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Quality evaluation of solvent-cast 3D printing of poly(lactic acid) films

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Abstract. This study aims to analyse the process conditions in the production of poly(lactic acid) (PLA) films by solvent-cast 3D printing. The films were evaluated according to thickness, roughness and visual aspect. An experimental design 2^2 was performed with centre point in triplicate to study solvent/PLA ratio and printing speed. The solvent/PLA ratio and printing speed had a significant negative effect on film thickness and positive effect on film roughness. The film that presented the best classification in the visual aspect was the one moulded with the highest printing speed and solvent/PLA ratio.

Keywords. Poly(lactic acid); solvent-cast 3D printing; liquid deposition modelling; experimental design.

1. Introduction

One of the new forms of polymer moulding is additive manufacturing, which is a technology used to fabricate materials from a computer aided data (CAD) file. The process consists of layer by layer deposition of a given material for the construction of the desired object in three-dimensional (3D) form. This allows an easy way to produce complex parts at relative low costs. The products have similar mechanical properties when compared with traditional methods [1,2]. Currently, the most common application of this method is in the production of functional models and prototypes, which shows that the market for additive manufacturing in industry is very promising [3] with potential applications in several areas, including aerospace, automotive, medical and pharmaceutical industries [4].

The liquid deposition modelling method, also called solvent-cast, was developed to manufacture geometric structures in 3D at room temperature, with thermoplastic polymers dissolved rather than melted. A schematic diagram of the apparatus and an example of its operation are shown in figure 1.

The solvent-cast 3D printing was described only recently [5,6]. The polymer is dissolved in a specific solvent and subsequently extruded onto a collecting surface to form the final object, which is previously modelled in a software, such as AutoCad. As the solvent evaporates, the solid polymer maintains the printed structure. This type of printing can be used with polymers that are sensitive to high temperatures or as a simpler way to model composites or nanocomposites with polymeric matrix, since one of the methods to disperse the particles/nanoparticles in the matrix is dissolving the polymer and use the ultrasound energy to improve the dispersion [7]. However, the success of the construction of 3D structures depends on process parameters, such as selected solvent, polymer concentration, printing speed and extrusion, among others [5].

Poly(lactic acid) (PLA) belongs to the class of aliphatic polyesters and is produced by the synthesis of lactic acid monomers [8,9]. The properties of PLA include high mechanical strength, excellent thermoforming, biocompatibility and compostability [10]. Although PLA has a Young's modulus comparable to PET, its low resistance and deformation have motivated studies in recent decades [11,12]. Still, the application field of PLA includes mainly the packaging and medical devices area [13]. The main forms of processing of PLA require the use of high temperatures at 185−190°C [14], but at these temperatures, chain breaks and consequent thermal degradation occurs, so that homopolymers of PLA have a very restricted processing window [14].

These factors motivated this study, which aims to print PLA films by solvent-cast 3D printing. As the method does not require high temperature, there is no thermal degradation, which can keep the PLA properties closer to the raw material. In addition, 3D printing allows the configuration of complex structures that conventional casting methods do not allow. We studied how the different parameters of initial solution and process parameters affected the thickness, surface roughness and quality of the films printed using PLA. Although the solvent-cast 3D printing method of PLA has been previously reported [5,15], there are few

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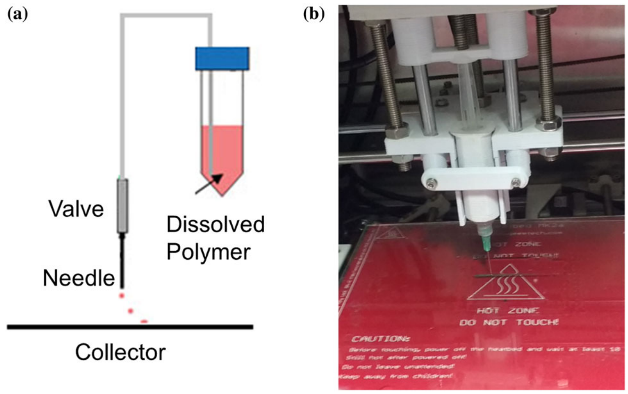

Figure 1. Process of solvent-cast 3D printing: (**a**) process diagram and (**b**) example of the operation of the printer to make polymer film (source: authors).

papers published about this technique and none of them try to understand more about the response that the printed material has in relation to the initial parameters (thickness, surface roughness and quality), which is the aim of this study.

2. Experimental

The materials used were the polylactide (PLA) Ingeo 4042D, manufactured by NatureWorks; and the solvent chloroform PA–ACS, stabilized with amylene. The 3D printer used was a prototype named Arion 210S developed by the company 3D Biotechnology Solutions for solvent casting. The PLA was dissolved for 24 h without stirring in chloroform at room temperature. A 2^2 factorial design was made according to the conditions described in table 1. An arbitrary composition was also made to validate the model.

For printing, a 5 ml syringe and a 0.8 mm diameter needle were used. After printing onto a glass substrate, the films were covered to slow the evaporation of the solvent. The evaporation of chloroform occurred at a room temperature of 18°C. After drying (24 h after printing), the films were removed from the glass substrate. Minitab® software was used for statistical analysis. The resulting model of the statistical analysis was tested considering a coded 50/12:1.

A flowchart of our printing method is presented in figure 2. The thicknesses of the films were measured using a Digimess digital external micrometer at five different points of the film (at the four corners and at the centre) to calculate the mean value among the five measurements.

The roughness determination was done by atomic force microscopy (AFM) on the equipment SPM-9600 (Shimadzu), using commercial Si tips. The roughness was measured on a surface of 10 μm.

The dynamic viscosity of the polymer solutions was measured with Vibro Viscometer SV-10 (A&D Company Limited) at room temperature.

The appearance of the films obtained in the seven trials was evaluated by an arbitrary scale ranging from 1 to 10, where 1 corresponds to non-continuous film, 5 corresponds to continuous film with imperfections and 10 corresponds to continuous film without imperfections. The films were analysed by three isolated evaluators, who did not know the evaluation of the others. The analysis of variance (ANOVA) of the generalized linear model with 95% confidence, was used to evaluate whether the score was affected by the evaluators and/or the tests.

3. Results and discussion

3.1 *Film thickness*

Figure 3 shows the contour plot and Pareto chart of film thickness. From the statistical results, equation (1) presents the regression equation in uncoded units of thickness. The R^2 is 85.42%.

$$\text{Thickness (mm)} = 0.1425 - 3 \times 10^3 \times A + 2.5 \times 10^4 \times B - 5 \times 10^5 \times A \times B, \quad (1)$$

where A stands for solvent/PLA ratio (ml g^{-1}) and B stands for printing speed (mm min^{-1}).

Table 2 shows a summary of the results of solution viscosity and of film thickness and roughness. Figure 3a and table 2 show that an increase in the solvent/PLA ratio causes a decrease in film thickness, which can be explained by the lower amount of polymer per square centimetre in more dilute solutions. As printing speed is increased, there is a small reduction in thickness. However, according to figure 3b, the only significant factor was solvent/PLA ratio, while the printing speed and the interaction between both factors were considered nonsignificant.

The lower thicknesses obtained for more dilute solutions (figure 3a) shows that solution viscosity decreases when compared to concentrated solutions (table 2) as well as shows an important role in 3D printing. The film formation on the substrate is also affected by the printing technique, which, in this case, occurs by the manufacture of continuous filament and by the solvent evaporation process [16]. The film drying is fast because of the presence of chloroform, an easy evaporation solvent, even at room temperature.

3.2 *Film roughness*

Figure 4 shows the contour plot and Pareto chart of film roughness. From the statistical results, equation (2) presents the regression equation in uncoded units of roughness. The R^2 is 97.36%.

$$\text{Roughness (mm)} = 2.3 - 0.7 \times A - 0.161 \times B + 0.0626 \times A \times B, \quad (2)$$

Table 1. Matrix of the experiments.

	Coded variables		Uncoded variables	
Sample*	Printing speed (mm min^{-1})	Solvent:PLA ratio (ml g^{-1})	Printing speed (mm min^{-1})	Solvent:PLA ratio (ml g^{-1})
40/5:1	−1	−1	40	5:1
40/15:1	−1	1	40	15:1
60/5:1	1	−1	60	5:1
60/15:1	1	1	60	15:1
50/10:1	0	0	50	10:1
50/10:1	0	0	50	10:1
50/10:1	0	0	50	10:1
50/12:1**	—	—	50	12:1

*Printing speed/solvent; PLA ratio.
**Arbitrary sample for model validation.

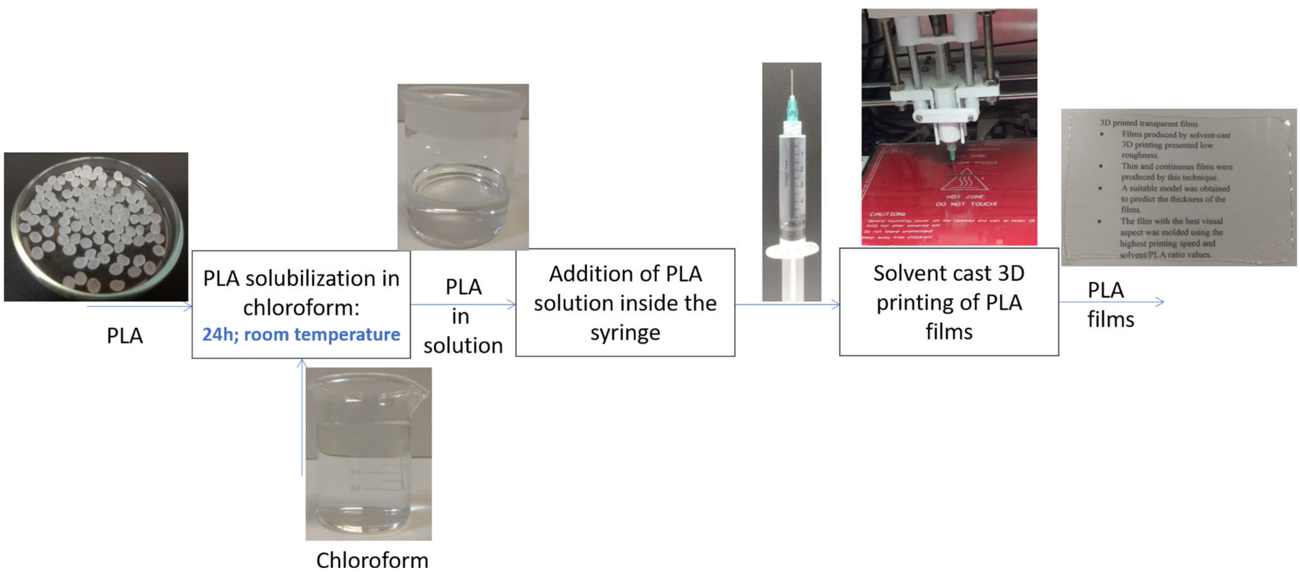

Figure 2. Solvent-cast 3D printing method by liquid deposition modelling.

where *A* stands for solvent/PLA ratio (ml g^{-1}) and *B* stands for printing speed (mm min^{-1}).

Table 2 shows the roughness values of PLA films. The obtained roughness values were considered low, when compared with results reported in the literature. For systems of polymethacrylate and polystyrene in chloroform, using casting technique, the film roughness obtained was 79 nm [17]. Although film roughness may vary depending on the solvent and the polymer used, we observed that the films obtained by Strawhecker *et al* [17] using chloroform have a higher roughness than those obtained in this study. According to the conditions used, 3D printing is a good method to produce less rough polymer films.

Figure 4a shows the contour plot of roughness, and one can observe an increase in roughness with the increment of printing speed and solvent/PLA ratio. This is corroborated by the Pareto chart (figure 4b), which shows that both main factors are significant.

A lower solvent/PLA ratio may lead to less polymer diffusivity in the solvent [18], affecting the final morphology and the polymeric macromolecules arrangement [19]. Solutions that present lower solvent/PLA ratio can become rougher films because of the lower diffusivity needed for PLA molecules to rearrange. A higher roughness may be induced by a greater convective instability, which can be originated from the greater concentration of polymer in the solvent [20]. Higher printing speed values may increase the roughness by enhancing the natural convective instability of the evaporation [21]. As more solution is extruded during printing, it can dissolve regions that are already solid and increase local convection.

The composition 50/12:1 was produced to verify the model. For these conditions, according to equation (1), the model predicts that thickness should be 0.09 mm. The thickness measured was 0.09 ± 0.02 mm, which fits the model. The roughness measured was 9.51±0.01 nm. For these conditions,

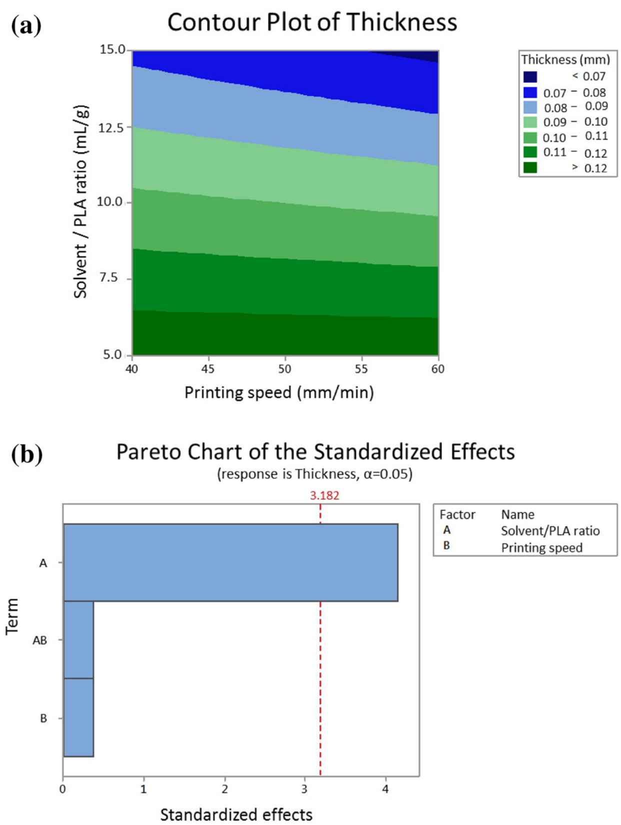

Figure 3. **(a)** Contour plot and **(b)** Pareto chart of thickness with 95% confidence.

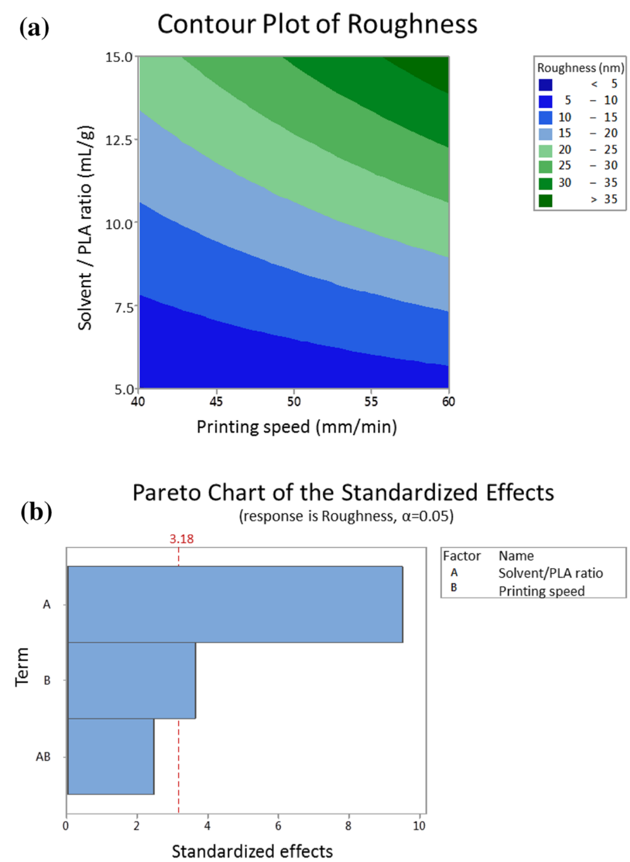

Figure 4. **(a)** Contour plot and **(b)** Pareto chart of roughness with 95% confidence.

Table 2. Summary of the results of viscosity of the solutions and of thickness and roughness of the films.

		Response	
Sample*	Viscosity (Pa s)	Thickness (mm)	Roughness (nm)
40/5:1	9.51 ± 0.09	0.13 ± 0.02	5.37 ± 0.01
40/15:1	0.19 ± 0.02	0.08 ± 0.02	23.40 ± 0.01
60/5:1	9.51 ± 0.09	0.13 ± 0.02	8.40 ± 0.01
60/15:1	0.19 ± 0.02	0.07 ± 0.01	38.95 ± 0.01
50/10:1	1.31 ± 0.01	0.08 ± 0.01	21.20 ± 0.01
50/10:1	1.31 ± 0.01	0.10 ± 0.01	15.63 ± 0.01
50/10:1	1.31 ± 0.01	0.11 ± 0.01	16.84 ± 0.01
50/12:1	0.14 ± 0.01	0.09 ± 0.02	9.51 ± 0.01

*Printing speed/solvent:PLA ratio.

according to equation (2), the model predicts that roughness should be 23.41 nm. The predicted result does not show a good approximation with the measured result, showing that other factors could affect roughness, such as humidity and temperature of the environment during the printing process. All samples were printed on the same day, which presented relative humidity of 70% and average room temperature of 18°C. Chloroform evaporation to form the films occurred at room temperature to simplify the printing process. The presence of humidity could influence PLA properties, as it is a polyester, which may undergo hydrolyses, reducing the size of its chains [22].

3.3 *Visual aspect of films*

Table 3 presents the results of the film visual aspect given by three evaluators. Figure 5 shows an example of the 3D printed film of the 60/15:1 sample. It is a transparent, homogeneous and continuous film, which presented the best evaluation in comparison with other films, according to table 3.

Films that were evaluated with the two lowest film aspects were cast in lower solvent/PLA ratio condition and higher dynamic viscosity (9.51 Pa s, table 2). To produce uniform films during e 3D printing process, the several lines printed in each layer must join in such a way that (1) they form a continuous film and (2) they maintain the stability of the model designed in AutoCad. For solutions with higher viscosities, the coalescence between the sequentially deposited solution lines may not have occurred. These films did not present a uniform appearance, since the film aspect scores were <5, which was considered the standard score for uniform films. As solvent/PLA ratio increases and solution viscosity

Table 3. Visual aspect results of 3D printed films.

Ranking	Sample*	Film aspect evaluator 1	Film aspect evaluator 2	Film aspect evaluator 3	Film aspect mean	Standard deviation
1	60/15:1	10.0	10.0	10.0	10.0	0.0
2	50/10:1	9.0	9.0	10.0	9.3	0.6
3	50/10:1	8.0	8.0	10.0	8.7	1.2
4	50/10:1	5.0	5.0	9.0	6.3	2.3
5	40/15:1	7.0	3.0	7.0	5.7	2.3
6	40/5:1	5.0	1.0	1.0	2.3	2.3
7	60/5:1	2.0	1.0	1.0	1.3	0.6

*Printing speed/solvent: PLA ratio.

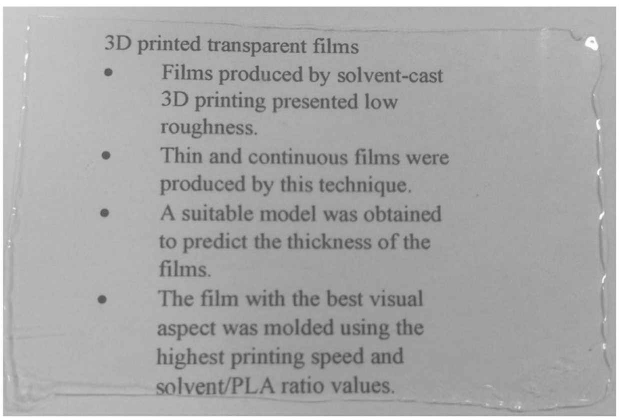

Figure 5. 3D printed film of the 60/15:1 sample.

Table 4. ANOVA with 95% confidence of the generalized linear model for film aspect as a function of the evaluator and the test.

Source	DF	SS (Ad.)	MS (Ad.)	F value	*P* value
Evaluator	2	9.810	4.905	2.25	0.148
Sample	6	207.810	34.635	15.87	0.000
Error	12	26.190	2.183		
Total	20	243.810			

decreases, the bond ability between the layers become higher, allowing a continuous film formation and improving the film aspect.

However, the 40/15:1 composition presented a lower film aspect, which was similar to the centre point (with 10:1 dilution). In this case, a slower printing speed increases the time in which each line is formed, which seems to affect the film aspect. As time passes and the printed line solvent evaporates, its local viscosity increases, which probably presents the same problems of the 5:1 dilution compositions with the difficulty to form uniform films.

Table 4 shows the ANOVA with 95% confidence, of the generalized linear model for film aspect as a function of the evaluator and the test.

Table 4 shows a P value >0.05 for the evaluator factor and <0.05 for the sample factor. A P value <0.05 indicates that only the sample factor showed a significant variation in the visual aspect of the films. The evaluation criterion was statistically the same for different evaluators, which means this subjective evaluation was reliable.

4. Conclusion

This study analysed the moulding process of solvent-cast 3D printing to produce PLA films. In the evaluated conditions, we obtained continuous films with good visual aspect; in addition, statistical analysis allowed us to evaluate the influence of the process conditions on the thickness and roughness of the studied range. However, the model was only able to predict the thickness. Solvent-cast 3D printing is an alternative process to manufacture test specimens in the form of thin films with low roughness.

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