Analysis of Thermal Degradation in the Annealing Process of Colored Parts Built by Extrusion-Based 3D Printing

K. Castro[1], L. Santana[2], J. Lino[3]

[1]University of Debrecen, Faculty of Engineering, leocastroskp18@gmail.com
[2]University of Porto, Faculty of Engineering, leonardosantana29@gmail.com
[3]University of Porto, Faculty of Engineering, falves@fe.up.pt

Abstrac. With the ever-increasing request of light materials, poly lactic (acid) PLA, have got much in consideration. Low-cost PLA materials have risen its use. Those possess some benefits but nevertheless insufficient mechanical strength. The printed PLA objects have a stumbling block for practical applications. Thus, annealing is an interested alternative to make 3D printed objects strong. This thermal treatment can significantly develop investigational studies and offer technical data. Hence the purpose of this paper is study and discuss how to increase the flexural strength through annealing process. Geometry distortions and color degradation will be analyzed. Differential Scanning Calorimetry, Taguchi Method (TM) and variance (ANOVA) were applied as part of the design experiments and analysis. Twenty-seven printed specimens were tested and factors as temperature, time and color were selected.

Keywords: Poli-lactic (Acid), Differential Scanning Calorimetry, Analysis of Variance, Taguchi Method.

Introduction

Due to the development of open source projects, there is not any standard which regularize technical properties of filaments used to in FDM (Fused deposition modelling) process. Many users set up parameters through experimental tests [1]. Most of the free-code 3D print equipment turn out interesting to the field of investigation, due to flexibility, capacity, and material as PLA-Poly lactic (acid). Some studies were developed to corroborate the properties of PLA filaments [2] [3] [4].

Thermally, PLA shows a glass transition about (55 to 65) °C [5] and fusion temperature of (170 -180) °C [3]. PLA can transit between an amorphous or semi crystalline polymer. When it is semi crystalline it has a melting temperature between 170 and 180 °C. PLA is widely used in some industries although the lowest impact resistance and tensile and flexural strength [6].

Nevertheless, lack of standardization and information about how to improve mechanical properties without geometrical and color distortion, makes this subject interesting for academic research.

Annealing of materials is used to decrease internal stress in objects and make those objects mechanically stronger, temperature resistant, less brittle, ductile, and less prone to warping [7].

An oven annealing temperature was settled at 70°C, above the glass transition but bellow the melting point. The specimens were treated for 1 hour and then leave it to cool. The results showed an increase of 40% in mechanical strength; however, it was evident the shrink in the X and Y directions, expansion in the Z direction and warped around the printed surface [7].

Annealing at 75°C increased tensile and compressive strength compared to samples tested at room temperature. The annealing effects on crystallinity relief residual stress, and make better inter-layer bonding, which causes changes in mechanical properties of 3D printed specimens [8].

Into some areas of engineering field and biomedical, 3D printed colors are used to get replicas of a real stress. Alteration in color appearance, may be perceived when 3D prints are exposed to annealing process and infiltration agents [9].

Temperature, time, and geometrical tolerance are essential in novel process as freeze nano 3D printing, where the dropped solidification, heat transfer, and time prediction behaviour is crucial [10].

As it can be seen, most of the available literature presents optimization of mechanical properties by considering controllable parameters such: extrusion temperature, print velocity, inner structure, layer height, material, and post processing. However, there is still little information regarding the influence of annealing to geometrical and color properties, thus this being the paper's intention.

1. Materials and Methods

Experimentally this work was divided in two groups of analysis *Figure 1*. The first group make a thermal analysis. The second group study the behaviour and alterations of the 3D printed specimens.

1.1. Flexion test specimens, Materials, Equipment and Thermal analysis

The flexion test specimen was prepared according to ASTM D790. PLA 'filament-PM', 1.75 mm was used. A 3D printer (Ender 3 by Creality3D) with a closed print chamber was operated. Data acquisition equipment 'NOVOS' measured a real approximation of temperature on the bed and the tip extruder. POL-EKD Apartura Incubator STD, used for annealing process. Colorimeter PCE-CSM 5, measured the differences of color before and after annealing treatment. MECMESIN multi test 2.5-dv, tensile and compression tester. Digital micrometre Mitutoyo, for measuring the width and thickness of specimens.
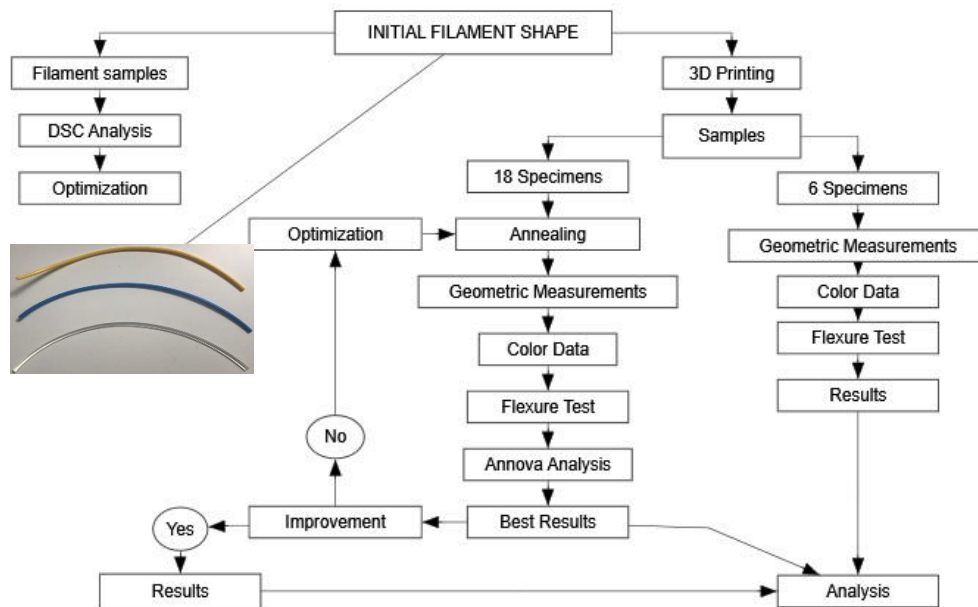
Figure 1 Methodology of Investigation (own source)

The DSG (Differential Scanning Calorimetry) analysis identified the PLA transitions of states as a function of temperature, as Tg-cooling, Tcr- Crystallization and Tf-Fusion. SDT Q6Ta Instruments was operated as equipment. The *Figure 2* identify important temperatures for annealing in this study (50, 90, 130) °Celsius. A thermal treatment between these temperatures will reorganize the internal crystalline structure, generating bigger grains setting up stronger objects [7].

1.2.   3D-Printing Process and Color Analysis

Printed parameters were setup as Layer height: 0.2 mm, Line width: 0.4 mm, Line wall: 5, Platform temperature: 60ºC, Infill density: 100%, Printing extrude temperature: 215ºC, Material flow rate: 102%, Print speed: 60 mm/s, Infill speed: 60 mm/s, Inner/wall speed: 30 mm/s, Print cooling: Enable, Fan speed: 100%. The specimens were stick off at 30°C of bed temperature. Controlling the temperature in the chamber can avoid internal stresses during solidification and cooling.

In this study, spectral values of printed specimens were compared, in terms of CIE L*a*b color shifts and color difference dE*± 0.500 tolerance equation 1, with CQCS3 SOFTWARE version 3.4.3.

The collected spectral data was converted into L*a*b values of color coordinates in CIELAB color system, where L* represents the lightness from luminance value while a* (redness-greenness plane) and b* (yellowness-blueness plane) symbolize the chromatic value of the color.

$$\textit{Difference color equation:}\quad dE* = \sqrt{dL^{*2} + da^{*2} + db^{*2}} \tag{1}$$

1.3.   Taguchi Method

Considering that customer's perception of quality is the most important factor, many companies look for quality through product and process optimization. This structure study was elaborated as shown *Figure 3*. The first stage defines the factors and the adequate orthogonal array (OA). The second stage is

essentially execution of experiments. Third stage deals with data examination, which was done using specialized software, and finally the fourth stage agrees to the corroboration of the experiment [11].
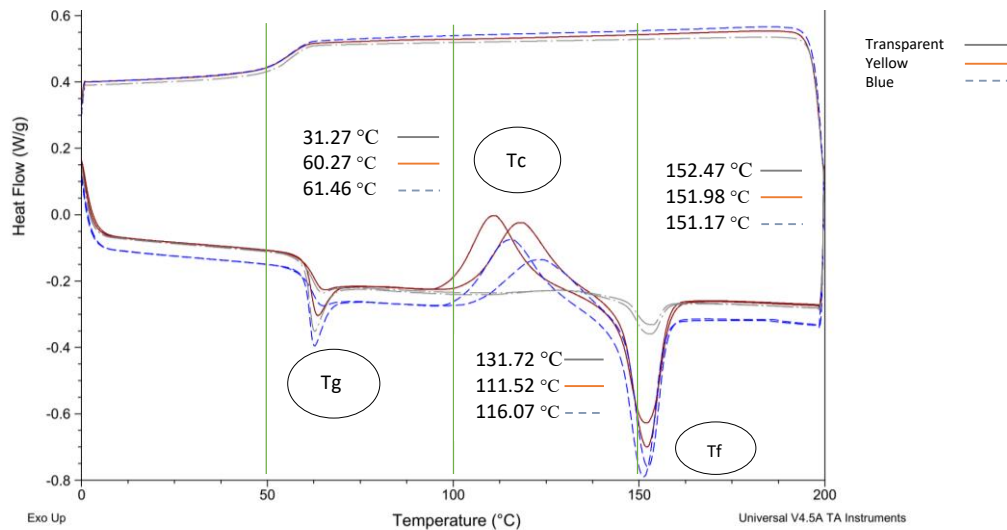

Figure 2 Thermograms obtained by DSC analysis. Tg-cooling, Tcr-crystallization and Tf-fusion temperatures (own source)
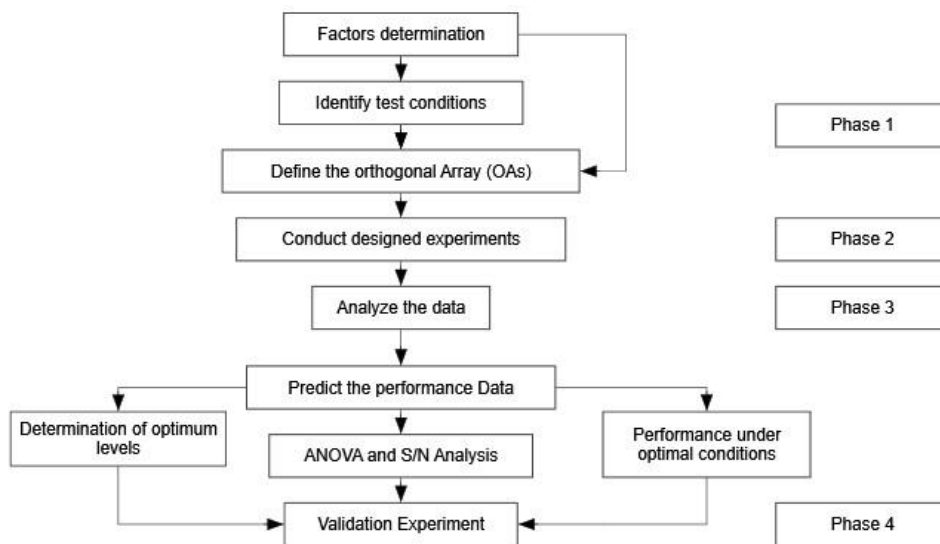

Figure 3 Scheme of the Taguchi Method approach (own source)

Three significant factors were identified: Incubator's Temperature (A), Time (B), and Color (C). Three levels for each factor were recognized as show in *Table 1*. The knowledge of the process is essential when sectioning the factors and levels to be considered with the experimentations [12].

FACTORS AND LEVELS

FACTORS	UNITS	LEVELS		
		1	**2**	**3**
A Incubator's temperature	Celsius	50	90	130
B Time	Minutes	20	40	60
C Color	Type	Transparent	Blue	Yellow

Table 1 Taguchi factors and levels

Defining the appropriate Orthogonal Array (OA) is an essence to assure truthfulness of the statistical model [12]. Thus, a L9 (OA) is chosen for this research. This experimental design shows the array selector for parameters and their interactions. Besides, the measurements and means trials *Table 2*.

TRIAL N°	(A)	(B)	(C)	S1 (MPa)	S2 (MPa)	S mean (MPa)	T1 (mm)	T2 (mm)	T mean (mm)	W1 (mm)	W2 (mm)	W mean (mm)	dE*
1	50	20	Transparent	91.963	96.752	94.357	3.372	3.045	3.209	12.552	12.666	12.609	1.744
2	50	40	Blue	106.876	105.499	106.188	3.089	3.05	3.070	12.723	12.877	12.800	2.216
3	50	60	Yellow	109.546	108.359	108.952	3.043	3.068	3.056	12.902	12.611	12.757	0.470
4	90	20	Blue	111.136	112.791	111.964	3.427	3.418	3.423	12.902	12.611	12.757	1.484
5	90	40	Yellow	110.350	117.039	113.695	3.437	3.301	3.369	12.485	12.732	12.609	1.508
6	90	60	Transparent	100.390	119.852	110.121	3.661	3.381	3.521	12.235	12.235	12.235	2.462
7	130	20	Yellow	96.050	98.198	97.124	3.567	3.586	3.577	12.274	12.235	12.255	3.468
8	130	40	Transparent	102.299	100.083	101.191	3.711	3.7103	3.711	12.271	12.248	12.260	7.394
9	130	60	Blue	106.801	99.715	103.258	3.583	3.753	3.668	12.335	12.202	12.269	4.202

Table 2 Experimental results after thermal exposure: flexural Stress (S), thickness (T) and width (W) mean, shift color difference (dE) based on L*a*b* measurements (own source).*

1.4. Annova Analysis and Performance Data

F-value is compared to the standard value F (0.05,2,2), which means at the 5% of significance level, degrees of freedom (DF) of the factor, and the DF of the error correspondingly. In this study a factor is significant only if the calculated F-value is greater than F (0.05, 2, 2) =19. For flexural analysis case, factor (A) is not statistically significant, despite 58% of influence *Table 3*.

Source	DF	S	V	F	%P	P value	F (0.05,2,2) = 19
Time	2	0.1847	0.0923	3.42	21.353	0.226	X
Color	2	0.1213	0.0600	2.25	14.023	0.308	X
Error	2	0.0540	0.0270		6.243		
Total	8	0.8650			100.035		

Table 3 Analysis of Variance flexural stress (own source)

In order to get the prediction model, an analysis of the factors was performed as shown in *Figure 4* . For the case of thickness analysis, factor (A) is statistically significant, as 92% influential factor towards a response. For the case of width, the factor (A) is statistically significant, about 78% of effect. In Color case, factor (A) is responsible about the 69% of final response. Factors (B) and (C) do not represent a significance to the result in all the cases.

Agreeing to the Taguchi model, the greatest performance for the experiment can be achieved with the next expression equation 2, [12]:

Optimal result equation: $Ropt = A + B + C - 2 * Rmean$ (2)

The values (A, B, C) for each factor are taken from response means tables. *Table 4* shows means and an optimized result of 115.49, for flexural stress case. On the other hand, 3.034 mm and 12.896 mm are the optimized results for thickness and width cases respectively *Table 4*. A confidence interval (CI) must be calculated for validation procedure as show equation 3.

Confidential interval equation: $CI = \sqrt{F(1, DFE) * Ve * \left[\frac{1}{Neff} + \frac{1}{R}\right]}; \quad Neff = \frac{N}{1+Vt}$ (3)

Where F (1, DFE) is taken form tables at 95% confidence. DFE is the number of DF related to the error, it is 2. F (1,2) = 18.513. Ve is the variance of the error for each case of study. For flexural stress case the information can be found in *Table 3*. R=2, is the number of the test repetitions. Neff is the effective number of replications. N=9, is the total number of trials in this study. Vt = 2 it is the total DF of influence factors. Thus, CI: flexural Stress= ± 0.645 MPa, thickness = ± 0.026 mm and width = ± 0.032 mm.

Level	Inc Temp(A)	Time(B)	Color(C)
1	103.2	101.1	107.1
2	111.9	107.0	101.9
3	100.5	107.4	106.6
Delta	11.4	6.3	5.2
Rank	1	2	3

	Factors			
	A	B	C	Predict response
F. s	90	60	Yellow	115.49± 0.645 MPa
T	50	40	Yellow	3.034 ± 0.026 mm
W	50	40	Yellow	12.896 ± 0.032 mm

Sopt=A(50°C) +B (60 Min) +C(Yellow)-2*Smean
Sopt= 111.9+107.4+106.6-2*105.205=115.49MPa

Table 4 Response means for Flexural Stress and predict responses for each case F.s (Flexural stress), T(Thickness), W (width) (own source)
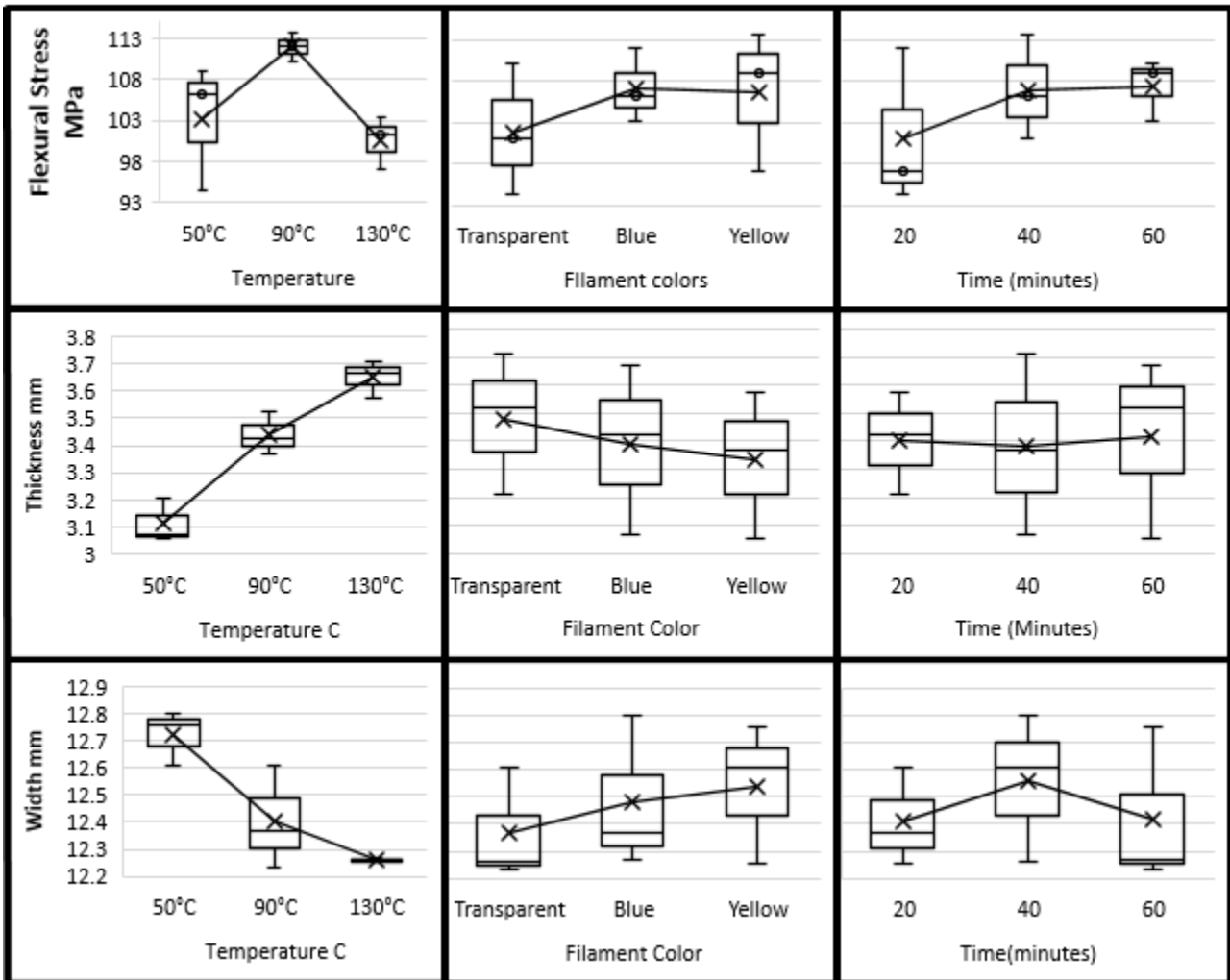
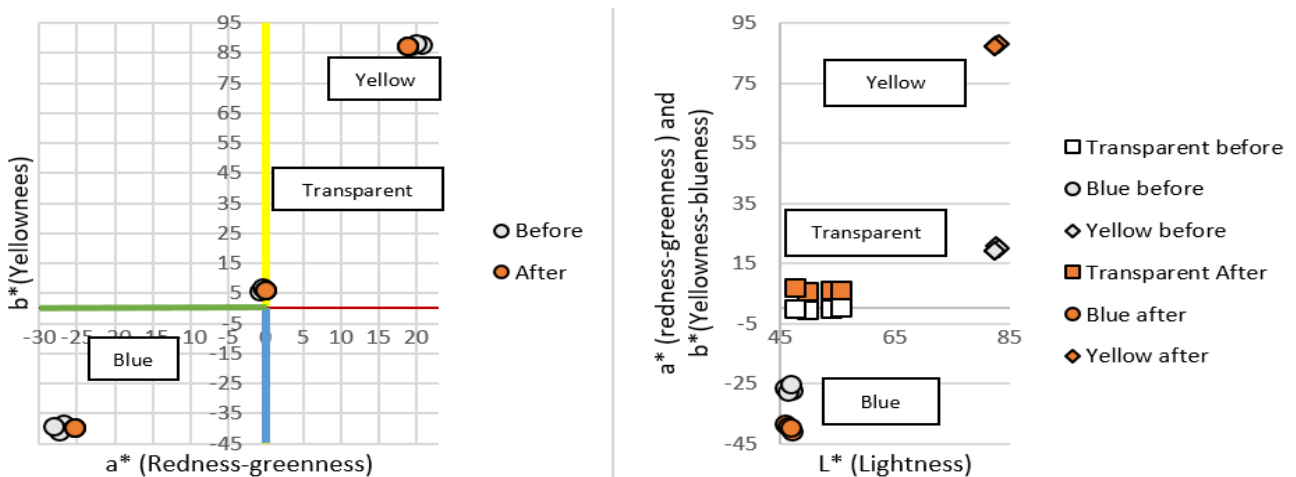*Figure 4 Response of main effect factors for flexural stress, thickness, and width cases*

Figure 5 Right. - a* vs b* color printed specimens' measurements. Left. - L* vs a* and L* vs b* samples Colored specimens (own source)

The *Figure 5* shows the CIELAB a*b* plot, of all the colored printed specimens (Left graph). When comparing the position of the marks before and after annealing. A depreciable shift in chroma can be

visible. The shift in lightness values L* (Right graph), an appreciable difference can be seen in yellow printed specimens.

2. Discussion and Conclusions

Validation experiments were performed for optimal combinations as it can be seen on *Table 5*. Yet as a temperature below 90°C and upper 50 °C, can be used as effect of significant positive results for future investigations. Factor time (B) correlates positively with the result. An increment of flexural stress can be seen in yellow filament test about 11.75% *Figure 6*, and insignificant variation in thickness, width and color properties. The values were compared with specimens without annealing treatment.

A judgment can be carried out whit this analysis to verify whether color difference can meet the requirements, after the thermal/time exposure, according to the allowed customer's tolerance and color standard. Thus, this study provides considerations and information to compare, about the behaviour of geometric, color and flexural properties of 3D printed specimens after annealing process.

The characterization of PLA enabled to corroborate thermal properties and relevant transitions of states as a function of temperature. The result shows aspects of semi crystalline polymer but amorphous and crystalline pre-eminence. The filament tested did not lose mass during the experiment.

Correlating the obtained results with previous studies [13], they presented as a result of 1 hour of annealing at (80 and 100) °Celsius a flexural strength about (118 and 125) MPa respectively for 3D printed PLA samples. These values are positives but, they do not consider the geometric and color deformation caused by the annealing temperature upper 50°Celcius.

The results display to 3D printing users, the importance of time and annealing temperature for an increment of the flexural strength without geometric and color significant alterations. The results are base for future investigations, where changes of parameters, equipment, software, materials, filling printing and cost can be implemented, improved, and compared with other technologies.
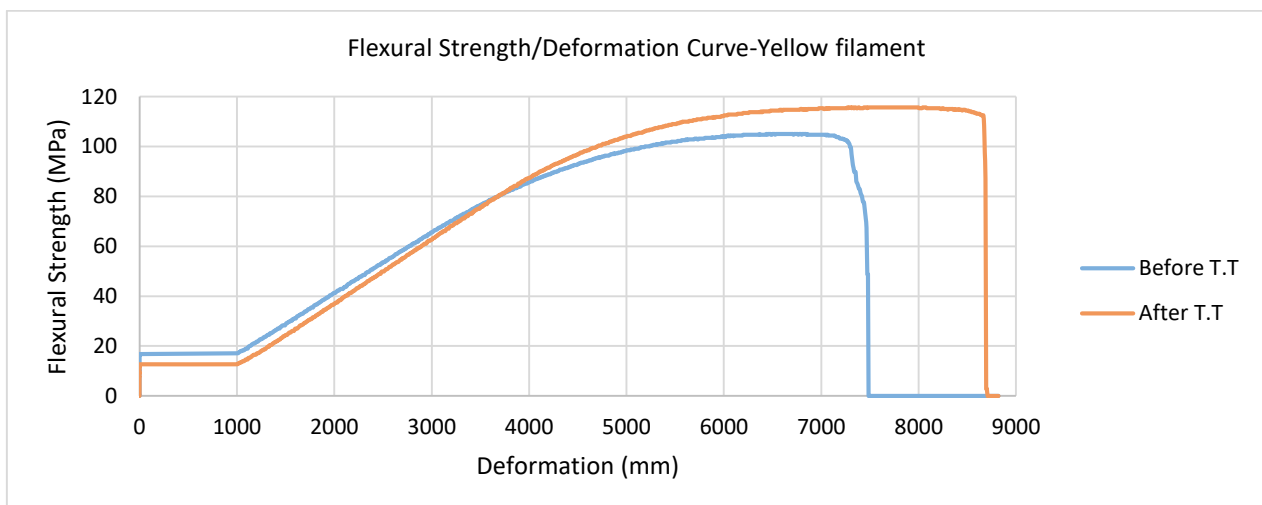

Figure 6 Force/Deformation curve, Before and after annealing, yellow color filament (own source)

TRIAL N°	Inc-Temp °C	Time (Minutes)	Color	S mean (MPa)	Thickness (mm)	Width (mm)	dE*
12	50	60	Transparent	104.232	3.098	12.587	5.285
11	50	60	Blue	116.723	3.061	12.481	4.274
10	50	60	Yellow	<u>115.703</u>	<u>3.072</u>	<u>12.501</u>	<u>0.455</u>

Table 5 Validation experiment Flexural Stress, Thickness, width, and Color Difference (own source)

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