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Production and characterization of thermo-mechanical properties of hydroxyapatite filled polycarbonate composite filaments for FDM printing

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Abstract

The number of 3D printer filament development studies are increasing day by day by using composite materials to respond the need to create implants which have personalized design by using fused deposition modelling (FDM) 3D printing technology in bone tissue engineering. The aim of this study is to investigate the effect of Hydroxyapatite content in properties of composites and to produce filaments from developed composite materials. 10%, 15%, 20% and 25 wt. % Hydroxyapatite (HA) filled Polycarbonate (PC) composite granules were produced by using twin-screw extruder. Filaments were produced by filament production line. Characterization samples were obtained by using hot press in accordance with the standard dimensions. Density and MFI (Melt Flow Index) measurements, thermogravimetric analysis (TGA), and mechanical tests including three-point bending, and Izod un-notched impact strength tests are performed. Scanning Electron Microscopy (SEM) analysis was carried out to investigate the morphological changes. Tensile strength and elongation at break values were decreased but Young's modulus was increased with increasing amount of HA in the composition. Similar results were obtained for flexural tests. Izod impact strength values were decreased by increasing HA amount. 3D printer filaments were produced and flexural test specimens were printed in 3D printer.

Keywords: Composite, Filament, Fused deposition modeling, Polycarbonate, Hydroxyapatite.

1. Introduction

Additive manufacturing techniques are frequently used for many industries such as aerospace, automotive and defense[1]. Biomedical industry is one of the main users to produce personalized bone implants for people who have bone losses because of many reasons such as accident, tumor and cancer [2]. Fused deposition modelling (FDM) is one of the additive manufacturing methods. It needs filament type material to produce the part in desired shape and geometry. The number of 3D printer filament development studies are done in academic and commercial side. Not only neat thermoplastic polymers but also their composite materials are used to manufacture these filaments. There are many composite material development studies for 3D-printing by using different matrices such as PLA [3], poly(L-lactic acid) [4], PLGA [5],Poly(3-hydroxybutyrate)/poly(d,l-lactide) blends [6], poly(e-caprolactone)/poly(D,L-lactide-co-glycolide) [7] and PVA [8] in the literature.
Especially for implant production neat thermoplastics do not provide the desired properties such as biocompatibility and bioactivity for bone healing. For that reason, bioactive fillers such as Hydroxyapatite, beta tricalcium phosphate and bioglass are used to produce implant materials. Hydroxyapatite exists naturally in bones and gives bioactive property to composites. Polycarbonate is used for many applications and industries. It has also used in biomedical applications. Coupling agents are used for compatibilization of HA with polymers to provide a good interphase in the composite [9].
In the literature, there is

The aim of this study is to investigate the effect of HA content for production of composite filaments. It examines the effect of the production technique on the bending properties of the material, which was carried out to reveal the flexural strength difference between the three-point bending test specimen produced by using a hot press and by FDM technique.

2. Material and methods

2.1. Materials Subsection

Four composite samples based on Polycarbonate (2203R, Sabic) and hydroxyapatite (nanoXIM.HAp203, Fluidinova) were used in all studies. Elvaloy PTW and Elvaloy AC1330 were supplied from Dow Chemical

Company and used for impact modifier and compatibilizer, respectively. The amounts of additives were kept same for all composites. Table 1 shows compositions of the composite samples.

Table 1. The compositions of the composite samples.

	Amount (%)			
Samples	**PC**	**HA**	**PTW**	**AC1330**
PC	100	0	0	0
PC-10HA	84	10	1	3
PC-15HA	81	15	1	3
PC-20HA	76	20	1	3
PC-25HA	71	25	1	3

2.2. Methods

10, 15, 20 and 25 wt. % hydroxyapatite (HA) filled polycarbonate (PC) composites were produced in twin screw extruder (Leistritz, ZSE 27 MAXX/HP, L/D:48, diameter is 27 mm). The temperature setting of the zones of the extruder were between 245-275 ˚C. The total production weight of the samples was around 25 kg/h.

Before filament production, composite granules were dried 4 hours in 100 ˚C to get rid of the moisture. Filaments were produced by using B1R RTX S16 filament production line (Figure 1) that includes single screw extruder which has 12 mm screw diameter, and its L/D ratio is 25. The final output was a polymeric composite filament with 1.75 mm in diameter.

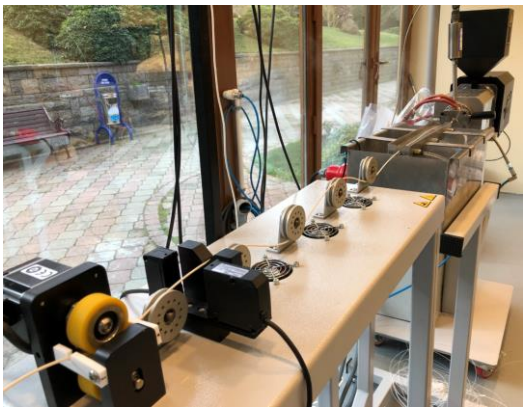

Fig 1. Filament production line.

Production of composite test samples from granules were done by using hot and cold press. Density and MFI measurements are performed according to ISO 1183 and ISO 1113 standards, respectively. TG analyses of the samples were conducted by TG analyzer (Q20 TA Instrument) performed according to ISO 11358 standard. Analyses were conducted up to 800°C under nitrogen atmosphere with a heating rate of 10°C/min.

Flexural properties of PC and its composites were determined by using three-point bending test. Flexural strength and modulus values of the samples were measured according to the ISO 178 standard.

Izod impact strength values of the samples were measured according to the ISO 180 standard. Within the scope of this standard, the dimensions of the test specimen are 80 mm long and 4 mm thick, and the notch depth is 2 mm.

3. Results and discussion

3.1. Density

The density values of composites are given in Figure 2. As it was seen from the graph, density of composites increased with the increasing amount of hydroxyapatite. This result is expectable since the density value of HA (3.18 g/cm^3) is higher than that of PC (1.21 g/cm^3).

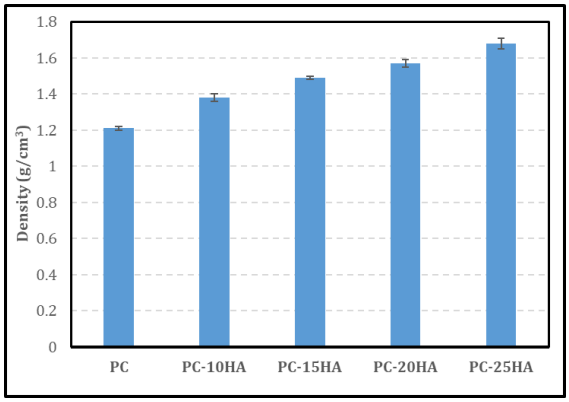

Fig 2. Density values of samples.

3.2. Melt Flow Index

MFI values are important parameters to produce filament and printing of filaments in FDM 3D printing. The graph which shows MFI values is given in Figure 3. The decrease in MFI values observed for the filled PC with the addition of HA. A sharp decrease in MFI was observed when 10 wt. % HA incorporated into the polymer. However, it can be said that this decrease is in a narrow range between 10 wt. % HA and 25 wt. % HA filling. The MFI value is an attribute to consider for 3d printing. Previous studies have reported that the MFI value of around 10g/min makes filament printable [10]. In addition, the quality of the printed product is also related to the MFI value. In this study, PC-10HA and PC-15HA samples were close to this value.

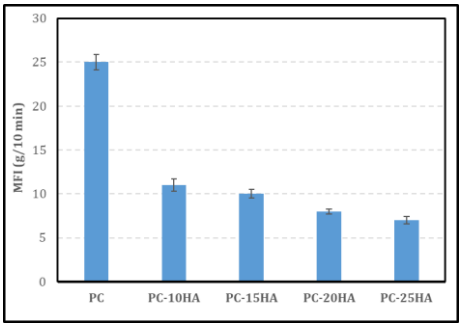

Fig 3. MFI values of the composites.

3.3. TG Analysis

Figure 4 shows the TG curves of PC and HA loaded PC composites. The TGA data obtained from TG curves are summarized in Table 2. As can be seen from Table 2, maximum degradation temperature values of PC, PC-10HA, PC-15HA, PC-20HA, and PC-25HA were obtained to be 527, 520, 519, 514, and 508 °C, respectively. Temperatures at 5% mass loss and 10% mass loss follows the same decreasing trend. It is seen that HA loading into PC decreased the thermal stability of PC. %25 HA loading into PC decreased the temperatures at 5% mass loss and 10% mass loss values by 112 and 124 ^{0}C, respectively. This decrease may be due to dihydroxylation of the HA as the temperature increases over the range 200-750°C[11]. Since PC is not completely degraded in the studied temperature range, TGA was not directly used to check HA contents. Since a small mass, about 2 mg, was used in TG analysis, the residual mass of the composite with 20% and 25% seems to be similar. Besides if one evaluates the bulk properties of the composites containing 20wt% and 30 wt% HA, differences can be seen, which indicates the different HA loading rates.

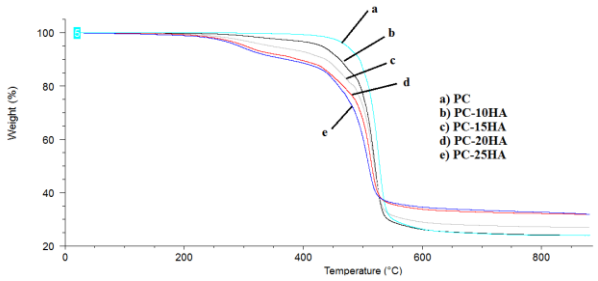

Fig 4. TG curve of PC and its composites.

Table 2. TG data of PC and its composites.

Sample	T_{max}, ^{0}C	Temperature at 5% Mass loss, ^{0}C	Temperature at 10% Mass loss, ^{0}C
PC	**527**	**474**	**495**
PC-10HA	**520**	**432**	**460**
PC-15HA	**519**	**346**	**436**
PC-20HA	**514**	**303**	**389**
PC-25HA	**508**	**292**	**371**

3.4. Flexural Test

Flexural strength and modulus values of PC and its composites containing various amount of HA is shown in Table 3. As can be seen from Table 3, the addition of HA led to a reduction in flexural strength to 75, 59, 36, and 25 MPA for 10, 15, 20, and 25 wt. % loadings, respectively. This may be associated with the low strength of HA as presented in literature [12, 13]. Moreover, it has been demonstrated that the mechanical properties are highly dependent on the dispersion of HA in the polymer matrix [14]. So, one can say that the possible agglomeration of HA particles at high weight fractions could serve as points for stress concentration which result in deterioration of the mechanical properties of the composites. It is seen from Table 3 that the flexural modulus of the HA added PC composites was noticeably improved especially at high weight fractions of HA studied. At 15 and 20 wt. % HA contents, composites revealed flexural modulus values of 6782 MPa and 10437 MPa, respectively. These results could be attributed to the higher modulus of HA composed with PC [12].

Table 3. Flexural strength and modulus of composites.

Sample	Flexural Strength (MPa)	Flexural Modulus (MPa)
PC	88	2300
PC-10HA	75	3851
PC-15HA	59	6782
PC-20HA	36	10437
PC-25HA	25	15921

3.5. Izod Impact Strength

Izod impact strength values of HA filled PC composites were shown in Figure 5. As it is seen from the graph, the highest impact strength is 34.43 kJ/m^2 found for 10 wt. % HA filled composite. Izod impact strength of polycarbonate used in this study is non broken. It could be understood that this non break value decreased with the incorporation of 10 wt. % HA to PC. When the ratio of HA increased to 15 wt.%, 21.75 kJ/m^2 was found. 10.32 kJ/m^2 and 5.76 kJ/m^2 were obtained for 20 wt. % HA and 25 wt. % HA filled composites, respectively. It could be concluded that decrease in impact strength was observed with increasing HA amount. While the impact strength of pure PC was non-broken, impact strength of PC materials filled with HA also decreased as the amount of HA increased.

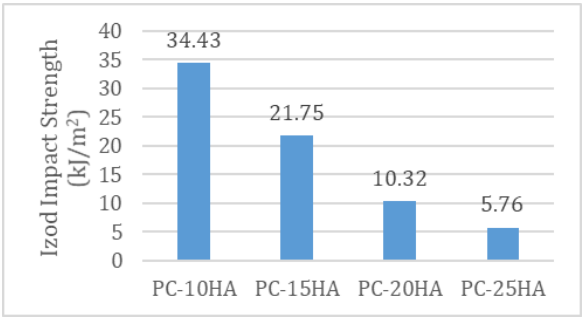

Fig 5. Izod impact strength values of composites.

3.6. Filament Production

Filaments are produced from composite granules with the parameters given in Table 4. The diameter of filament was set 1.75 mm for all productions. When processing parameters were analyzed, it could be seen that barrel temperatures and pulling rpm were increased slightly when HA amounts of composites

increased. Filaments produced could be seen in Figure 6. When the surface of composite filaments was evaluated, it could be seen that only PC-10HA and PC-15HA composite filament had smooth surface but PC-10HA and PC-25HA composite filaments has rough surfaces.

Table 4. Process parameters of filament production.

	Barrel Temperatures (°C)					
	1.	2.	3.	4.	Pulling (rpm)	Main Motor
PC-10HA	275	265	260	200	207	25
PC-15HA	275	270	265	220	229	27
PC-20HA	270	265	255	190	262	29
PC-25HA	273	262	260	200	254	29

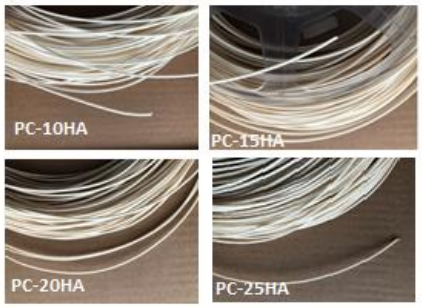

Fig 6. Filament produced from HA filled PC composites for 3D printing.

3.7. 3D Printing

All 3D printed samples (Figure 7) were printed two times in 3D printer according to parameters given in Table 5. Missing print was observed in produced parts due to instable flow observed in PC-10HA, PC-20HA and PC-25HA composites. Only PC-15HA composite showed no missing print during processing. Processing conditions could be optimized for other composite samples. As it is seen from Figure 7, the surfaces of PC-10HA, PC-20HA and PC-25HA composites has rough appearance compared with PC-15HA composite. It could be considered that compatibilization of 15 wt. % HA with PC could be better for the ratios used in formulations. 20 wt. % and 25 wt. % HA could be not compatibilized with the matrix. The second reason for surface difference could be the moisture. Maybe drying conditions could be enough for 15 wt. % HA composites but must be optimized for others. During filament production, flow was tried to be stabilized but 20 wt.% and 25 wt. % composite filament production it was difficult to perform, and it effects 3D printing process.

Fig 7. 3D printed flexural test samples numbered as 1. PC-10HA, 2. PC-15HA, 3. PC-20HA and 4. PC-25HA.

Table 5. 3D printing parameters of composite filaments.

Parameters	Values
Nozzle Diameter	0.6 mm
Layer Height	0.25
Width of printing layer	0.6 mm
Perimeter printing speed	40 mm/s
Fill print speed	40 mm/s
Heat bed temperature (°C)	125°C
Number of layers	16
Chamber temperature (°C)	90°C
Nozzle Temperature (°C)	220
Wall Thickness	0.7
Number of walls	2

3.8. Flexural test of 3D printed PC-15HA

As can be observed within Figure 8, the bottom surface of the 3D printer produces part has a smoother appearance when compared to the upper surface. This is due to the fact the bottom surface is in contact with the heated table of the 3D printer. This difference is surface structure also has a major effect on the results of the bending test about the positioning of the test sample on the device. Figure 9 was given for better understanding of three-point bending positioning. The upper part of the sample where the force-applied tip is, the lower part of the samples where the tip does not touch. The bending test results have been observed to be at a much better level when the force applied tip is in contact with the smooth surface with the rough surface is facing down.

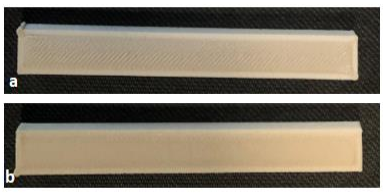

Fig 8. a) The top surface of PC-15HA sample, b) Bottom surface of PC-15HA sample which is contact with the heated table of 3D printer.

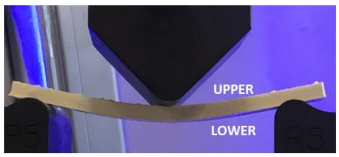

Fig 9. The upper part of the sample where the force-applied tip is, the lower part of the samples where the tip does not touch.

Table 6. Three-point bending test results of the samples prepared by using hot and cold press and 3D printing.

Three Point Bending Sample	Flexural Strength (MPa)	Flexural Modulus (MPa)
Hot and cold press	59	6782
3D printing (hot plated surface on upper)	38	1372
3D printing (hot plated surface on lower)	31	1184

4. Conclusions

The important of this study is the successful production of 3D filaments from the developed composite granules. Optimum amount of HA was found as 15 wt. % for 3D printing. The bending test results have been observed to be at a much better level when the force applied tip is in contact with the smooth surface with the rough surface is facing down. Drying time and temperature could be optimized by increasing both as a recommendation.

Acknowledgments

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References

1. Milazzo, M., et al., *Additive Manufacturing Approaches for Hydroxyapatite-Reinforced Composites.* Advanced Functional Materials, 2019. **29**(35).
2. Jariwala, S.H., et al., *3D Printing of Personalized Artificial Bone Scaffolds.* 3D Print Addit Manuf, 2015. **2**(2): p. 56-64.
3. Amnael Orozco-Diaz, C., et al., *Characterization of a composite polylactic acid-hydroxyapatite 3D-printing filament for bone-regeneration.* Biomed Phys Eng Express, 2020. **6**(2): p. 025007.
4. Dubinenko, G., et al., *Highly filled poly(l-lactic acid)/hydroxyapatite composite for 3D printing of personalized bone tissue engineering scaffolds.* Journal of Applied Polymer Science, 2020. **138**(2).
5. Babilotte, J., et al., *Development and characterization of a PLGA-HA composite material to fabricate 3D-printed scaffolds for bone tissue engineering.* Mater Sci Eng C Mater Biol Appl, 2021. **118**: p. 111334.
6. Melcova, V., et al., *FDM 3D Printed Composites for Bone Tissue Engineering Based on Plasticized Poly(3-hydroxybutyrate)/poly(d,l-lactide) Blends.* Polymers (Basel), 2020. **12**(12).
7. Moncal, K.K., et al., *3D printing of poly(ε-caprolactone)/poly(D,L-lactide-co-glycolide)/hydroxyapatite composite constructs for bone tissue engineering.* Journal of Materials Research, 2018. **33**(14): p. 1972-1986.
8. Aki, D., et al., *3D printing of PVA/hexagonal boron nitride/bacterial cellulose composite scaffolds for bone tissue engineering.* Materials & Design, 2020. **196**.
9. Di Silvio, L., M.J. Dalby, and W. Bonfield, *Osteoblast behaviour on HA/PE composite surfaces with different HA volumes.* Biomaterials, 2002. **23**(1): p. 101-7.
10. León-Cabezas, M.A., A. Martínez-García, and F.J. Varela-Gandía, *Innovative functionalized monofilaments for 3D printing using fused deposition modeling for the toy industry.* Procedia Manufacturing, 2017. **13**: p. 738-745.
11. Meenan, B.J., C. McClorey, and M. Akay, *Thermal analysis studies of poly(etheretherketone)/hydroxyapatite biocomposite mixtures.* Journal of Materials Science: Materials in Medicine, 2000. **11**(8): p. 481-489.
12. Akindoyo, J.O., et al., *Effects of surface modification on dispersion, mechanical, thermal and dynamic mechanical properties of injection molded PLA-hydroxyapatite composites.* Composites Part A: Applied Science and Manufacturing, 2017. **103**: p. 96-105.
13. Cucuruz, A.T., et al., *Synthesis and characterization of new composite materials based on poly (methacrylic acid) and hydroxyapatite with applications in dentistry.* International journal of pharmaceutics, 2016. **510**(2): p. 516-523.
14. Liuyun, J., et al., *Effect of n-HA content on the isothermal crystallization, morphology and mechanical property of n-HA/PLGA composites.* Materials Research Bulletin, 2013. **48**(3): p. 1233-1238.