The effect of 3D printing temperature on PLA/HA/TiO2 composite filaments

[Mikail Olam, Nihat Tosun]

Abstract— **Polylactic acid (PLA) based polymer composites containing titanium dioxide (TiO$_2$), synthetic hydroxy apatite (HA) and natural hydroxy apatite (nHA) have been developed for biomedical applications. These extruded composite materials were printed using Fused Deposition Modeling (FDM). 3D printing parameters and mechanical properties were characterized. According to the tensile dimensional accuracy analysis; Maximum tensile strength (59.85 N/mm^2) and maximum elongation to break (1.62 mm) were obtained from a mixture of 98% PLA, 1% nHA and 1% TiO$_2$ at 220°C printing temperature.**

Keywords—**filament, tensile strength, PLA, TiO$_2$, HA, fused deposition modeling,**

I.   Introduction

Today, the tasks loaded on the materials used in many areas are increasing day by day. It is very important to expand the range of products used for therapeutic purposes especially in living organisms and to produce new products. In order for a biomaterial placed in a living organism to function properly, it must have at least enough features to replace / provide additional support. Composite filaments can be used in these applications because they have the properties of more than one material. 3D printers are one of the most important options in terms of both production cost and time and product features of applications specific to the person and the place of use [1]. 3D printer technology is used in industrial design, engineering, architecture, military, medical (orthotics, prosthetics), biotechnology (human tissue identities), fashion, food and many other fields [2]. 3D printing ushered in a revolutionary era in medical product design and development. It is widely used in the production of anatomically correct tissue skeletons where biomaterials are placed at specific points in 3D space via a computer-controlled distribution system [3,4]. Fused deposition modelling (FDM) printers are among the most common and inexpensive 3D printers today. In this study, filaments produced with polylactic acid (PLA), synthetic / natural hydroxyapatite (HA, nHA) and TiO$_2$ mixtures were 3D printed by FDM printer.

Polylactic Acid, which can be produced from annually renewable resources and are biodegradable polymer [5], is a biocompatible material used in living tissues. Polylactic acid (PLA) has an important place in bone tissue engineering due to its biodegradable environmental friendliness, biocompatibility, thermal plasticity, and suitable mechanical properties [6]. Hydroxyapatite (HA) is an excellent biomaterial for bone repair and regeneration [7,8]. HA enhances biological functions of nanoscale particles such as biological mineralization, cell interaction and cell proliferation [9]. TiO$_2$, which it has biocompatible and chemical stability, nontoxicity and nanocrystalline, has been employed for many significant applications as the self-cleaning coatings for buildings materials [10,11], glasses and tiles [12], self-sterilizing solid surfaces [13,14], bone-implant fixation [15,16].

To improve the thermal properties of the PLA filament; By increasing the amount of nano-SiO$_2$ in the PLA / nano-SiO$_2$ composite filament, it improves properties such as the degree of orientation, coefficient of friction, thermal decomposition temperature and glass transition temperature [17]. In composite filaments obtained from SiC/C/PLA mixtures; As the SiC and C ratio increases, the thermal conductivity feature increases and the shape recovery time decreases [18]. Biocompatible polyurethane (TPU) / PLA (polylactic acid) / Graphene Oxide (GO) mixture filaments; The addition of GO from the mechanical properties of the polymer matrix increases the compression modulus by 167% and the tensile modulus by 75.5%, the adherent demonstrates excellent cell viability in the cell culture test and is also useful for small amounts of GO cell proliferation [19]. In 3D printing of filaments formed in micro fibrillated cellulose (MFC) / PLA mixture; MFC significantly reduced clumping [20]. By adding micro-sized particles (ZrB$_2$ and Al alloy) to ABS composite filaments reinforced with different nano / micro particles (MWCNTs, SiO$_2$, ZrB$_2$, Al), it increases the tensile strength by at least 18% [21]. It increases the tensile strength of the filaments produced by using 1/9 wood / PLA from 55 MPa to 57 MPa [22]. Cellulose / PLA blend filament increases impact strength by 34-60% and tensile strength by 43-52% than pure PLA filament [23]. PEG in a polycaprolactone / polylactide / polyethylene glycol (PCL/PLA/ PEG) blend; It significantly improves the tensile, impact strength and modulus of elasticity of PCL/PLA [24]. Filaments from PLA and biphasic calcium phosphates (BCP) are somewhat brittle, but suitable for use in FDM printers [25]. With the increase in chitosan ratio (1.1.5.2%, wt.) in chitosan reinforced PLA scaffolds, it decreases the tensile and bending strength, but also increases the compressive strength [25].

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In this study, PLA based polymer composites containing TiO_2, synthetic HA and natural HA have been developed for biomedical applications at FDM. These composite materials were printed using FDM. 3D printing parameters and mechanical properties were characterized. According to the tensile dimensional accuracy analysis; Maximum tensile strength and maximum elongation were obtained from a mixture of 98% PLA, 1% nHA and 1% TiO_2 at 220°C printing temperature. Studies involving HA/TiO_2/PLA mixtures have been carried out, but there are coating studies on material surfaces using methods such as dipping [26,27], not to be printed on the FDM 3D printer. In this study, 3D prints produced with FDM 3D printers, mechanical properties such as tensile, tensile strength, tensile stress, max tensile, max tensile elongation; existing composite filaments / pure PLA (100% PLA) filaments have properties or are intended to improve these properties.

II. Material and Method

A. Material

In this study; a granular PLA (Purapol LX175, crystalline white pellets, melt flow index: 8 g/10 min), a hydroxyapatite (NG10SM0104, CAS: 12167-74-7, average particle size: 50 nm), a TiO2 (CAS: 13463- 67-7, average particle size: 200 nm) and commercial PLA (PLA Max) was used as material. Natural hydroxyapatite (nHA) is obtained by cleaning the soft tissue inside and outside of the beef bones and drying them under atmospheric conditions.

B. Method

The process parameters were made by following the process steps shown in Figure 1. The granules PLA and nHA were ground and dried in an oven at 60 °C for 24 hours, then they were prepared in desired mixing ratios. The prepared mixtures were turned into filaments with a single screw extruder at 190 °C. The obtained filaments are FDM 3D printer (3D printing temperature: 190-220 °C, printing speed: 2880 mm / min, bed temperature: 45 °C, interior fill percentage: 100 %, layer height: 0.15mm, internal & external fill pattern: rectilinear, internal & external infill angle: 45 deg.) samples were 3D printed. Then, tensile stress (pulling speed:1 mm/min., Shimadzu autograph AGS-X series) and dimensional accuracy analyzes were performed on 3D printing samples obtained.
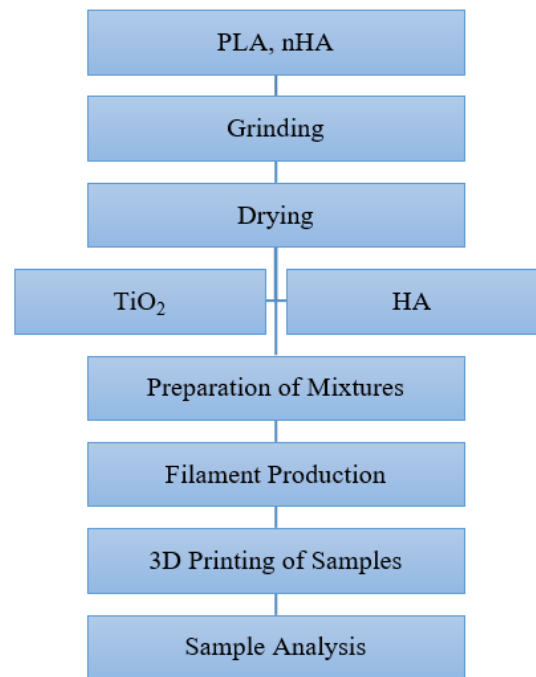

Figure 1.   The process parameters

1) Natural hydroxyapatite (nHA) production

Natural hydroxylapatite (nHA) was ground in a Fritsch Pulverisette 6 Mono Mill model planetary ball mill, after cleaning the soft tissue inside and outside the beef bones, first natural drying in the laboratory for 24 hours, then dried in an oven at 60 °C under atmospheric conditions for 24 hours. Dimensional analysis was performed using the ironed natural hydroxyapatite Mastersizer 2000 (Hydro 2000 MU) model device (Figure 2). SEM (LEO-EVO 40) analysis of beef bone powder obtained in Figure 3 and XRD (Rigaku Miniflex 600) analysis can be seen in Figure 4. According to the results of XRD, it is seen that the nHA obtained consists of Ca5(PO4)3(OH) compound.
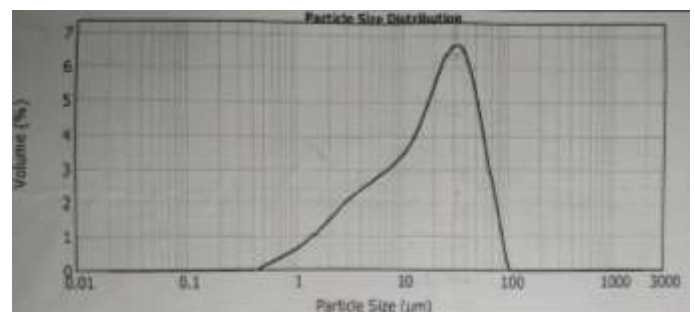

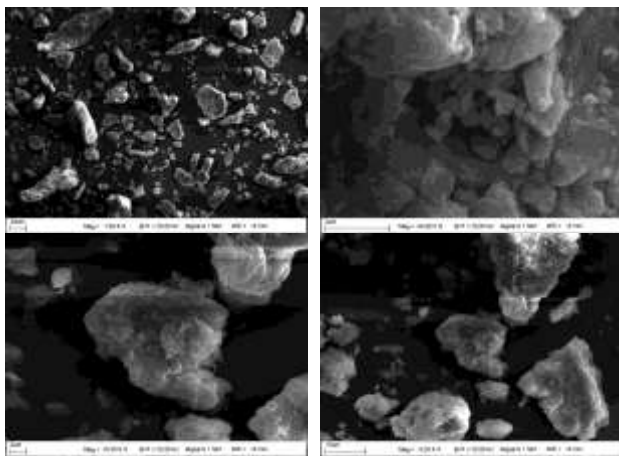Figure 2.   Particle size analysis of nHA samples
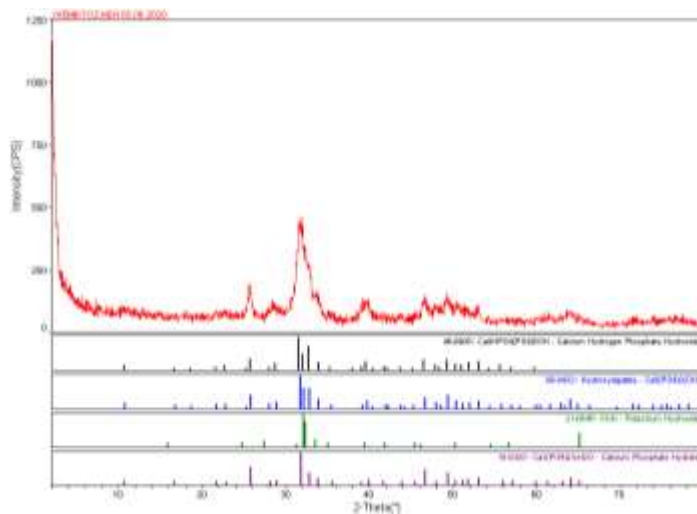
Figure 3. SEM image of beef bone powder

TABLE I. SAMPLES AND MIXING RATIOS

Sample Name	PLA (wt. %)	TiO$_2$ (wt. %)	Hydroxyapatite (HA, wt.%)	Natural Hydroxyapatite (nHA, wt. %)	3D printing Temperature (°C)
S1_190	98%	1%	1%	-	190
S1_205	98%	1%	1%	-	205
S1_220	98%	1%	1%	-	220
S2_190	98%	1%	-	1%	190
S2_205	98%	1%	-	1%	205
S2_220	98%	1%	-	1%	220
S3_190	100%	-	-	-	190
S3_205	100%	-	-	-	205
S3_220	100%	-	-	-	220
ST_205	100%	-	-	-	205

Figure 4. XRD diagram of beef bone powder

Figure 5. 3D printing of samples

2) Filament preparation

PLA granules are ground in a Diamond mill. The PLA powders were obtained in a size of 250-700 µm. The PLA, HA, DHA and TiO$_2$ used in the mixtures were dried in a vacuum oven (Core EV 018) at 60°C under atmospheric conditions for 24 hours. The sample quantities given in Table I were adjusted using precision scales (Kiwi kks-1151), mixed with a mechanical mixer (IKA RW 20 Digital) under laboratory conditions for 24 hours, and then filaments were produced using a single screw filament extruder (Polartek). For the tensile analysis, the 3D model of the sample was created in the ISO 527-2 5A standard and then printed on a 3D printer (3D+++ Xperia) (Fig. 5).
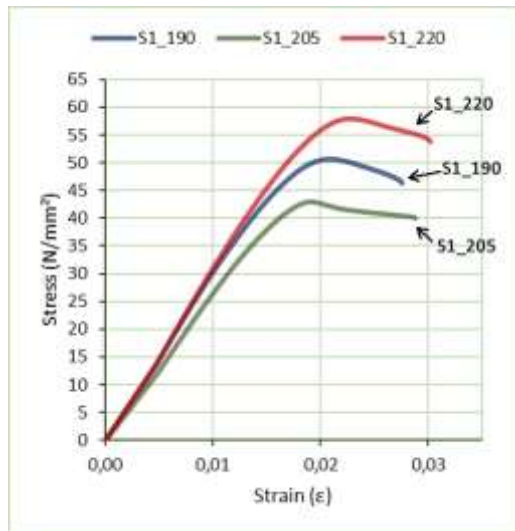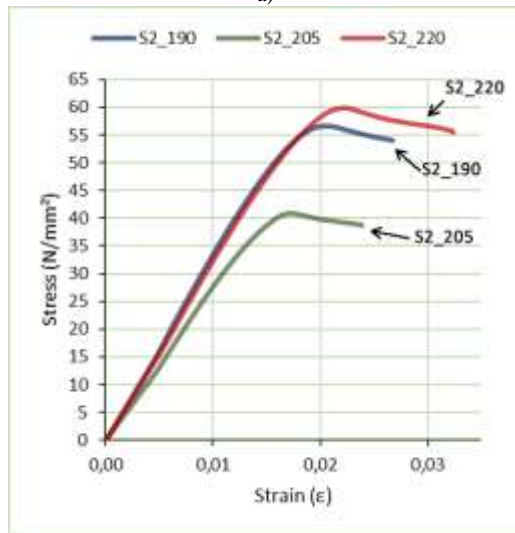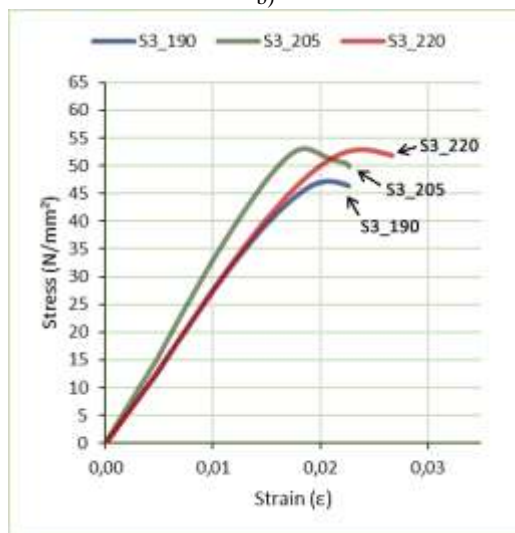
III. Results and discussion

According to the stress-strain curves of the 3D printed samples at 190, 205 and 220 °C shown in Figure 6; For 98% PLA, 1% HA, 1% TiO$_2$ mixture, maximum tensile strength and unit elongation were obtained in the sample printed at the 3D printing temperature of 220 °C (Fig. 6a). For 98% PLA, 1% nHA, 1% TiO$_2$ mixture, although the elastic modulus (E) at 205 and 220°C was the same, the maximum tensile strength and unit elongation amount were obtained in the sample printed at the 3D printing temperature of 220 °C. Although nHA slightly improved its maximum tensile strength, it behaved similarly to HA (Fig. 6b). The best maximum tensile strength is better at 3D printing temperatures between 205 and 220 °C, and the unit elongation amount is better at 220 °C. However, according to the elastic modulus and maximum tensile strength results, the ideal 3D printing temperature of 100% PLA is 220 °C (Fig. 6c).

a)

b)

According to the 3D printing results of the produced composite filaments at 205 °C (Fig. 7); In all mixing ratios of PLA/HA/nHA/TiO$_2$, elasticity modulus, maximum tensile strength and unit elongation were worse than 100% PLA. The stress-strain curves obtained from the 205 °C 3D print samples of the commercially purchased PLA filament (ST_205) with the 100% PLA filament produced (S3_205) are approximately the same (Fig. 7). According to the stress-strain curves of 3D prints obtained from PLA/HA/nHA/TiO$_2$ composites (Fig. 8), pure PLA and commercial PLA filaments at optimum 3D printing temperature; the elastic moduli are the same, but the max. tensile values were higher in PLA/HA/nHA/TiO$_2$ composites. When looking at the unit elongation amounts; Although commercial PLA (ST_205) was higher, was obtained in PLA/HA/nHA/TiO$_2$ (S1_220, S2_220) composites more than pure PLA (S3_205). 205 °C 3D printing temperature is suitable for 100% PLA filaments, but not sufficient for PLA/HA/nHA/TiO$_2$ composites. The max tensile, max strain and elastic modulus of PLA/HA/nHA/TiO$_2$ composite filaments were obtained better at 220 °C 3D printing temperature. Therefore, the 3D printing temperature of PLA/HA/nHA/TiO$_2$ composites was found to be 220 °C.
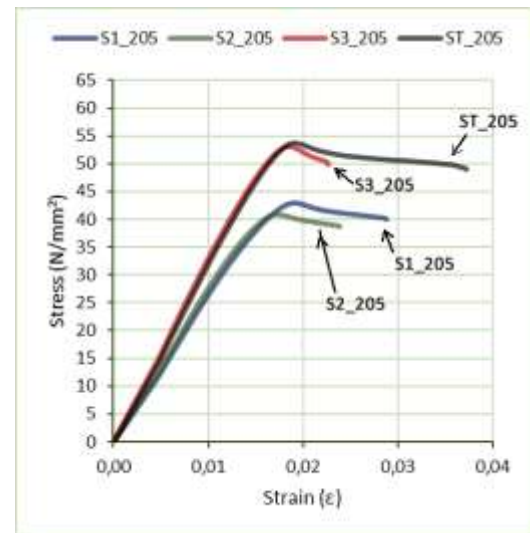

Figure 7. Stress-strain of the mixtures at 205 ° C 3D printing temperature

c)

Figure 6. Effect of 3D printing temperature on tensile strength; a)98%PLA, 1%HA, 1%TiO$_2$; b) 98%PLA, 1%nHA, 1%TiO$_2$; c)100%PLA
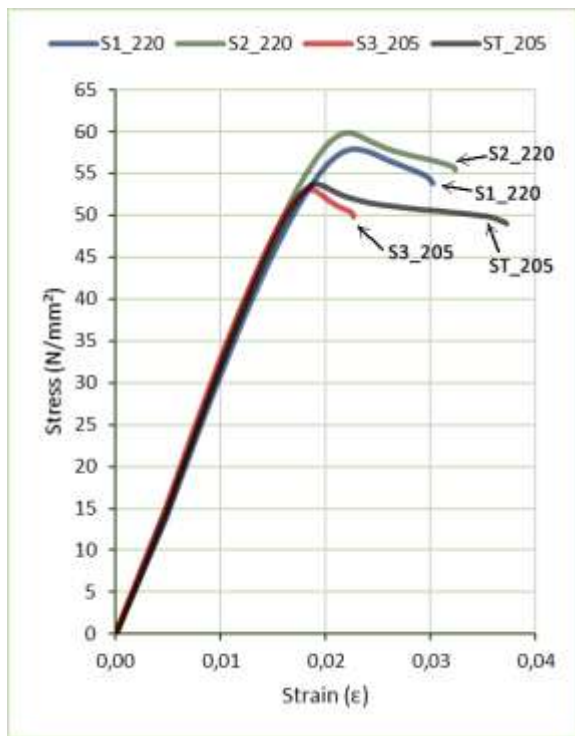
Figure 8.   The Optimum 3D printing temperature of samples

Both the maximum tensile and the maximum elongation at break of PLA/HA/nHA/TiO$_2$ composites were obtained more than pure PLA (Fig. 9,10).
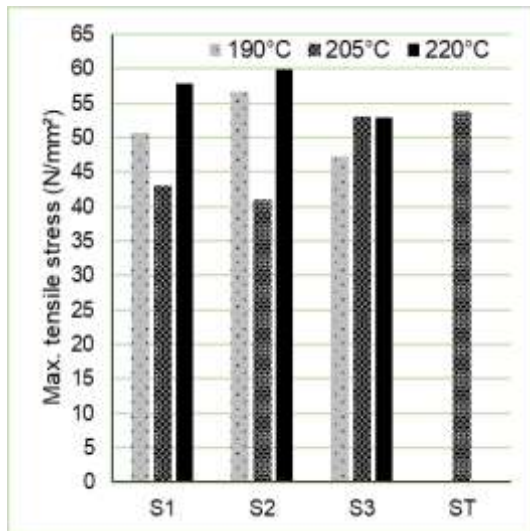

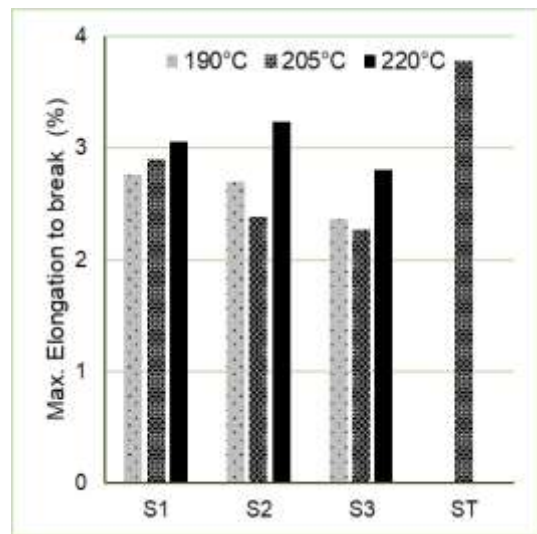Figure 9.   3D printing samples at 190, 205 and 220 °C max. tensile stresses

Figure 10. 3D printing samples at 190, 205 and 220 °C max. elongation to break

Dimensional analysis cube with 20mm edge length was produced from composite filaments at the 3D printing temperature of 190, 205 and 220°C by FDM method (Fig. 11). The arithmetic averages of the data obtained by taking measurements at 4 different locations on each axis in the X, Y and Z axes of the 3D printed dimensional analysis cube (Fig. 11) samples were taken. According to the data obtained, there was not much dimensional change in dimensional analysis cubes (Fig. 12,13,14). In addition, it has been observed that the dimensional cube does not adhere well to the building tray during 3D printing at 190 °C. No such problem was observed at 205 and 220°C, and there was no significant change in their dimensional analysis.
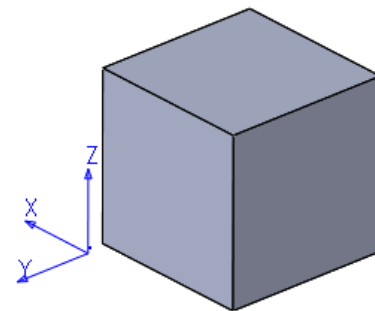

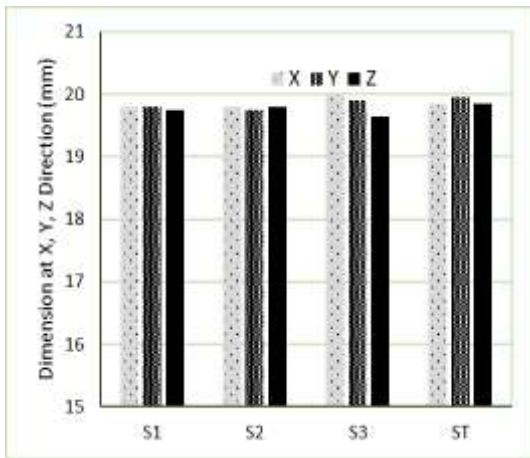Figure 11. Dimensional analysis cube

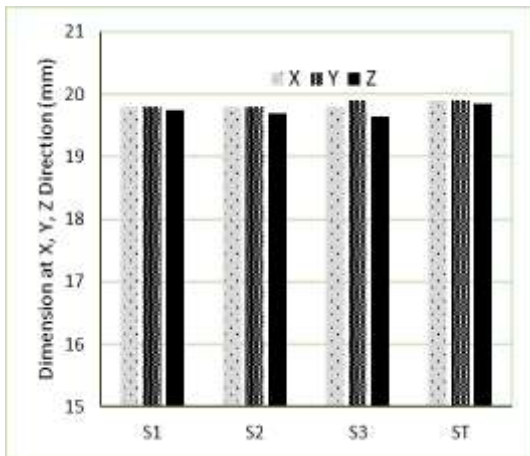Figure 12. Dimensional values of samples made 3D viewed at 190°C

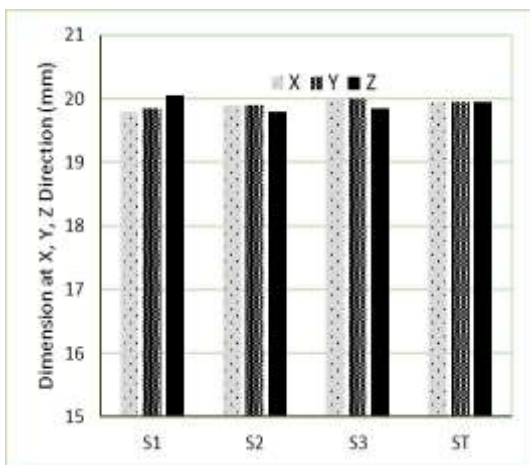Figure 13. Dimensional values of samples made 3D viewed at 205°C

Figure 14. Dimensional values of samples made 3D viewed at 220 ° C

IV. Conclusion

Composite filaments obtained by mixing PLA/HA/nHA/TiO$_2$ in the proportions given in Table I; It was produced at 190, 205 and 220 °C 3D printing temperature. There was no significant change in the dimensional analysis of 3D printed samples from these filaments with the increase of 190-220 °C 3D printing temperature. According to the tensile analysis, the PLA/HA/nHA/TiO$_2$ mixture showed good mechanical properties and the nHA in the mixture showed better properties than HA. The optimum 3D printing temperature of the composites was found to be 220 °C.

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