Characterization of Polymers Used by Additive Manufacturing Technologies in Development of Medical Equipment

Thesis

Author:
Péter Maróti, MD

Doctoral School of Interdisciplinary Medical Sciences D93
Leader of Doctoral School: Balázs Sümegi PhD, DSc

Supervisors:
Miklós Nyitrai, PhD, DSc
Dénes Lőrinczy, PhD, DSc

University of Pecs, Medical School
Department of Biophysics
2019

1.) Introduction: History of 3D printing

Today additive manufacturing technologies (AM – Additive Manufacturing) are emerging in both fields of science and industry. Specifically, highly tuned 3D printing technologies can be found in common households, thanks to the rapid development of the technology and the remarkable corresponding IT solutions. Additive manufacturing bears a significant impact upon fundamental (e.g., material science) and applied areas of research (e.g., medical and clinical studies, industrial, mechanical and electrical applications). Most recent international studies have aptly demonstrated how 3D printing is the midst of an exploding, developmental era. The appearance of new materials and device manufacturing demands the scientific, critical evaluation of the technology, aligned with their practical implementation.

Despite the prominence of additive manufacturing in the field of emerging technologies dating from the 1980's, it has gained immense international attention in the past decade. On a global scale, several research groups worked towards a solution not to 'remove' (e.g., CNC – computer numerical control) the material from the initial object, but to 'add' to it, therefore the manufactured object is built up in numerous layers, reducing material loss, saving time and costs. The first successful patent was filed by Charles Hull in the United States in 1984 in support of the process defined as SLA (SLA – stereolitography apparatus), in which the material was liquid-state photopolymer and hardened through the use of UV light. The first commercially available 3D printers operated very much the same as in the case of the 3D Systems, model SLA-1, 1987. In 1989, SLA 3D printers first appeared in Japan (products of NTT Data CMET and Sony/DMEC) and shortly afterwards followed by the German business entity, EOS (EOS - Electro Optical Systems). Several years later, in 1991, three new technologies appeared on the market, the filament-based Fused Deposit Modelling (FDM™), the ‘solid-ground-curing’ (SGC, Cubital), which is similar to SLA and the ‘laminated-object-manufacturing’ (LOM, by Helisys), in which a laser cuts out the structure from layers positioned on the top of one another. The next important milestone was the appearance of SLS (SLS – selective laser sintering) in 1992, which was the proprietary of DTM, and currently known as 3D Systems. The polymer powder based technology initiated the development of DMLS (DMLS – Direct Metal Laser sintering by Fraunhofer Institute, ILT, from Germany), which used metal powders as its material source. Both technologies are deemed relevant in both industrial and medical applications. The widening dispersion regarding 3D printing technology burst onto the scene in the middle of the 1990s when several manufacturers lowered the retail price regarding 3D print consumer goods. A superb example was the model Z402 inkjet 3D printer, which was the product of Z. Corp, or the paper-based 3D printer, which originated from Schroff Development, and featured a retail cost under $10,000.

Up through the middle of the 2000s retail costs underwent a consistent decrease making the new technology more affordable, and the trend was coupled with an increase in product solutions and development. Today 3D printers are available to the general public for a few hundred dollars and are marketed in the form of household use. These desktop devices are referred to as FFF (FFF – Fused Filament Fabrication), such as in the model RepRap. The fall in retail costs obviously served as an immense impact regarding professional use, particularly in the applications of medical research and industrial manufacturing. Thanks to the academic and market-based start-up business entities, not only did FFF, DLP and SLA solutions undergo a substantial drop in retail costs, the availability of industrial scale devices soared.

2.) Theoretical Fundamentals - Aims of the Study

2.1) Additive Manufacturing in Medicine

The presence of 3D printing throughout medical applications resurrected preventive, diagnostic, interventive and rehabilitative technologies. All of which served in the contribution towards increasing of effectivity of healthcare education, decreasing the time needed for diagnostic steps or intervention, and in the longer run a distinctive increase in the quality of life among patients.

In healthcare education it is primarily relevant with regards to the curriculum of anatomy and pathology, – alongside with other fundamental, pre-clinical and clinical subjects - however, prevention and patient education are also important areas and fundamentally aligned to effective patient-doctor communication. Today 3D printing provides a cost-effective, variable production of various models, in reference to size, quality and hue, and printing is considerably simplified in contrast to the past. Another main aspect in today’s world of 3D printing is the ease-of-use regarding file sharing. File-sharing is quick, easy and global. Depending on the technology some portions can be highlighted (e.g., with colour or a variety of strata regarding quality), supporting effective communication and interpretation.

Personalized medicine is one of the most important aspects of our days’ healthcare system. The additive manufacturing technologies are proving beneficial not only in pharmaceutical applications, but they are useful in creating personalized drilling and cutting templates in support of defining shape, form and dimension. It is also used in the planning and visualization of surgical procedures (e.g., liver, hearth, aorta and aesthetic surgery). Additionally, there is also a significant area regarding dental use in which significant results have been achieved by professionals in the field of invisible orthodontics and case-specific drilling and cutting templates and recently have become an important tool in the field of maxillofacial surgery.

Radiology has a prominent role in the spread of 3D printing technologies throughout healthcare, as CT, MRI and ultrasound devices are essential in the production of three-dimensional case-specific models as imaging techniques. Patient-specific models can be produced relatively easily with dicom (.dcm) files using open source (e.g., Slicer) or professional market software (e.g., Materialise Mimics).

2.3) Aims of Our Study

The aim of our research was to carry out a comprehensive study regarding 3D printing of raw materials preferred in medical device development from the aspect of mechanical, structural and thermoanalytical characterization. Nearly all of the 3D printing technologies possess medical and health-related aspects. Our research team analyzed the most commonly used FDM ™/FFF, selective laser sintering (SLS) and photopolymer based techniques. In the case of photopolymer based techniques the focus was on Stratasys PolyJet ™ technology. The tests were conducted through practical use problems which generally arises in the prototype development regarding medical devices and aids. Structural and mechanical tests were carried out during prosthetic and robotics development, and the thermoanalytical analysis was performed in reference to materials in which the thermal effect may likely be a significant factor regarding its functionality. Additionally, thermal analysis of the raw material (pellets) of the filaments proved to be an important issue. In the case of photopolymer processes the use of dental and oral surgery was the subject of our study, in which biocompatibility and accuracy are the determining factors.

3.) Materials and Methods

3.1) 3D Printing Technologies, Materials and Test Specimens

Standard specimens were prepared for the mechanical and structural analysis regarding polymers and composites according to ISO and ASTM standards. In the case of structural tests the fracture surfaces of the specimens were examined. We have examined the following technologies and materials:

3.1.1) 3D Printers:

- **FFF Technology**: CraftUnique, Craftbot 2 FFF 3D printer (Craftunique Kft. Hungary, 1087, Budapest, Salgótarjáni út 12-14).
- **FDM™ Technology**. Stratasys Fortus 400 mc Large (Stratasys Ltd., Eden Prairie, Minnesota, USA).
- **SLS Technology:** EOS Formiga P110 (EOS GmBH – Electro Optical Systems Headquarters – Robert Stirling-Ring 1 D-82152, Krailling, Germany).
- **Photopolymer Based Technology**: Stratasys Objet™350 Connex, Stratasys PolyJet™ J70 és Stratasys Objet™ Eden260VS Dental Advantage.

3.1.2) Materials:

- **FDM™/FFF:** ABS (M30), neat PLA, PLA-$CaCO_3$ composit (20 m / m%: ‘Modell’ and 50 m / m %: “Gypsum”, PLA HDT (HDT-heat deflection temperature), neat PLA granule, ULTEM™ 9085.
- **SLS:** polyamide (PA2200).
- **PolyJet™:** Objet™Vero Grey™, Objet™ Digital ABS and MED670 VeroDent™.

From the test specimens 5-5 pieces were fabricated in accordance to the test standards.

3.2) DTA/TG – Thermoanalytical Characterization

An SC 5200 SII DTA/TG (Seiko, Japan) was used in support of thermal analysis. The temperature and enthalpy calibration, based on international standards, was made using Indium (Alfa Aesar, PURA-TRONIC, Johnson Matthey Company, Ward Hill, MA, USA), and the temperature parameters were also selected in accordance to the standards of Thermal Applications Note TA Instruments (TN-11). Samples were placed in an open aluminium sample holder with a diameter of 5 mm. The heating rate varied from 10 to 40 °C / minutes in a working space filled with N_2 gas at a flow rate of 50 ml / min. The maximum temperature reached 250 °C. External cooling unit was not used during the cooling phase. The conventional PLA and HDT PLA pellets were tested with and without prior heat treatment (105 °C for 1 hour) to best map the differences between the initial form and the extruded form from a thermal point of view. Subsequently, the 3D printer fibers and filaments were examined: PLA HDT, PLA Model and Gypsum, natural PLA. The average weight of the samples was 9 ± 1 mg.

The Tested Materials Were as Follows:

- PLA granule;
- PLA – HDT granule;
- PLA (neat);
- PLA (transparent);
- PLA + 20m/m % CaCO3 composite (PLA Modell);
- PLA + 50m/m % CaCO3 composite (PLA Gypsum).

In the case of the pellet form heat-treated and non-heat-treated samples were also examined.

3.3) Static and Dynamic Mechanical Tests

Of the static mechanical tests the three-point bending test was carried out in accordance to ASTM-D 790-3 (bending speed of 2 mm / s) and Shore D hardness was measured (with a 15 s measurement duration), in accordance to ASTM-D 2240-03 standard. In the latter case the specimens were measured each time on the side of the printing bed. Additionally, a tensile test was performed regarding several technologies and materials in accordance with ASTM-D 6378-03. The number of items in the tests consistently was five, in accordance to the standards. In the dynamic tests a Charpy impact test was performed without incision in accordance to ISO 179-1. During the testing of the materials the individual tests were selected based on the expected physical use of the objects to be printed and the subsequent practical use was calibrated. The room temperature was 27.1 °C and the relative humidity was 48.8 %. The following test were carried out**:**

- **3 Point Bending Test:** PA, neat PLA, PLA Gypsum, PLA Model, Objet™ Vero Grey™, Objet™ Digital ABS, ABS M30, ULTEM™ 9085;
- **Shore D Measurement:** : PA, neat PLA, PLA Gypsum, PLA Modell, Vero Grey™, Objet™ Digital ABS ,ABS M30, ULTEM™ 9085;
- **Tensile Test:** neat PLA, PLA Gypsum, PLA Model;
- **Charpy Impact Test:** PA, neat PLA, PLA Gypsum, PLA Model, Objet™ Vero Grey™, Objet™ Digital ABS, ABS M30, ULTEM™ 9085.

It is important to note that in the case of neat PLA, PLA Gypsum and PLA Model specimens, the specimens were printed only in the X orientation, as the purpose of the tests was specifically to prepare 3D printed fracture fixes, splints and casts. In these cases, the printed medical aids always positioned according to the X orientation.

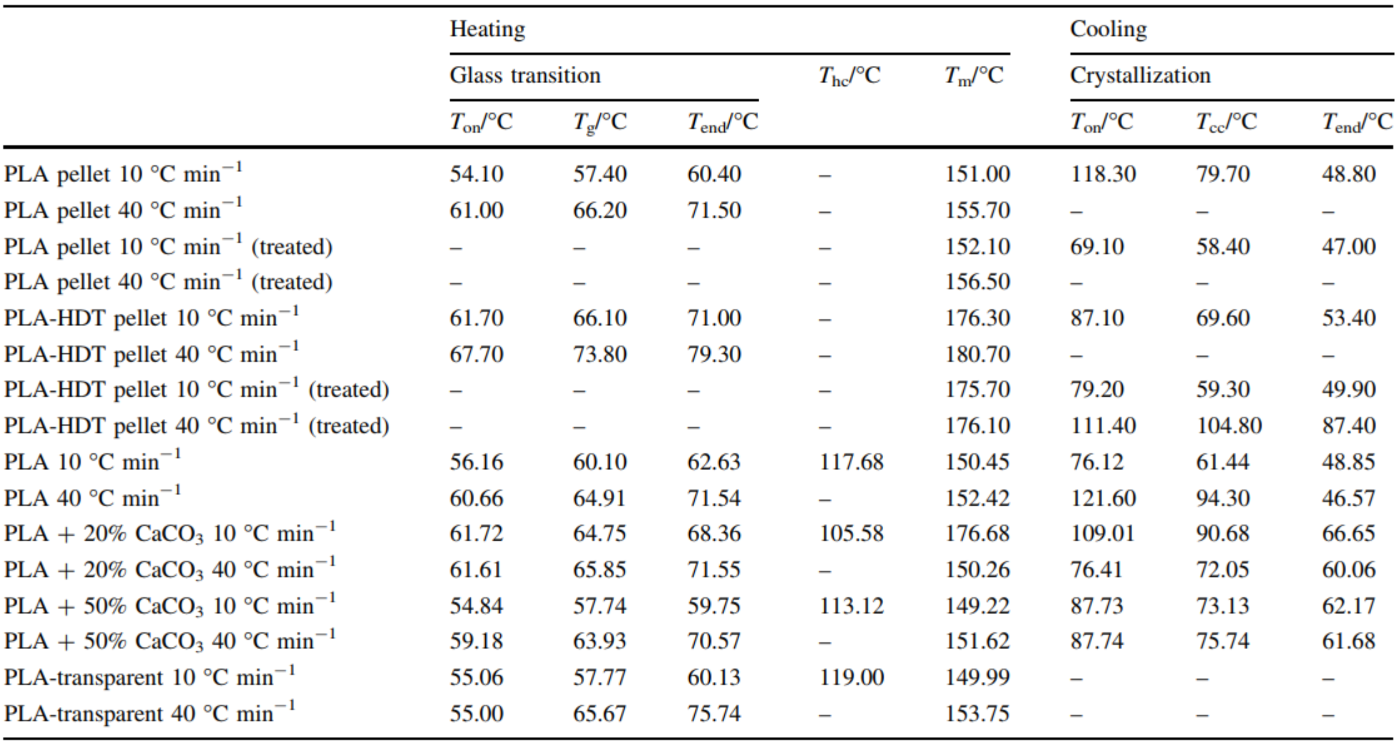
3.4) Structural Analysis with SEM

The structural analysis was performed by scanning electron microscopy (SEM), which is a common method for characterizing structures of different materials. We used a JEOL JSM 6300 device for our tests. The fracture surfaces of the specimens, which were broken at Charpy impact tests were gold-sheated, thereby making the structure visible for the electron microscope. All test materials were analyzed at 15X, 60X and 200X magnification.

4.) Results

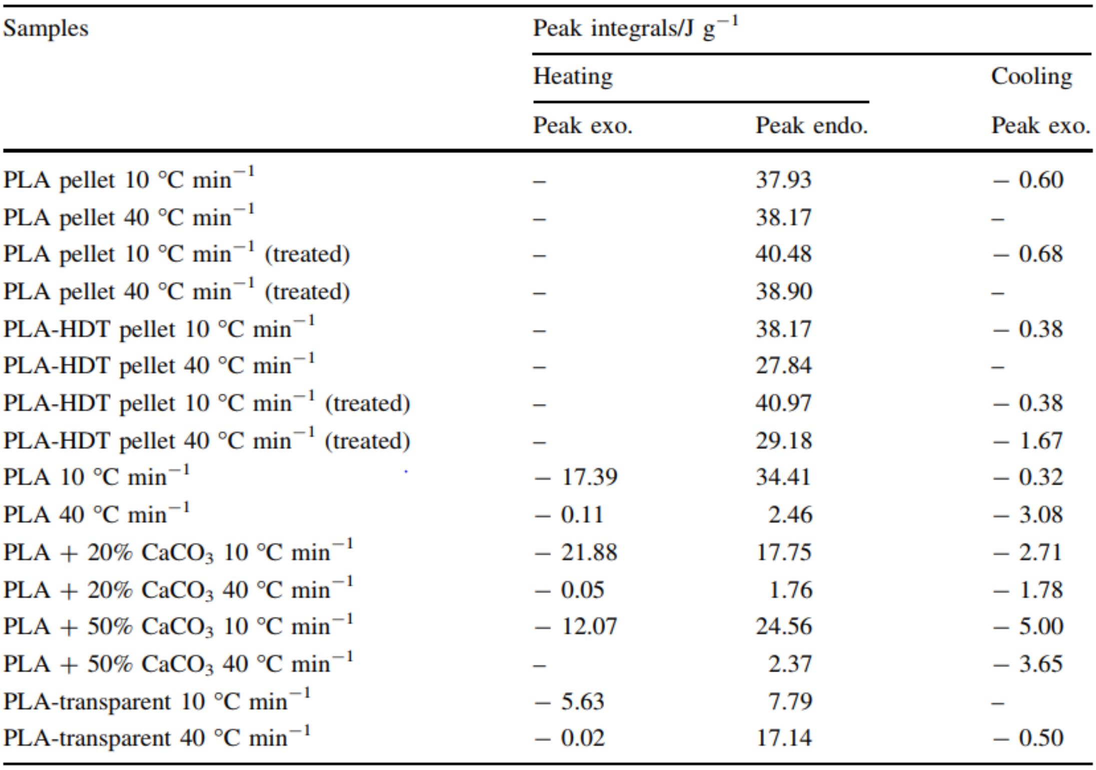
4.1) DTA/TG – Results of Thermal Analysis

The results of the DTA / TG test are summarized in Tables 1 and 2. The calculated enthalpy values were determined from the integral regarding the area under the heat flow curves. The curves can be used to separate individual phase transitions and internal structural transformations. In the case of pellets preliminary heat treatment resulted in the disappearance of Tg (glass transition temperature) for each heating rate. It is an interesting observation, in which an unexpected exothermic transition is observed in these samples, which is not observed in previous studies. We assume this is the likely result of environmental impact (humidity and / or low concentration of contamination) among the production of pellets. The fusion (melting) endotherm curves depict the absolute dependence regarding the heating rate. During cooling (cooling rate is unknown yet presumably constant) crystallization at 80 °C (non-heat-treated pellet) was observed, as at 58 °C (10 °C min^{-1} heating rate – in case of heat-treated pellet). These temperature ranges are particularly important for the use of additive manufacturing technologies (extrusion heating, initial layering, heating of a chamber or print tray, etc.). Pre-treatment increased the melt enthalpy at the indicated heating rate compared to the untreated sample. In regards to PLA-HDT the Tg value was also higher in the untreated case compared to conventional PLA at about 8 °C, and the endothermic curve peak at about 25 °C higher for both heating rates. The measured data demonstrated using the appropriate pre-treatment, the PLA HDT form is more thermally stable and structurally more coherent than when compared to that of the conventional PLA, although their crystal structure is very similar. HDT-PLA can withstand temperatures up to 130-150 °C, without significant macroscopic physical deformation. This observation is especially relevant in the design and manufacture of sterilized medical devices, in which we can expect an obviously significant heat effect. In the case of PLA where processes are well known: glass transition (60-65° C, dependent upon the heating rate), crystallization and melting. No crystallization was observed at 40 °C min^{-1} heating rate. Interestingly, the fusion transition temperatures regarding the composites containing $CaCO_3$ differed from that of the natural PLA. This resulted in an increase in case of 20 m / m % material and in the case of the 50 m / m% composite, a decrease was observed, when the heating rate was 10 °C min^{-1}. It can be stated, that the lower $CaCO_3$ concentration results in a higher temperature tolerance and a more resistant internal structure, which also is manifested in mechanical tests. Another important aspect of the close relationship between structural stability and temperature parameters is that we cannot see crystallization at a temperature of 40 °C min^{-1} (around 110 °C). The fusion enthalpy peaks are significantly lower when compared to those of conventional PLAs, yet their decrease at the rate of heating is similar. The results of the transparent PLA were very similar to those of the natural PLA, so it is likely that their internal structure is almost the same, hence, there is no difference regarding their potential use. The lack of cooling crystallization (in the case of spontaneous cooling) and the significant increase in melting enthalpy suggest that the areas of application should be carefully selected. For example, it is not advisable to develop and prepare devices using this material which are about to undergo routine sterilization.



	Heading					Cooling		
	Glass transition			T_{hc}/°C	T_m/°C	Crystallization		
	T_{on}/°C	T_g/°C	T_{end}/°C			T_{on}/°C	T_{cc}/°C	T_{end}/°C
PLA pellet 10 °C min^{-1}	54.10	57.40	60.40	–	151.00	118.30	79.70	48.80
PLA pellet 40 °C min^{-1}	61.00	66.20	71.50	–	155.70	–	–	–
PLA pellet 10 °C min^{-1} (treated)	–	–	–	–	152.10	69.10	58.40	47.00
PLA pellet 40 °C min^{-1} (treated)	–	–	–	–	156.50	–	–	–
PLA-HDT pellet 10 °C min^{-1}	61.70	66.10	71.00	–	176.30	87.10	69.60	53.40
PLA-HDT pellet 40 °C min^{-1}	67.70	73.80	79.30	–	180.70	–	–	–
PLA-HDT pellet 10 °C min^{-1} (treated)	–	–	–	–	175.70	79.20	59.30	49.90
PLA-HDT pellet 40 °C min^{-1} (treated)	–	–	–	–	176.10	111.40	104.80	87.40
PLA 10 °C min^{-1}	56.16	60.10	62.63	117.68	150.45	76.12	61.44	48.85
PLA 40 °C min^{-1}	60.66	64.91	71.54	–	152.42	121.60	94.30	46.57
PLA + 20% $CaCO_3$ 10 °C min^{-1}	61.72	64.75	68.36	105.58	176.68	109.01	90.68	66.65
PLA + 20% $CaCO_3$ 40 °C min^{-1}	61.61	65.85	71.55	–	150.26	76.41	72.05	60.06
PLA + 50% $CaCO_3$ 10 °C min^{-1}	54.84	57.74	59.75	113.12	149.22	87.73	73.13	62.17
PLA + 50% $CaCO_3$ 40 °C min^{-1}	59.18	63.93	70.57	–	151.62	87.74	75.74	61.68
PLA-transparent 10 °C min^{-1}	55.06	57.77	60.13	119.00	149.99	–	–	–
PLA-transparent 40 °C min^{-1}	55.00	65.67	75.74	–	153.75	–	–	–

1. Table: Enthalpy values of PLA samples – heating and cooling cycles. Source: Maróti et al. 2018: Testing of Innovate Materials for Medical Additive Manufacturing by DTA



Samples	Peak integrals/J g^{-1}		
	Heating		Cooling
	Peak exo.	Peak endo.	Peak exo.
PLA pellet 10 °C min^{-1}	–	37.93	− 0.60
PLA pellet 40 °C min^{-1}	–	38.17	–
PLA pellet 10 °C min^{-1} (treated)	–	40.48	− 0.68
PLA pellet 40 °C min^{-1} (treated)	–	38.90	–
PLA-HDT pellet 10 °C min^{-1}	–	38.17	− 0.38
PLA-HDT pellet 40 °C min^{-1}	–	27.84	–
PLA-HDT pellet 10 °C min^{-1} (treated)	–	40.97	− 0.38
PLA-HDT pellet 40 °C min^{-1} (treated)	–	29.18	− 1.67
PLA 10 °C min^{-1}	− 17.39	34.41	− 0.32
PLA 40 °C min^{-1}	− 0.11	2.46	− 3.08
PLA + 20% $CaCO_3$ 10 °C min^{-1}	− 21.88	17.75	− 2.71
PLA + 20% $CaCO_3$ 40 °C min^{-1}	− 0.05	1.76	− 1.78
PLA + 50% $CaCO_3$ 10 °C min^{-1}	− 12.07	24.56	− 5.00
PLA + 50% $CaCO_3$ 40 °C min^{-1}	–	2.37	− 3.65
PLA-transparent 10 °C min^{-1}	− 5.63	7.79	–
PLA-transparent 40 °C min^{-1}	− 0.02	17.14	− 0.50

2. Table: Results of thermal anlysis, PLA samples –heating and cooling cycles. ($T_{on:}$: onset of measurement, T_{end}: end of measurement. T_g: glass-transition temperature, T_{mexo}: crystallization at heating, T_m: crystallization at cooling.) Forrás: Maróti et al. 2018: Testing of Innovate Materials for Medical Additive Manufacturing by DTA

4.2) Results of Static and Dynamic Tests

4.2.1) Static Tests

In static measurements it was observed regarding the use of SLS technology that there is no significant differences among the values of the different printing orientations. In the three-point bending test 40.5 ± 1.5 MPa was obtained in the X printing orientation, while 45.3 ± 1.2 MPa in the Y orientation, and 40.1 ± 1.9 MPa in the Y orientation. In regards to other technologies and materials there are significant differences among the individual orientations. In the case of FDM™ and PolyJet™ this is remarkable in reference to the Z direction, in which we measured significantly less results compared to other orientations. When comparing materials we noticed there are no significant differences in orientation among the results of the PolyJet™ technology (Vero Grey™ and Digital ABS). In the use of industrial FDM™ technology, and consistently in all cases, the values of flexural strength in case of the specimens printed in the Y orientation are the highest of all materials and resolutions, with 53.6 ± 2.2 MPa printed at 0.178 mm layer height, in the case of ABS specimens, while the value was 57.6 ± 1.9 MPa 0.330 mm resolution. ULTEM ™ showed an outstanding result of 86.6 ± 0.8 MPa. Shore D hardness values was independent of printing orientation and was consistent with the values on the technical data sheets and literature data. Measuring the PLA-$CaCO_3$ composite – which can be used in desktop FFF 3D printing - the limit bending stress was 52.5 ± 1.6 MPa for Gypsum and 59.2 ± 1.2 MPa for the Model materials. These values are significantly lower than that of the natural PLAs, which was 82.2 ± 5.7 MPa. The results of the tensile test showed a similar tendency (Figure 1.). Relative elongation was measured for both the tensile and the three-point bending tests. In both cases, the elongation values decreased by increasing the $CaCO_3$ concentration. No significant difference was detected among the results of the Shore D measurements (77.0-77.9).

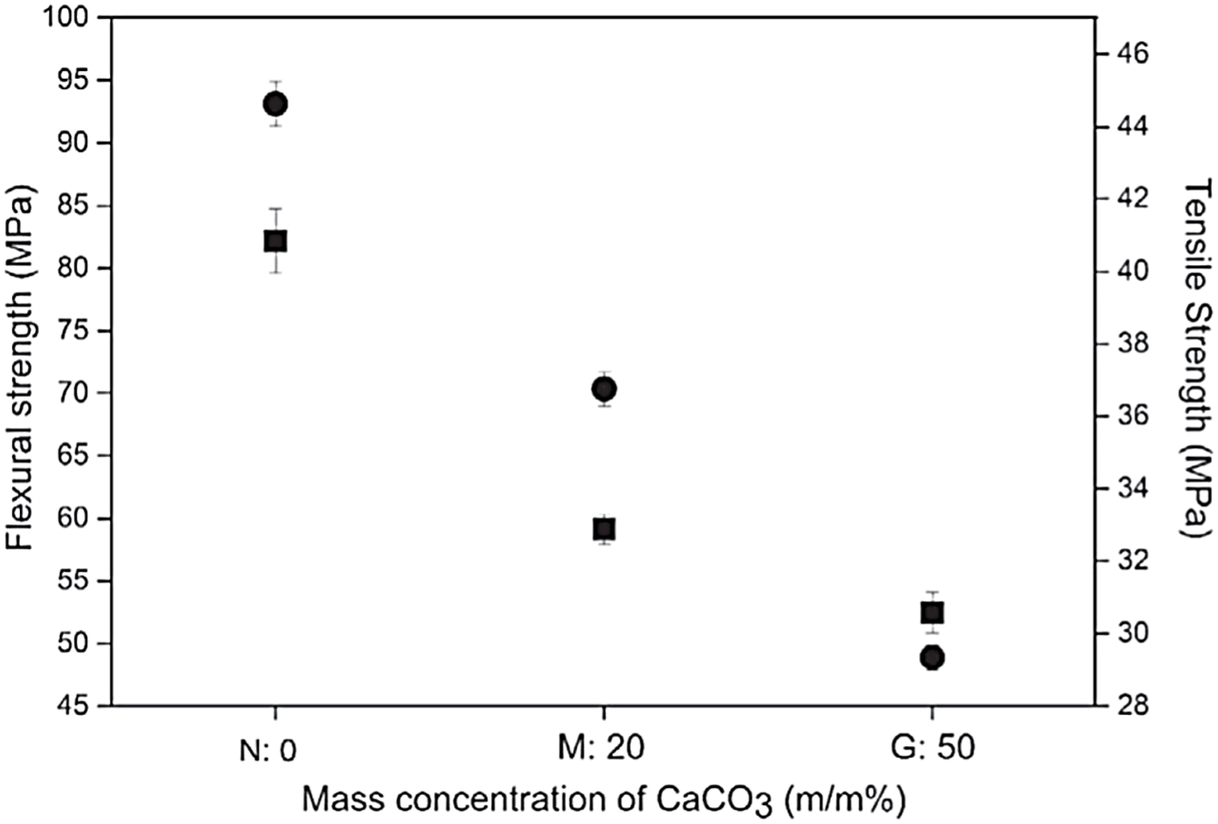


Figure 1. Results of static mechanical tests of PLA-$CaCO_3$ composites. N: neat PLA, G: Gypsum PLA, M: Modell PLA. Varga et al 2019: Novel PLA-$CaCO_3$ Composites in Additive Manufacturing of Upper Limb Casts And Orthotics – A Feasibility Study

4.2.2) Dynamic Tests

As a dynamic measurement, we performed the Charpy impact test. Similarly to static measurements the Z orientation was the weakest in all cases. The ULTEM™ has outstanding value in the X orientation (36.7 ± 0.5 kJ m^{-2}). Polyamide specimens proved to be more mechanically resistant in all cases than those of the PolyJet ™ materials, with the lowest value shown by Vero Grey ™, 2.2 ± 0.1 kJ m^{-2} in case of X orientation, 2.2 ± 0.2 kJ m^{-2} in Y and 1.2 ± 0.1 kJ m^{-2} at Z orientation. The results of the SLS technology showed a smaller standard deviation even during the dynamic test, although the value measured at the Z orientation is significantly lower – with 10.6 ± 2.2 kJ m^{-2} - than those for the Y (14.3 ± 4.2 kJ $m^{-2)}$ and X (17.6 ± 1.24 kJ m^{-2}) orientations.. It is interesting to note that among the ABS materials produced by PolyJet ™ and FDM ™ technology the highest value was measured at 0.330 mm layer height FDM ™ test specimens in X orientation (24.9 ± 0.7 kJ m^{-2}). This is the only case regarding the Charpy impact tests in which the Y direction reaches a higher value than the X orientation. It is important to mention that for dynamic measurements the 0.330 mm layer resolution results in a stronger structure than when compared with the finer, more detailed 0.178 mm printing resolution. In the case of $CaCO_3$-PLA composites the impact strength was 3.8 ± 0.3 kJ m^{-2} in regards to the materialcontaining 20 m / m % $CaCO_3$ and it was 3.1 ± 0.5 kJ m^{-2} at the 50 m / m % material. Compared to natural PLA these values are significantly lower, as we obtained 6,0 ± 1.0 kJ m^{-2} as impacts strength value.

4.3) Scanning Electron Microscopy (SEM)

The analysis of fracture surfaces provided beneficial information about the internal structure of 3D printed specimens, demonstrating the characteristics of each technology. On the basis of mechanical tests, in the case of specimens printed in the Y orientation, greater strength can be achieved than in when compared with printing or outputting them in either Z or X orientation.

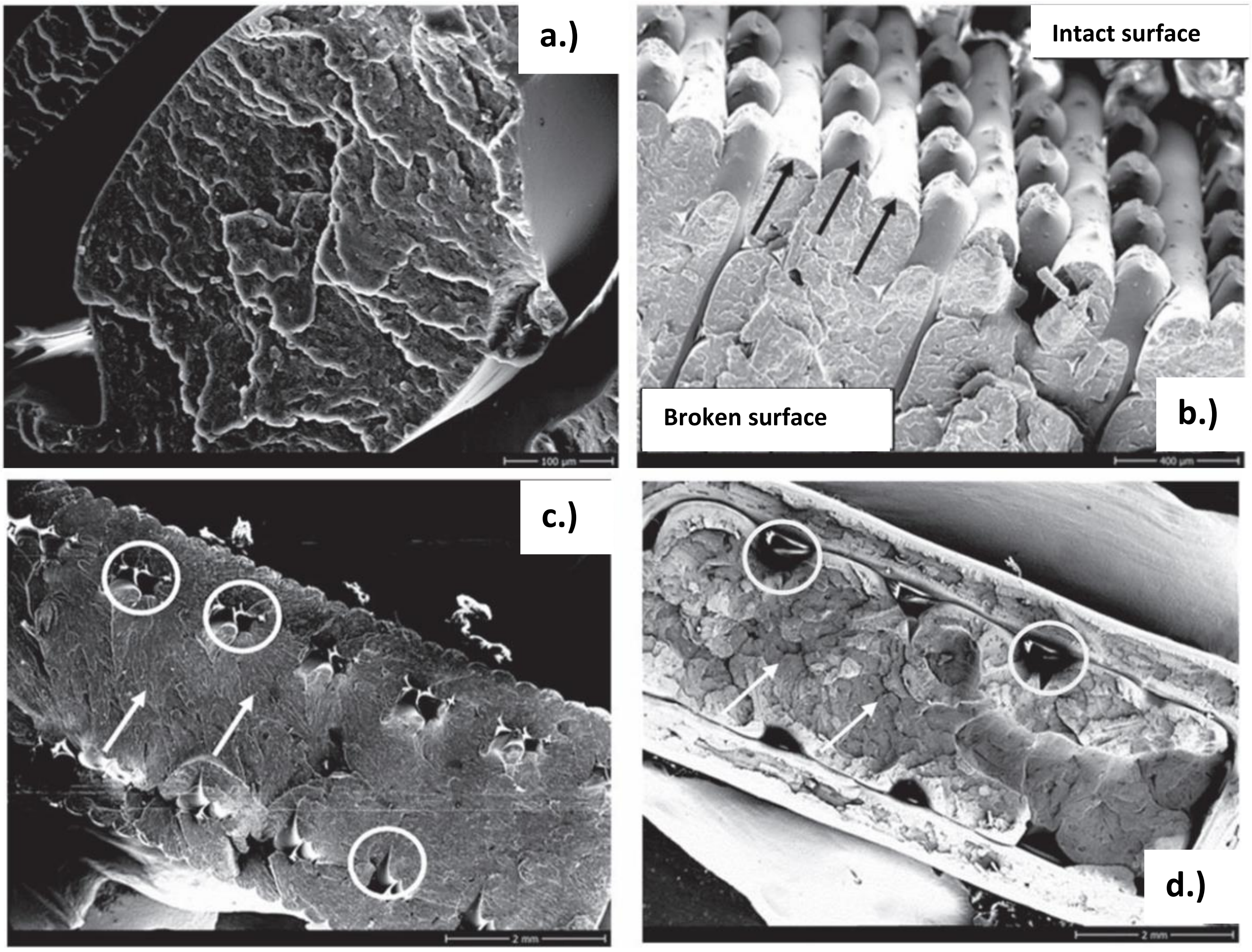


Figure 2. : FDM™ SEM images of ABS test specimens printed with 0.178 mm layer height a.) FDM™ 3D printing (ABS M30, 0.178 mm): platelet-like broken surface, 200X magnification. b.) Broken and intact surface, black arrows indicate the orthogonal columns, 60x magnification c.) Broken surface of test specimens printed in Y orientation. The white circles indicate the gaps between layers, arrows points to the characteristic broken suface, 15x magnification d.) Specimen printed in Z orientation. The circles show the gaps and the arrows the tearing between layers. Source: Maróti et al 2019: Printing Orientation Defines Anisotropic Mechanical Properties in Additive Manufacturing of Upper Limb Prosthetics

Regarding the ABS M30 (FDM™) Y samples smaller gaps (0.3-0.4 mm) can be seen between the neighbouring layers at 15x magnification, while in the Z orientation they are larger (0.65-0.85 mm). This observation is generally true for all FDM ™ and FFF printing technology, including ULTEM™. Connections between the layers in the case of samples with a resolution of 330 microns are more pronounced than those observed at 178 microns (Figure 2). Each layer is rotated by 90 ° relative to one another, which is a primary function in the design intended to provide greater stability. In the examination of the structure regarding the ‘columns’ which make up each layer, we can observe, at 200x magnification, a plate-like fractured surface and a deformation of the ‘columns’. This deformation can be caused as a result of cooling, after the polymer flows out from the extruder. Armed with FFF technology the natural surface of the PLA fracture features remarkable similarity to FDM™ technology. The individual columns are well separated. However, the $CaCO_3$-PLA composites possess a far more uniform, homogeneous structure. In the case of the PLA Model the columns melted together, presumably due to the changed rheological parameters associated with $CaCO_3$ concentration. In the case of Gypsum samples the column structure disappears, and more porous surfaces appears. The pore size is in the range of 30-50 microns. In the case of composites $CaCO_3$ particles can also be identified. The structure explains the mechanical behaviour regarding the materials. Photopolymer specimens proved to be far more rigid, likely explains the glass-like fractured pattern. At 60x magnification it can be clearly seen that the surface is nearly uniform, without gaps, homogeneous, and is supported by the larger, 200x magnification images. There was no significant difference among the individual orientations. In the case of polyamide samples, due to laser fusion, the internal structure is identical in the X, Y and Z orientation, which is consistent with the results supporting the mechanical tests. There is no visible gap between the layers, yet the material is generally porous.

5.) Conclusions

Our studies provided the characterization of additive manufacturing technologies most commonly used in medical technology development from the point of view of material science, including the possibility to answer important practical questions. In the light of data from previously published studies at the international level and our own results, we state, FDM ™, FFF, SLS and PolyJet ™ technologies can be used independently and in combination for the development in support of medical devices, medical aids and small run production. Based on the literature data, our research team determined the orientation dependence of the individual printing methods, extending the tests to static and dynamic methods. The effective completion of mechanical tests by scanning electron microscopy was only partially realized among internationally published studies. The thermoanalytical analysis of composites, including $CaCO_3$ designed for 3D printing, was not previously performed by a research group, nor was it characterized for practical use (e.g. cost-effectiveness analysis, manufacturability and pre-clinical studies), although several publications are available regarding 3D printed upper limb prostheses , development of orthoses and dental applications. Based on the results of our research, the following main findings can be made about the additive manufacturing technology solutions which can be used in medical device development:

5.1) Practical Aspects:

- FDM™, FFF, SLS and PolyJet™ technologies can be successfully used in medical device development, thanks to the relatively wide range of materials, resulting in a broad spectrum of mechanical, thermal and structural features.
- Strikingly, and in consideration of the first time in our research, we effectively and systematically prepared a complex material technology study involving complex

additive manufacturing technology solutions at international level, involving several additive manufacturing technology solutions through the solving of practical problems

- During our research, several new medical technology products and aids (Phoenix Smart Orthosis, dental drill sleeve) were developed
- The various forms of technologies tested can be used in initial modelling, product/idea visualization, prototype production and small run production too. FFF technology is primarily used in modelling and early-stage prototyping, and FDM™ technology proved ideally suitable regarding industrial materials (e.g., ULTEM ™), in particular, for small run production. The advantages of SLS are primarily in functional prototype production and small series production, while PolyJet ™ is advantageous in the design of highly detailed, finely printed structures.
- All of the devices developed and implemented into routine practice can potentially be considered operationally suitable throughout healthcare education and/or clinical practice. Ideally, clinical testing regarding ongoing developments will soon see fruition in the near future, including the appropriate ethical permission, since their practical testing has, thus far, proven successful.

5.2) Material Characteristics and Manufacturability:

- In the case of thread-pulling (FDM™ and FFF) technologies, the use of X and Y orientation is indeed, more favorable regarding both static and dynamic parameters, which is a general finding in the development of all medical devices and aids. Some parts, models which can only be printed in Z orientation and require industrial technologies (e.g., SLS or FDM™ with ULTEM™ material)

- Our research team is the first to effectively test the PLA-$CaCO_3$ composites (PLA Model, PLA Gypsum) regarding 3D printing from a mechanical and thermoanalytic perspective.
- Larger layer resolution results in a stronger internal structure, resulting in a more mechanically stable workpiece, including an increase in efficient manufacturing processes (time, cost and efficiency), which is an important aspect in regards to prosthesis development and manufacturing.
- Addition of additives - in this case, $CaCO_3$- the thermoplastic polymer base material greatly influences static and dynamic mechanical parameters. In the case of fracture fixations, this means less flexibility and elongation, thus, potentially being effective in the fixation of upper limb fractures and increasing patient-friendly use.
- The results of the thermal analysis have highlighted how PLA-$CaCO_3$ composites can potentially be used to produce fracture fixings, and HDT PLA is particularly suitable for the development regarding such devices undergoing routine thermal sterilization. Structural studies have also confirmed this very aspect.
- It can be stated in which Shore D hardness, as a static parameter, is independent of printing orientation.
- Cost-effectiveness analyses of break fixations and dental drilling sleeves have highlighted the potential for technology to be deployed within a relatively short span of time regarding day-to-day clinical activity.
- In the production of complex devices (for example, limb prostheses), it may be advisable to use several different technologies and/or printing parameters, taking into consideration, the mechanical stress of each component and its functionality.

6.) Publications, conferences

6.1) Publications from the topic:

1.) P. Maróti, P. Varga, A. Ferencz, Z. Ujfalusi, M. Nyitrai, D. Lőrinczy, Testing of innovative materials for medical additive manufacturing by DTA, Journal of Thermal Analysis and Calorimetry 2019;136:2041-48.

DOI: https://doi.org/10.1007/s10973-018-7839-x

IF: 2.209

2.) P. Maroti, P. Varga, H. Abraham, G. Falk, T. Zsebe, Z. Meiszterics, S. Mano, Z. Csernatony, S. Rendeki, M. Nyitrai, Printing orientation defines anisotropic mechanical properties in additive manufacturing of upper limb prosthetics, Materials Research Expres (2018)

DOI: https://doi.org/10.1088/2053-1591/aaf5a9

IF: 1.449

3.) J. Szalma, B.V. Lovász, E. Lempel, P. Maróti, Three-Dimensionally Printed Individual Drill Sleeve for Depth-Controlled Sections Third Molar Surgery, Journal of Oral and Maxillofacial Surgery (2018)

DOI: https://doi.org/10.1016/j.joms.2018.11.028

IF: 1.779

4.) P. Varga, D. Lorinczy, L. Toth, A. Pentek, M. Nyitrai, P. Maroti, Novel PLA-CaCO3 composites in additive manufacturing of upper limb casts and orthotics—A feasibility study, Materials Research Express 6(4) (2019) 045317

DOI: https://doi.org/10.1088/2053-1591/aafdbc

IF: 1.449

6.2) Other Papers:

6.2.1) Publications and Papers:

1.) Horváth Orsolya, Maróti Péter
3D Nyomtatott fegyverek – Vélt vagy valós veszélyek?
PÉCSI HATÁRŐR TUDOMÁNYOS KÖZLEMÉNYEK 20. p. 73 (2018)

2.) Henter I, Figler M, Maróti P, Berényi K
A praxisközösségi működés tapasztalatai a dietetikus szemszögéből
NÉPEGÉSZSÉGÜGY 95 : 1 pp. 47-51. , 5 p. (2017)

3.) Keresztes Dóra, Woth Gábor, Nagy Bálint János, Farkas József, Németh Zsuzsanna, Maróti Péter, Rendeki Mátyás, Rendeki Szilárd: Kárhelyszíni elsősegélynyújtás - a disaster medic képzés első tapasztalatai tűzoltók körében: VédelemTudomány online folyóirat II/1 2017.03

4.) An International Association for Medical Education (AMEE) Conference 2016, Barcelona, Spain, - poster presentation: Adam Tibor Schlegl MD, Peter Varga MD, Peter Maroti MD, Ian O'Sullivan MD, Csaba Vermes MD, Peter Than MD: Patient specific 3D printed hip models for easier understanding the total hip arthroplasty in developmental dsysplasia of the hip – poster presentation

5.) An International Association for Medical Education (AMEE) Conference 2015, Glasgow -e poszter: Peter Maroti, Adam Tibor Schlegl MD, Peter Varga, Szilard Rendeki MD: Multidisciplinary simulations to improve teamwork and medical skills at the same time – e-poster presentation

6.) 3rd International Interdisciplinary 3D Conference: The Role of Additive Manufacturing in Upper Limb Prosthetic Development V. Potári, A. Péntek, P. Varga, M. Bene, D. Berki, Á. Árvai, P. Maróti, M. Nyitrai

6.2.2) Conferences:

1.) 1st International Interdisciplinary 3D Conference founder, organiser, workshop participant, oral presentation – 2015

2.) 2nd International Interdisciplinary 3D Conference - Chief Organizer, Conference Abstract Book Editor ISBN 978-963-429-066-7 – 2016

3.) 3rd International Interdisciplinary 3D Conference – Chief Organizer, Conference Abstract Book Editor ISBN 978-963-429-165-7 – 2017

4.) 2nd International Interdisciplinary 3D Conference: The mechanical and structural effects of printing orientation in 3D printed upper limb prosthetics: Péter Maróti ,János Móczár, Péter Varga, Zoltán Meiszterics,Tamás Zsebe,Hajnalka Ábrahám, Miklós Nyitrai – oral presentation

5.) 2nd International Interdisciplinary 3D Conference: Anastomosis Quality Analysis Using 3D Technologies: B. Gasz, P. Varga and P. Maróti – poster presentation

6.) PTE Grastyán Endre Szakkollégium VII. International and XIII. National Interdisciplinary Conference – 2015- Maróti Péter, Schlégl Ádám Tibor, Varga Péter: A simulation based method to improve medical skills in emergency situations - Best Oral Presentation Award

7.) PTE Grastyán Endre Szakkollégium VII. International and XIII. National Interdisciplinary Conference – 2015 - Peter Maroti, Szilard Rendeki: A possible reaction to CBRN threats, involving the Operational Medicine Concept – oral presentation

8.) NATO RWS 267 Advanced Medical Training Workshop, 2016, Romania, Bukarest - Advanced Medical Technologies of Training" lecutre, Szilard Rendeki MD, Peter Varga MD, Peter Maroti MD, Brief Introduction to Simulation Education in Operational Medicine

9.) An International Association for Medical Education (AMEE) Conference 2016, Barcelona, Spain, Patil Teaching In Innovation Award nomination - Peter Maroti MD, Peter Varga MD, Miklos Nyitrai MD, Adam Tibor Schlegl MD, Robert Pilisi, Szilard Rendeki MD: 3D Printing in Cost Effective Simulation Education – Intraosseus Trainer – oral presentation