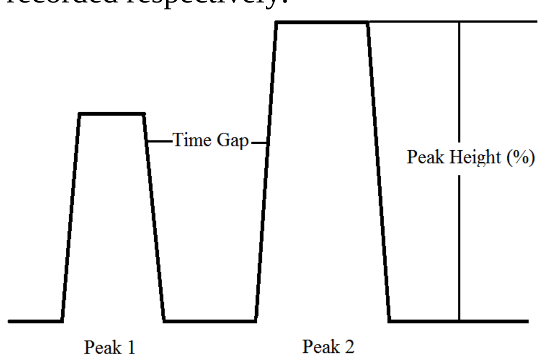


Fig 2: Printing waveform used in this research.

It was observed that droplet formation is closely related to the Total Printing Voltage Input (TPVI) when printing voltage was between 21V-23V and time gap was 3μs. Too high or too low TPVI both led to failure of droplet formation. TPVI can be calculated by following equation and it is proportional to the total energy input for droplet formation. By combining TPVI with droplet formation state, a figure was developed and shown in Figure 3.

$$\text{Total Printing Voltage Input (TPVI)} = V_p \times [H_1+H_2] \qquad \text{Eq2}$$

(Where V_p stand for printing voltage, the unit of it is volt, V; H_1 and H_2 stand for height of peak 1 and peak 2 and the unit of them are percentage,%)

From Figure 3, it can be seen that when the TPVI value was low, the PCL ink cannot obtain enough energy to form a droplet and droplet formation failure occurred. As TPVI value increases, ink at the nozzle obtained more energy and started coming out. When the TPVI increased, the printed droplet obtained more energy and the formed droplet started to break into a primary droplet and satellites; however these satellites can still catch up with the primary droplet and form a single droplet when travelling between nozzle plate and substrate. This procedure is referred to satellites with recombination. If TPVI keep increasing, satellites would not have enough speed to catch up with the primary droplet and satellite without recombination happened. Finally when the TPVI was too high, the droplet started to break up and no regular single droplet formation was observed anymore resulting in droplet formation failure.

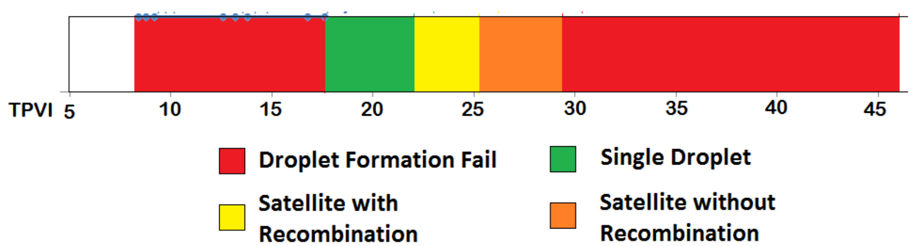


Fig 3: Droplet formation state under different Total Printing Voltage Input with 3μs time gap.

The influence of the time gap between two voltage peaks on droplet formation and the droplet speed were also investigated. From Figure 4, it can be found that droplet velocity increased when time gap started to increase from 1μs and reached maximum speed with a time gap of around 4μs and 5μs. After that, as the time gap increased, the droplet velocity gradually reduced. Experiments were carried out at different printing voltages showing the same trend. Also, the higher printing voltage induced a higher droplet velocity. It was also observed that if droplet velocity exceeded 7m/s during time gap modification, satellite effect without recombination would occur.

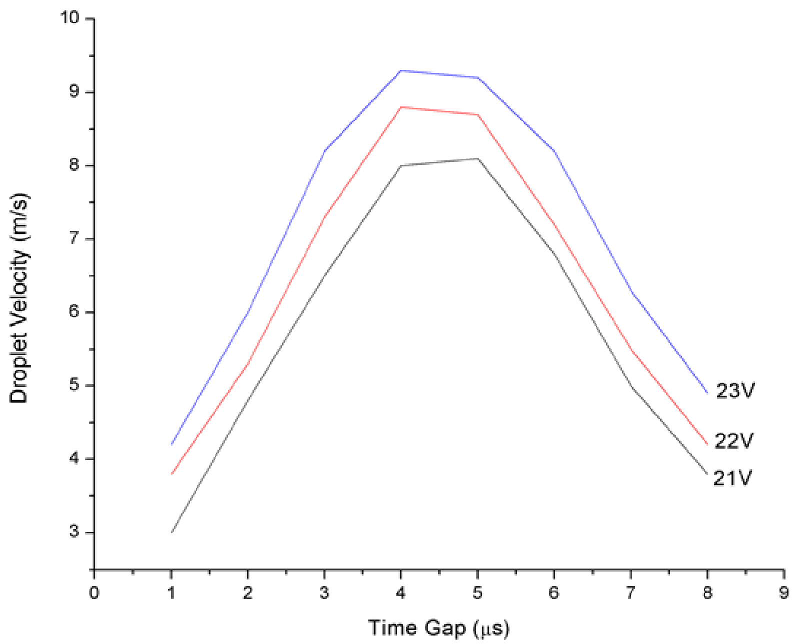
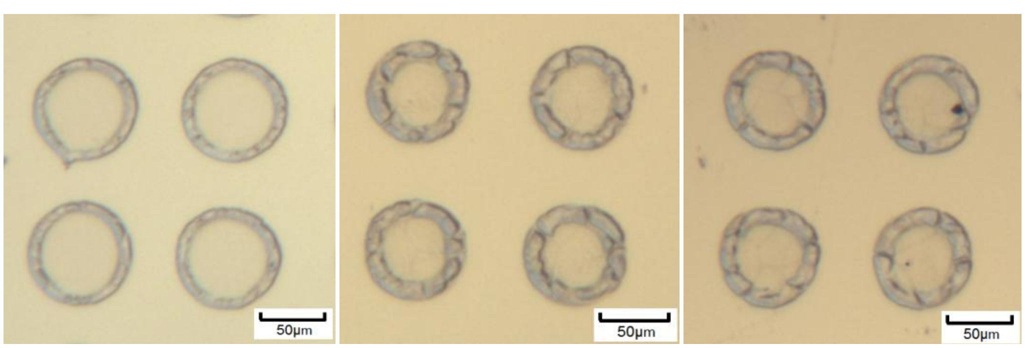


Fig 4: Droplet Velocity change under different time gap and printing voltage.

From the experiments above, it was found that in order to get single regular droplet formation, the TPVI value should stay between 18.4-25.2V. Modifying the time gap could change droplet velocity with fixed TPVI value, however droplets with higher velocity tended to induce satellite effects. Droplet formation with TPVI between 18-25V and velocity between 5m/s to 7m/s were found to be most suitable for single droplet formation.

Droplet Deposition

The effect of changing droplet velocities on the deposited droplet shape was investigated. In order to observe each single droplet after deposition, 5wt% PCL solvent ink was printed with 100μm droplet spacing which was much larger than the droplet size to ensure every deposited droplet would be separate. The droplet deposition microscopy pictures of printed and solidified PCL solvent ink are in Figure 5. After measuring the solidified droplet size, it was found that the deposited droplet size gradually decreased as droplet velocity increased.



(a) (b) (c)

	(a)(5m/s)	(b)(6m/s)	(c)(7m/s)
Droplet Size	83.9±1.7μm	78.7±0.8μm	77.1±1.2μm

Fig. 5: Optical microscopy images of solidified 5wt% PCL solvent ink printed at different droplet velocity (a) 5m/s (b) 6m/s (c) 7m/s (Droplet spacing=100μm, substrate temperature=25 ℃)

As solidification procedure of PCL solvent ink is based on evaporation, substrate temperature will also have an impact on deposited droplet shape. Therefore, similar experiment was carried out with different substrate temperatures from 25 ℃ to 35 ℃ and solidified droplet shapes were observed by optical microscopy. Figure 6 and Table 2 shows the droplet printed at different droplet velocities with different substrate temperatures. A trend can still be found in Table 2, droplet size reducing at higher printing droplet velocity. Moreover, when the droplet velocity was at 6m/s, the deposited droplet had a lower standard deviation compared with 5m/s or 7m/s droplet velocity. Therefore, 6m/s was chosen as optimum printing velocity to carry out line formation test. It can also be noticed that with higher substrate temperature, the deposited droplet size tended to become smaller.

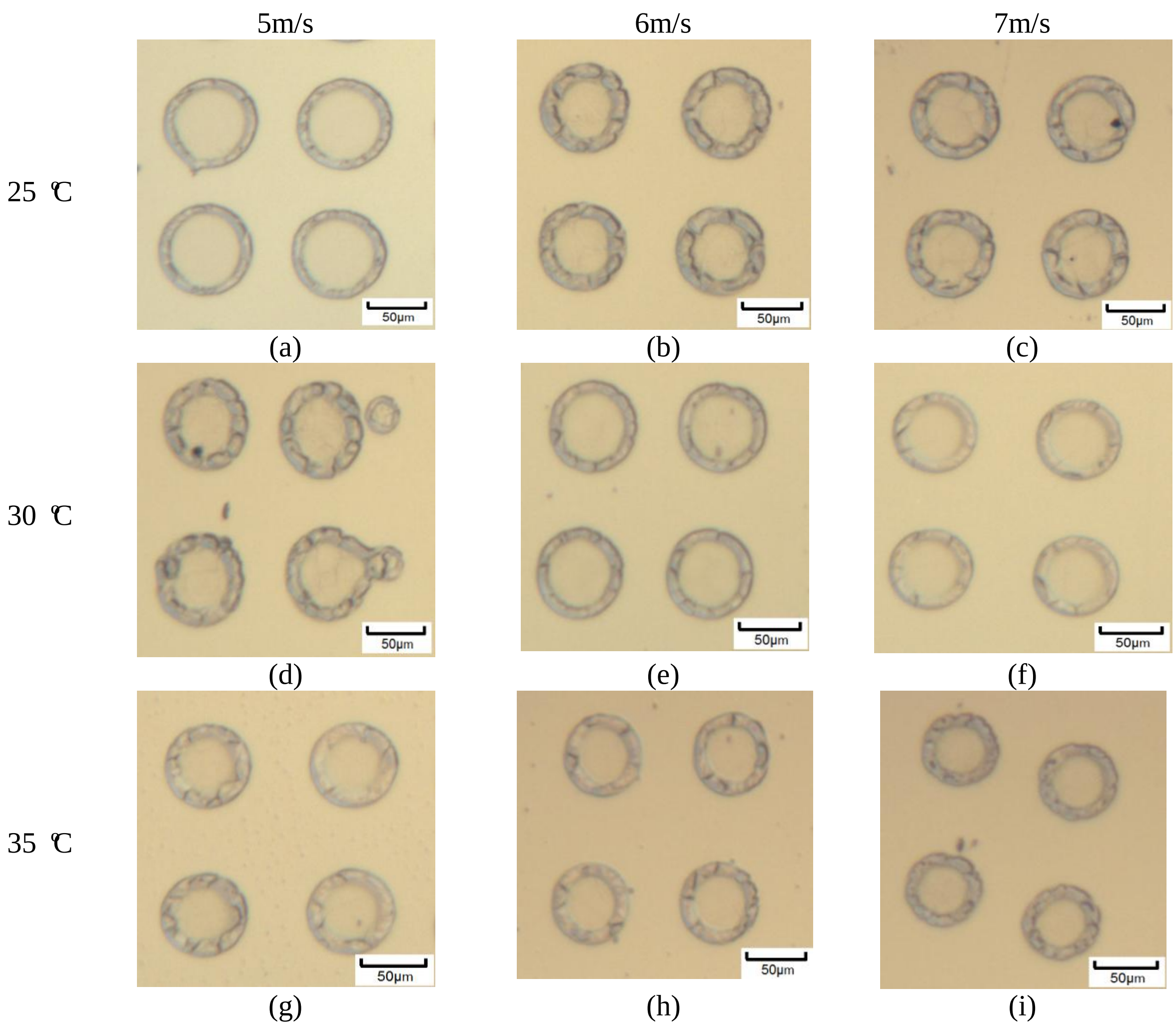
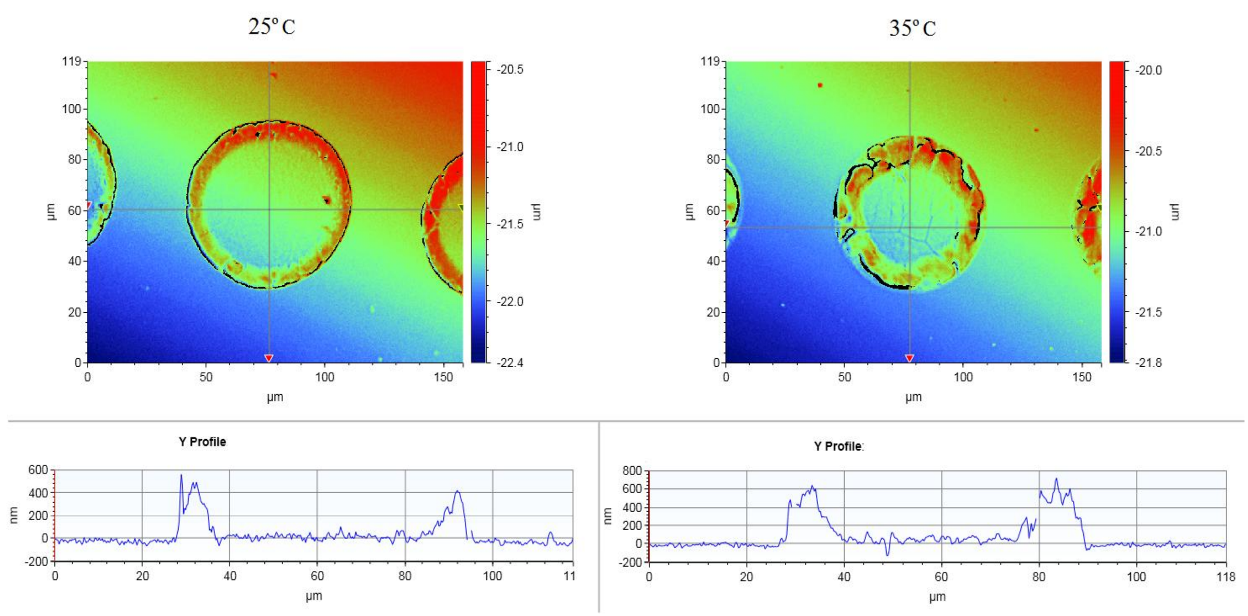


Fig.6: Optical Microscopy result of deposited and solidified PCL printed with different droplet velocity and substrate temperature.

Table 2: Solidified droplet diameter of PCL solvent ink printing under velocity of 5m/s, 6m/s and 7m/s with substrate temperature equals to 25 ℃, 30 ℃ and 35 ℃ respectively

	Droplet Diameter (μm)		
Substrate Temperature	Velocity		
	5m/s	6m/s	7m/s
25 ℃	83.9±1.7	78.7±0.8	77.1±1.2
30 ℃	76.1±1.5	75.0±0.9	69.1±1.3
35 ℃	68.6±1.2	67.6±0.7	64.4±1.2

From both Figure 5 and Figure 6, it can also be noticed that solidified PCL tends to concentrate at outer ring of the droplet under all printing conditions. This phenomenon is called 'Coffee Ring' effect which is caused by different evaporation speed on the edge and central surface of the droplet and can occur with suspension based inks [12-14]. Figure 7 shows surface profiling of a droplet printed with 5m/s velocity and dried with substrate temperatures of 25 ℃ and 35 ℃ respectively. It shows that PCL was concentrated at the droplets outer ring and as substrate temperature was increased, the solidified droplet edge height increased from 400nm (25 ℃) to 600nm (35 ℃).



(a) (b)

Fig. 7: Surface profiling of solidified PCL droplet deposited onto (a) 25 ℃ and (b) 35 ℃ substrate.

Line Formation

In this section, the effects of different droplet spacing on PCL line formation were investigated. From previous experiments, it was found that droplet deposition was more uniform when droplet velocity was 6m/s. In order to make every single droplet combine together to form a line, the droplet spacing needs to be smaller than the deposited droplet size. Therefore three different droplet spacing (20μm, 40μm and 60μm) were chosen to investigate how droplet overlap level influences the printed line. Experiments were also carried out under different substrate temperatures as mentioned previously different substrate temperature can cause droplet size differences which may also have effects on line formation.

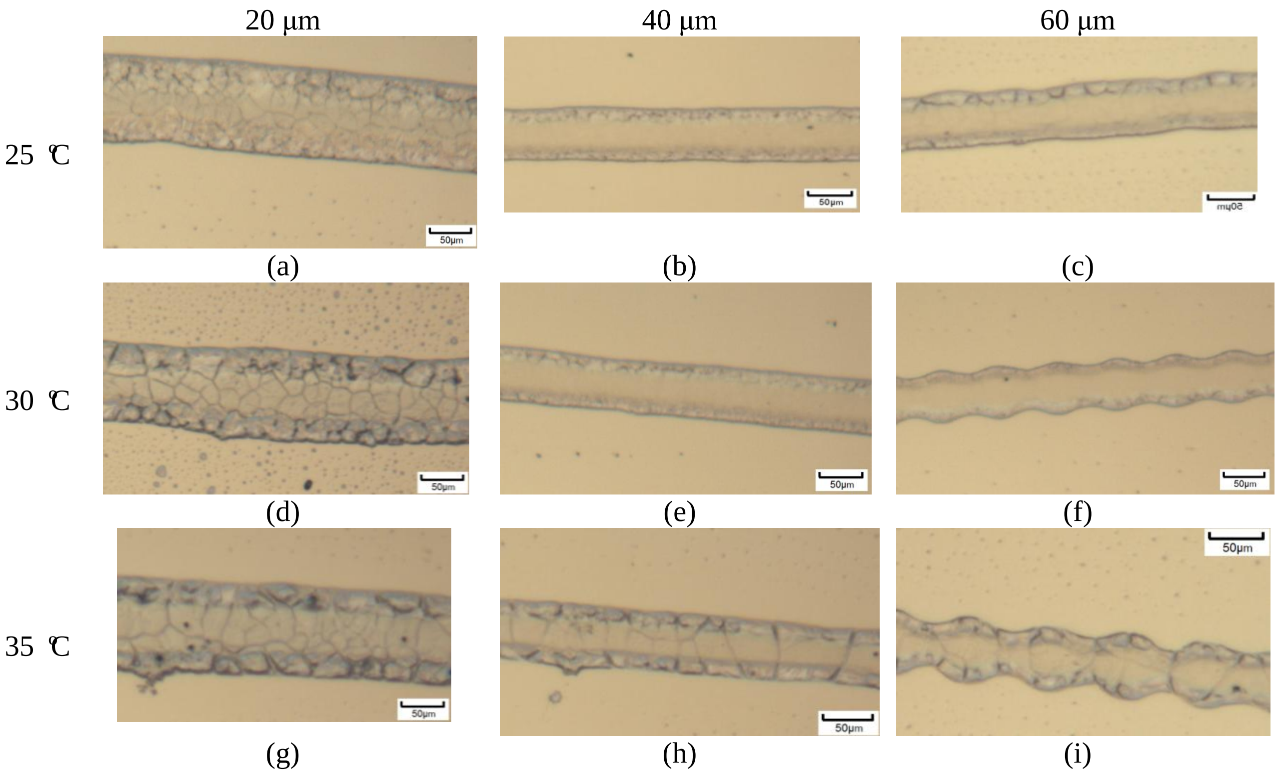


Fig. 8. Optical microscopy result of line formation test for PCL solvent ink printed with different droplet spacing and substrate temperature with droplet velocity=6m/s

Table 3: Width of printed PCL solvent ink line under different droplet spacing and substrate temperature with droplet velocity=6m/s

	Line Width (μm)		
Substrate Temperature	Droplet spacing 20μm	40μm	60μm
25 ℃	104.3 ±1.2	69.7 ±1.9	69.1 ±2.2
30 ℃	97.9 ±3.1	64.4 ±2.0	61.2 ±10.0
35 ℃	96.8 ±2.8	63.3 ±2.1	60.1 ±10.2

Figure 8 and Table 3 shows optical microscopy pictures and width measurement of printed line with 5wt% PCL solvent ink. It can be noticed that the width of the line tends to increase with printing droplet spacing decreasing. When the droplet spacing was 20μm, the line width was even larger than single droplet diameter. This is due to the fact that with the droplet spacing being too low, a large amount of ink droplets were printed horizontally with a high overlap to form a line. Before the ink is solidified, droplets tend to merge with each other until the surface tension cannot hold such large amount of ink on its original location. Then printed ink will expand vertically to achieve balancing state which caused line width at 20μm to be bigger than the maximum width of single droplet measured before. Moreover, the expansion of printed PCL solvent will also compete with solvent evaporation. If evaporation speed increases, printed PCL solvent will have less time to expand before it is solidified and locked to its location. Therefore, accelerating the evaporation speed by increasing the substrate temperature will cause a decrease of printed line width. This was confirmed in line formation experiment results as shown in Table 3.

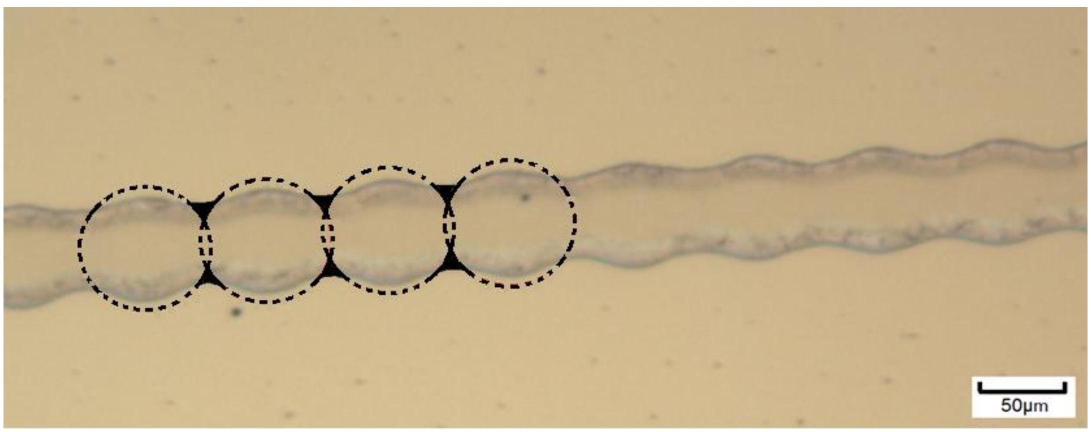
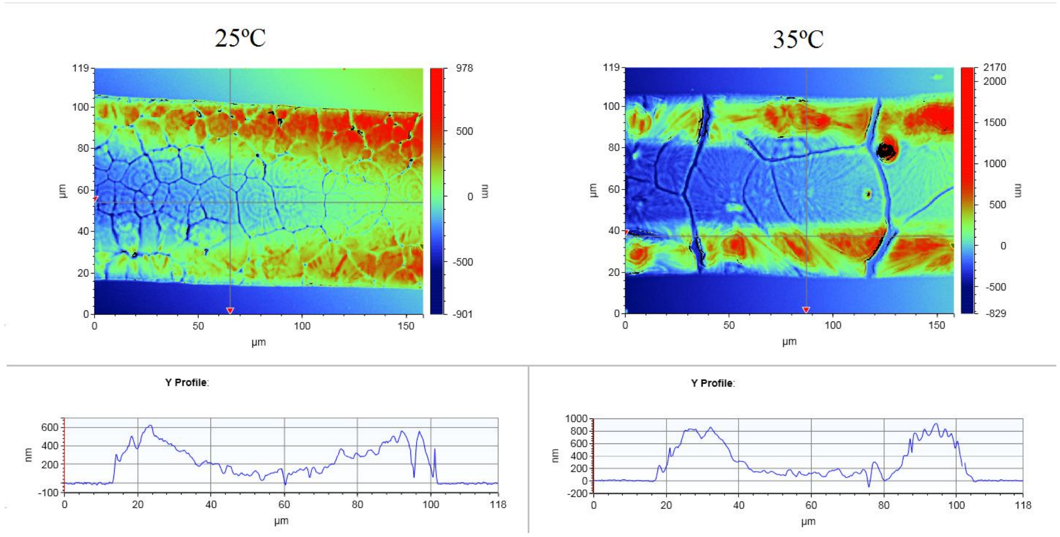


Fig.9: Inkjet printed PCL solvent ink track with 60μm and 35 ℃ substrate temperature.

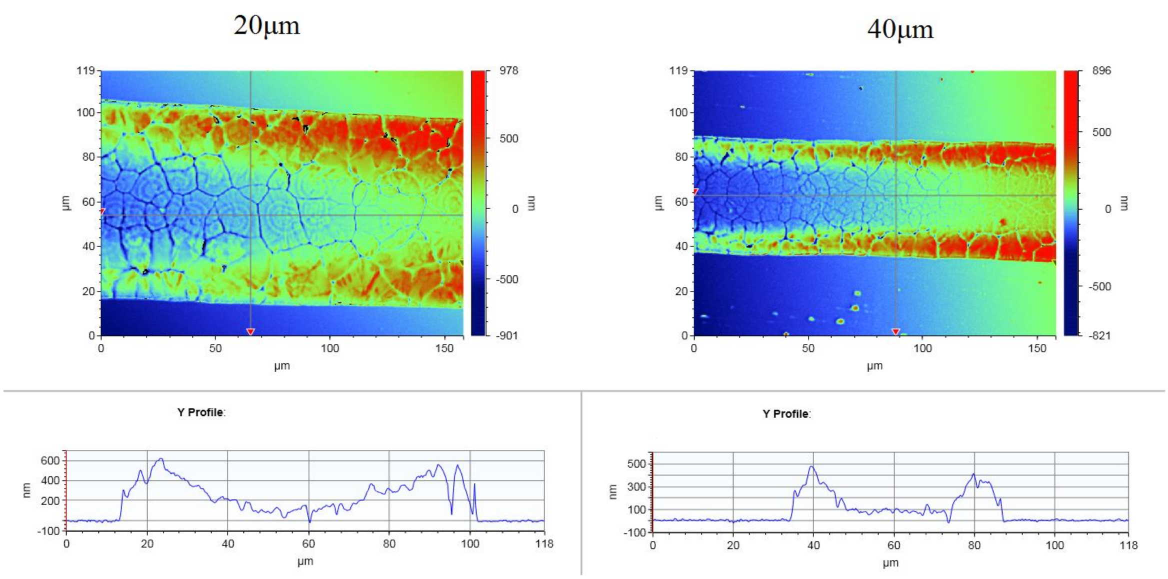
Another phenomenon observed from Figure 9 was that when PCL solvent ink was printed with 40μm and 60μm droplet spacing, the line width became smaller than the single droplet diameter. This phenomenon can be explained by Figure 10. Within Figure 9, the approximate printed droplet size and location is labeled out (based on droplet size measured before) by dash line circle. As soon as overlapped droplets were printed on to the substrate and before it solidified, it tended to move together to form a line and fill up the gap between them (black area in Figure 9). Therefore, part of the printed PCL solvent ink went to the gap between droplets and caused shrinkage of final solidified line width. When droplet spacing is larger, the gap to fill up between droplets also became bigger which requires more ink and longer time for the droplets to merge together and form a uniform liner track. Therefore, when the droplet spacing increased, the solidified PCL track width decreased. When the substrate temperature reached 30 ℃ and 35 ℃, due to evaporation speed increasing, necking between printed droplet were also observed when the droplet spacing equaled 60μm which showed a situation that droplet did not fully merged together before it was solidified.



(a) (b)

Fig.10 Surface profiling of solidified PCL tracks deposited onto (a) 25 ℃ and (b) 35 ℃ substrate with droplet spacing equals to 20μm.

Figure 10 shows surface profiling data of printed PCL track with different substrate temperatures. It can be noticed that due to the coffee ring effect, PCL was still concentrated at the edge after solidification. It also showed that at higher substrate temperature, besides the width reducing, the height of the solidified track also increased significantly. The maximum height of PCL track with 20μm droplet spacing and solidified at 25 ℃ was around 600μm, while for 35 ℃, the value increased to around 800μm.



(a) (b)

Fig 11: Surface profiling of solidified PCL tracks deposited onto 25 ℃ substrate with droplet spacing equals to (a) 20μm and (b) 40μm.

Figure 11 showed PCL tracks printed under the sample plate temperature of 25 ℃ with droplet spacing equal to 20μm and 40μm respectively. It showed that the total width of printed track decreased and the maximum height of solidified PCL also decreased slightly.

Film Formation

PCL solvent ink (5wt%) was printed with 20µm, 40µm and 60µm with substrate temperatures of 25 ℃, 30 ℃ and 35 ℃ respectively to investigate the effect of droplet spacing as well as substrate temperature on PCL film formation (Figure 12). From Figure 12, it can be noticed that when droplet spacing was 40µm and 60µm, edges between different printed tracks across at the whole temperature range. For films printed with 20µm droplet spacing, no significant edge was observed with substrate temperature of 25 ℃ and 30 ℃ until it reached 35 ℃. This is because at the low plate temperatures, due to lower evaporation rate, the ink had enough time to merge with each other both within and between different tracks after it was printed. Moreover, when the ink was printed at low droplet spacing, more droplets were printed within a unit area which mean higher ink volume and more evaporation was required before solidification. Therefore, droplets between different tracks have enough time to merge together. With increasing temperature, the solidification speed raised and edges start to appear for 20µm droplet spacing sample when the substrate temperature reached 35 ℃. For film samples printed with 40µm and 60µm droplet spacing, the ink volume within a unit area reduce to 26% and 13.5% respectively comparing with 20µm, which will significantly reduce the solidification time. Therefore the previously printed PCL track was solidified before the next track was printed and edges between them appeared.

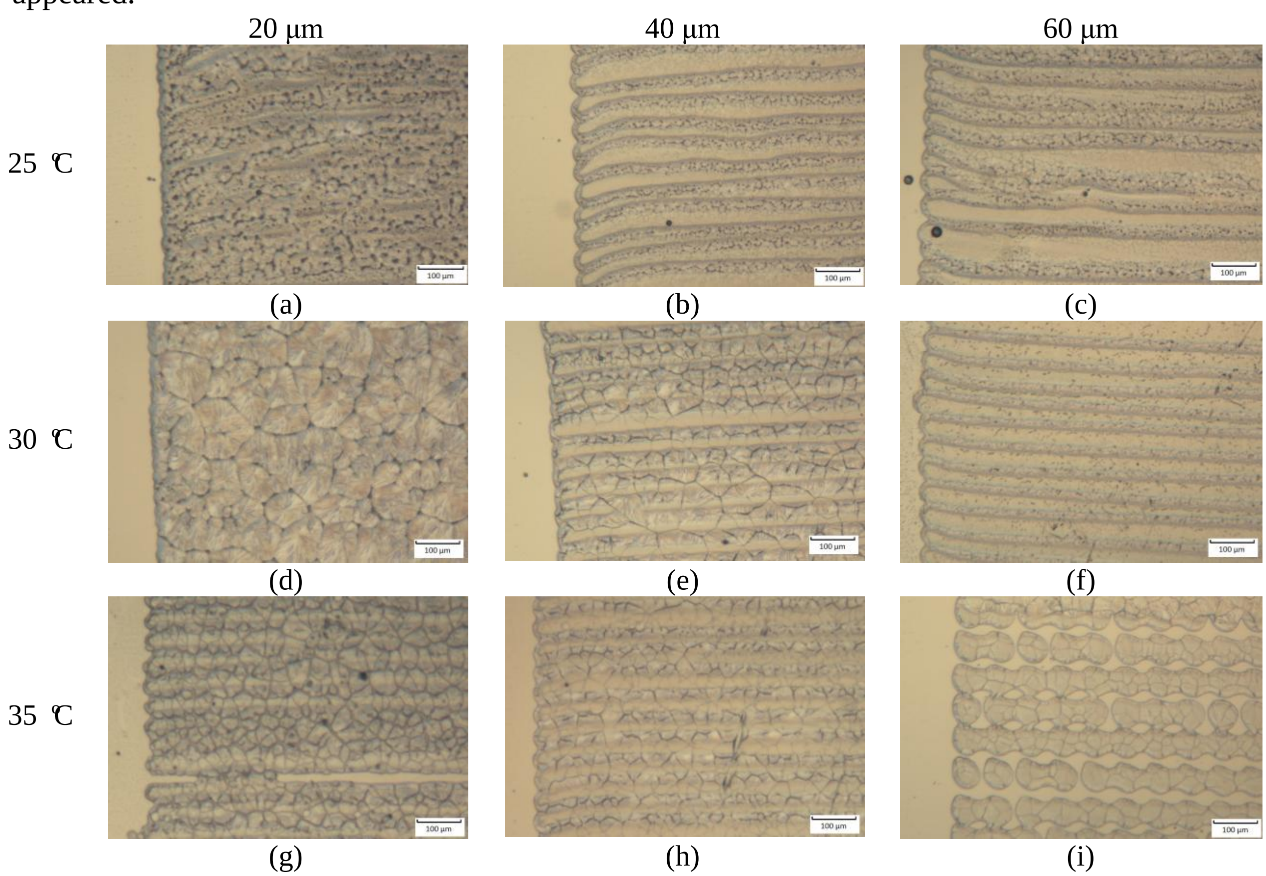


Fig.12: Microscopy picture of printed PCL solvent film with different droplet spacing and substrate temperature.

The edges between different printed tracks tended to be more regular and uniform at higher temperature i.e. 35 ℃. This is because at higher temperatures, the printed PCL track evaporates faster and locked to its deposited position. Meanwhile, the solvent within the ink will have less time to re-dissolve into the overlapping solidified part of a previous track to cause edge irregularity. However, the regularity of the printed film did not increase by increasing substrate temperature. From Figure 12 (i), it can also be noticed that some blank areas caused by nozzle failure during printing started to appear when the substrate temperature reached 35℃. During printing, the nozzle plate of the printhead was close to the substrate (1mm in this research) to minimize the air flow influence during droplet flight. This means that a heated substrate can warm up the nozzle plate easily through radiation which caused the PCL to solidify around the nozzle resulting in nozzle failure. It was found that when the substrate temperature was 30℃, PCL solvent ink can achieve stable printing and regular film formation.

The quality of printed films under different printing parameters were characterized by measuring Ten-point Mean Roughness value (Rz) through a Bruker ContourGT-I microscopy, results are shown in Table 4. Rz value of each film was measured at four points to calculate the mean value and standard deviation. From Table 4, it can be concluded that a 40μm droplet spacing with 30℃ substrate gave best film quality (both low Rz value and standard deviation). For films printed at 35 ℃ with 60μm, as it did not cover the whole substrate, the Rz value cannot show the real state of surface roughness, therefore, it was not included. It can also be noticed that as droplet spacing decreases, the film tends to be less uniform as the standard deviation value of Rz increased significantly.

Table 4: Ten-point Mean Roughness of printed film for 5wt% PCL solvent ink:

Ten-point Mean Roughness value (Rz)			
Substrate Temperature	Droplet Spacing 20μm	40μm	60μm
25℃	0.569±0.251μm	0.411±0.030μm	0.394±0.040μm
30℃	0.387±0.157μm	0.278±0.040μm	0.384±0.030μm
35℃	0.467±0.200μm	0.372±0.070μm	N/A

Multi-Layer Printing

Based on previous experiments, it was found that when PCL 5wt% solvent ink was printed with 6m/s droplet velocity (1mm printing gap), 40μm droplet spacing as well as 30 ℃ substrate temperature, the most uniform PCL film can be achieved (Table 4). Multi-Layer samples were then printed with these printing parameters.

Printed PCL samples were characterized by using Talysurf 2000. Figure 13 shows the surface profiling result of 3 printed layers PCL sample. Three different sizes of squares were printed (including 6mm*6mm, 4mm*4mm and 2mm*2mm). From Figure 13, it can be noticed that the edge of each layer was clear and the layer thickness was around 0.6 μm.

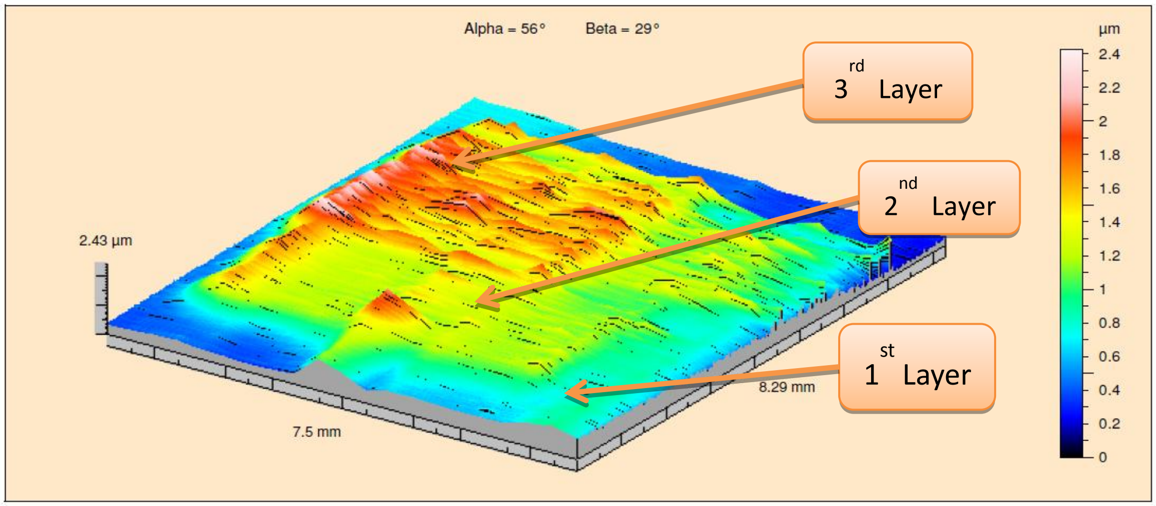


Fig. 13: Surface profiling result of printed PCL square sample

CONCLUSION

In this study, inkjet printing was used as a processing method to produce biodegradable polycaprolactone. It is found that high polycaprolactone concentration (10wt%) with 1,4-dioxane can easily cause nozzle blocking due to fast evaporation and precipitation of PCL at the nozzle plate at room temperature. During the droplet formation stage, in order to achieve uniform single droplet formation, the Total Printing Voltage Input needs to be carefully controlled and too high or too low TPVI will both cause droplet failure. When the time gap of the waveform equals to 3µs, the optimum TPVI value was found between 18.4-25.2V. As the time gap of the waveform increases, the velocity of droplet firstly increased and reached a maximum around 4 to 5µs and then reduced. With printing voltage increasing, the velocity of droplet will also increase. At droplet deposition stage, it was found that PCL tended to concentrate at an outer ring deposited droplet after solidification. Higher substrate temperature reduced the size of solidified PCL droplet and increased its thickness. When droplet velocity was 6m/s, the droplet diameter showed minimum deviation. During line formation tests, it was found that higher substrate temperature and larger droplet spacing will both cause printed PCL track width decrease. During film formation test, films formed at 40µm and 60µm droplet spacing showed edges between different printed PCL tracks. Higher substrate temperature made the edge between different printing tracks became clearer and more uniform. However, when substrate temperature reached 35℃, nozzle started to become instable due to heat radiation from substrate heat nozzle up and cause PCL precipitation which gradually blocked the nozzle. Based on our studies, it was found that when droplet speed equals to 6m/s, substrate temperature equals to 30℃, PCL film printed with 40µm tends to have best film formation. This described processing method offers a possibility of processing polycaprolactone through inkjet printing. Further works need to be carried out to modify the stability of the PCL solvent ink by reducing its volatility. Multi-solvent system is a potential solution to increase the PCL solvent ink stability.

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