Materials Research Express

PAPER

Novel PLA-CaCO₃ composites in additive manufacturing of upper limb casts and orthotics—A feasibility study

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Keywords: material testing, mechanical properties, polymer composites, biocompatible polymers, scanning electron microscopy, CaCO₃

Abstract

Additive manufacturing technologies provide rapidly developing and promising solutions in many fields of healthcare. Traumatic upper limb injuries are among the most common conditions worldwide. In the case of a traumatic bone fracture it is crucial to provide immobilisation of the affected limb in the correct anatomical position to achieve the desirable healing process. Thus, splints and casts play an essential role in the healing and rehabilitation progress. 3D printing is a powerful tool in creating personalized biomedical devices, therefore, medical aids for the treatment of bone fractures are amongst the most promising fields of medical 3D printing. In medical care, the most extensively used area of additive manufacturing is Fused-Filament-Fabrication (FFF). In our study we have investigated two different unique PLA-CaCO₃ composites. To access the characteristics of the composites, dynamic and static mechanical stability tests were performed along with scanning electron microscopy for the structural analysis, and also manufactured splints with the help of 3D design and thermoforming methods. According to our results the new materials are potentially viable in clinical environment, but further laboratory and clinical investigations are necessary. Our aim is to continue the feasibility tests and establish the appropriate clinical trials.

1. Introduction

Additive manufacturing (AM) and three-dimensional (3D) visualization technologies are essential parts of innovative biomedical solutions [1, 2]. By using 3D printing we are able to manufacture customized external prosthetics [3, 4], create models for surgical applications e.g. operating guides [4, 5] or develop new methodologies and devices for orthotics. Traumatic upper limb injuries and other pathologies affecting the upper extremities are common medical conditions. In support of that, a study conducted in England and Wales showed that the most prevalent fractures are related to the upper limb (men: carpal bones, 26.2 cases per 10 000 person/years, women: radius and ulna 30.2 cases per 10 000 person/years) [6]. Another research highlighted that the incidence of forearm fractures are significantly higher in elderly people (men: 33.8 per 10 000 person/years, women 124.6 per 10 000 person/years) [7]. 3D printing, as a unique and innovative solution in personalized medicine, could be a great tool for the treatment of traumatic fractures, considering that different lower- and upper limb orthoses and casts can be manufactured with this approach [8–11].

In the course of fracture treatment, the primary goal is to fix the bones in the correct anatomical position along with minimization the pain of the patient. The choice of the treatment method depends on several factors and the decision should be based on patients’ individual needs. Conservative treatment encompasses the closed reduction if required, followed by a period of immobilization with casting or splinting until the periosteal callus appears and the healing process accomplishes [12, 13].
Traditional casting involves the application of circumferential gypsum plaster onto the damaged limb [14]. This solution is rapid and relatively cost effective. While the gypsum plaster casts are widely used in medical therapy, recently several attempts have been made to modernize the technique; supplementary materials such as fiberglass and plastics have been used to improve the technical features of casts [15]. In the 21st century, one of the most important ways to amend existing methods is to personalise treatments based on individual needs.

3D printing is an influential tool for personalized medical treatment. According to a recent review, rapid prototyping (RP) is widely used in anatomical modelling to generate surgical instruments as well as producing implants and prostheses [5]. The desired object can be created by using computer-assisted design (CAD), either segmentation from radiological data or a precision scanner. Both methods support sufficient fitting, based on the patients’ personal anatomy and specific pathology [4, 5].

In our research we aimed to test three different materials which could be potentially used for manufacturing casts, splints and orthoses, using FFF additive manufacturing technologies. Two of them are new and unique developments of Filamania Ltd (Hungary, 2310 Szígtzentmiklós, Fenyőfa utca 23/A). These composites were compared to neat, standard PLA polymers, suitable for 3D printing. The mechanical characteristics and features of PLA 3D printing is well known, thus this material served as a reference point in our work [16].

Composites containing Ca\(^{2+}\) salts (carbonates and phosphates) are well-described and have been widely used in biotechnology [17–20]. However, we have only limited information regarding 3D printed CaCO\(_3\) composites. A previous study revealed the mechanical and thermal properties of CaCO\(_3\)-PLA-nanocomposites and showed that both static and dynamic parameters decreased, compared to neat PLA [21]. Another publication indicated that lower concentrations of CaCO\(_3\) can function as a plasticizer [17]. In our study we aim to describe the materials by their mechanical characteristics and structure. These investigations also served as feasibility tests for the 3D printing and thermoforming process of upper limb orthotics and casts. The results and conclusions may be beneficially used in clinical research in the near future.

2. Materials and methods

2.1. Materials and 3D printing

The experiment was started with the selection of the materials. We have chosen standard PLA (N) as a reference, and the two other materials were PLA composites, mixed with fine CaCO\(_3\) powder (granule size: 1.5–3 μms). The ‘PLA Modell’ (M): contained 20 m m\(^{-1}\)% of CaCO\(_3\) and ‘PLA Gypsum’ (G) 50 m m\(^{-1}\)% of CaCO\(_3\). Mixing ratios are given as percentage of CaCO\(_3\) mass divided by the mass of the end product per unit. These materials are manufactured and provided by Filamania Ltd and for 3D Printing technology, we used FFF desktop printing (Craftunique Ltd—Craftbot 2 desktop 3D printer). The ‘Z’ resolution of printing was 200 micrometres and 2 outlying shells were used. The printing (nozzle) temperature was set to 215 °C in each cases, and the infill density was 100% in case of the test bars. The diameter of filament was 1.75 mm +/− 0.05 mm.

2.2. Mechanical tests and morphology

For the mechanical analysis, Charpy Impact test (ISO 179–1), 3-point-bending test (ASTM D 790—03), tensile strength test (ASTM D 638–03) were performed and also the Shore D hardness of the test bars (ASTM D 2240-03, print-bed side) were measured. All of the test bars were laid on the printing bed with the biggest surface facing downwards. Room temperature was 27.1 °C, relative humidity was: 48.8%. According to the standards, 5 pieces of test bars were produced for each test. The broken surface of test specimens was examined using scanning electron microscopy (SEM - JSM-6300, Jeol Japan), with 15x, 60x and 200x magnification, and we applied golden sheeting for the test bars. For the statistical analysis OriginPro 2016 software was used.

2.3. Feasibility test for thermoforming and 3D printing

We investigated the materials in terms of the possible production methods of casts and splints. First, thermoforming process was examined. The open source ‘.stl’ model was downloaded from Thingiverse (by: ‘rider12’). This pre-designed splint model has a flat, hexagonal based structure. For the three different types of materials the printing resolution was 200 micrometres constantly. The water temperature which we used for heating, was 75 °C, and the thickness of the models were 2 mm, infill density was set to 100%. Another common method, using CAD/CAM technologies was also tested (figure 1). A 27 years old healthy volunteer man’s hand was modelled using different CAD/CAM softwares. The initial photos (45 pieces) were taken by an iPhone 5 smart phone, and the 3D model was created using Autodesk ReMake. The Boolean-operations conducted with NetFabb, post-processing steps and design of clippers was performed by AutoDesk Meshmixer and 3ds Max. Slicing was carried out with Craftunique CraftWare, with 200 micrometres of ‘Z’ resolution. All of the mentioned software have an academic licence. The infill density was 40% in the latter case.
3. Results and discussion

3.1. Mechanical tests

To characterise the mechanical properties of the investigated material we first carried out dynamic mechanical test experiments. The impact strength values obtained for the neat PLA and for the two investigated composites are presented in figure 2. For M:20 the impact strength was $3822 \pm 254 \text{ J m}^{-2}$, while for the G:50 it was $3142 \pm 488 \text{ J m}^{-2}$. Comparing (two-sample t-test, $p = 0.05$ significance level) these results with the value of $5971 \pm 973 \text{ J m}^{-2}$ measured for the neat PLA indicates that the resistance of the PLA to dynamic mechanical stress has decreased during the formation of composites. The effect was greater in the case of G:50 than for the M:20 (figure 2).

Then we investigated how strain is generated in the composites under mechanical stress. In these analysis the mechanical properties were evaluated by using 3-point bending test and tensile test. Furthermore, the values of

Figure 1. Steps of 3D Scanning of the arm: The 3D scanning process was started with Autodesk Remake, using photos (45 pcs) taken by an Iphone 5 smartphone. The post-processing phase was done with Autodesk Meshmixer (a) and (c). For Boolean operations NetFab was used, and the clip was designed with Autodesk 3ds Max ((b) and (d)).

Figure 2. Results of impact strength ($\text{J m}^{-2}$), means with standard error. N: neat PLA, G: Gypsum PLA, M: Modell PLA.
strain and elongation were also investigated. The results are presented in figure 3. The data showed that the behaviour of the materials under static loads correlated well with those observed in the dynamic tests. Both the strain and elongation data indicated that the composites have more rigid structures than neat PLA and they are also more resistant against deformations (figure 3).

To further describe the mechanical properties of the composites, the flexural strength and tensile strength values were characterized in each materials as well (figure 4). In the case of the 'PLA Model' the flexural strength was 59.2 ± 1.2 MPa, greater, than that observed for the 'PLA Gypsum' (52.5 ± 1.6 MPa). However, both 'PLA Model' and 'PLA Gypsum' showed less sturdy nature than the standard PLA (82.2 ± 5.7 MPa). The results obtained in the tensile tests correlated strongly with those of the bending tests (figure 4). During the measurement of the Shore D hardness values, the results were between 77.0 and 77.9, thus there were no significant differences between the specified materials. This finding was interesting, since fillers usually increase the Shore D hardness, but we can find exceptions in the literature - like in the case of glycerol plasticized DDGS (distillers dried grain solubles) and PLA blends [21]. In our case, we can not observe significant (two-sample t-test, $p = 0.05$ significance level) change in this parameter, which can be correlated with the granule size of the

![Figure 3](image1.png)

**Figure 3.** Strain of the test specimens (%), means with standard error. N: neat PLA, G: Gypsum PLA, M: Modell PLA. The squares show the strain at flexion, the dots indicates the elongation in case of tensile test. The errors indicated in the figure are smaller in some cases than the applied symbols.

![Figure 4](image2.png)

**Figure 4.** Results of 3 point bending and tensile strength tests (MPa)The black squares indicates the means with standard error in the case of flexural strength, the dots show the means of tensile strength, with standard error. N: neat PLA, G: Gypsum PLA, M: Modell PLA. The errors indicated in the figure are smaller in some cases than the applied symbols.
powder. Also, the work of Kasuga and colleagues [18] showed that the increase in the concentration of CaCO₃ in the blend increases the overall porosity, especially from 40 wt.% which can avert the increase of the Shore D hardness value.

These experiments on the mechanical properties of the composites showed that with the increase of CaCO₃ concentration, the observed alterations were significantly larger. These effects are apparently much greater than those reported in previous studies from moulded test specimens [22, 23].

3.2. Morphology
To provide a structural framework for the understanding of the results of mechanical test we carried out scanning electron microscopic investigation on these materials. The images obtained in the experiments are shown in figure 5. These results indicated important differences in the deep structure of the tested materials. At 15x magnification the results showed that the pure PLA test bars are characterized by well-defined, column-like structures, compared to the composite materials, where the infill is more heterogeneous. In the case of PLA the outer shell is more differentiated from the inner structures. At 60x magnification the thickness of each column was measured. In the case of standard PLA the columns were 400 μm wide and 200 μm high (Z printing resolution), while the ‘PLA Model’ columns were more symmetrical, which is possibly explained by the modification of the rheological parameters. The ‘PLA Gypsum’ material had a hollow, heterogeneous structure, therefore the detection of the components was challenging and problematic. The diameters of the holes were in the range of 30–50 μm. The images obtained at 200x magnification showed that the characteristic, platelet-like broken surface appears in all of the materials. PLA has the smoothest, most structured form. In case of ‘PLA Model’ and ‘PLA Gypsum’ a porous infill was evident, and it was possible to identify the particles of CaCO₃. The images also revealed that the surface of the two composites are not differentiated, the printing layers were not
detectable. Considering all these observations we concluded that these scanning electron microscopic images give explanation for the mechanical behaviour of the composites.

3.3. Thermoformed and 3D scanned models—price and time

It is well known that PLA, as a thermoplastic polymer, can be thermoformed in water above 70 °C, however, it has its certain limitations. The two new materials are considerably simpler to form, and due to their observed rigid structure, they preserve the desired, anatomically accurate fitting position as shown on figures 6(a) and (b). In case of the 3D scanned version the overall production time was reasonably higher (2 h versus 19 h respectively) and the models cost more (average price per piece was 1.3 EUR versus 4.4 EUR respectively), but the fitting was found to be more precise (table 1). Furthermore, the volunteer stated that the resistance against the small movements were higher in case of using 3D scanning, he felt it more stable, which is a key element in case of upper limb bone fractures and other pathologies. The material costs for a conventional plaster casts varies around 1–2.5 Euros, depending on the size and the manufacturer. According to these results, we can conclude that, the AM (additive manufacturing) technology is still more expensive than classical methods, but the costs are getting closer and the differences are declining as a result of the development of new materials and 3D printers.

Figure 6. (a) Thermoformed models of wrist splints. N: neat PLA, G: Gypsum PLA, M: Modell PLA. (b) 3D scanned models of wrist splints. N: neat PLA, G: Gypsum PLA, M: Modell PLA.
Table 1. Costs and overall time of production of the splints.

| Material and method | Dry mass [g] | Price/kg [EUR] | Price of model [EUR] | Time of construction |
|---------------------|--------------|----------------|----------------------|---------------------|
| Pure PLA – T        | 29.34        | 26             | 0.76                 | 2 h for printing    |
| PLA, Gypsum - T     | 31.04        | 50.5           | 1.57                 |                     |
| PLA, Modell - T     | 32.01        | 45             | 1.44                 |                     |
| Pure PLA – 3D       | 111.16       | 26             | 2.89                 | 3 h for design, 16 h for printing |
| PLA, Gypsum – 3D    | 111.16       | 50.5           | 5.61                 |                     |
| PLA, Modell – 3D    | 102.25       | 45             | 4.60                 |                     |

*EUR/HUF: 321.86 2018. 07. 30

4. Conclusions

According to previous studies the 3D printing process of upper limb orthotics and casts are rapidly advancing [2, 3, 8]. New methods and materials can hasten the speed of technology and increase the effectiveness of the process. Nevertheless, while there are previous data regarding the mechanical properties of PLA-CaCO₃ composites [16–19], we have only limited information regarding the properties of these materials after they were 3D printed. In this work we concluded that, the examined composites are suitable for manufacturing 3D printed casts and orthoses. These materials do not absorb significant amount of water, has a lightweight structure and has the advantage of rigidity, which potentially improves the stability of the broken upper limb during the rehabilitation phase. Also, from the perspective of the patients it is more comfortable, since it could be worn under clothing, it is water resistant and the user can be more independent in case of performing activities of the daily life.

With the addition of CaCO₃, the dynamic and static parameters of the composite were altered significantly (figures (2)–(4)); they became more rigid and brittle. The observed modifications of the mechanical properties are even more interesting when compared to the results of previous works [23, 24] and they also differ from the results of the work published by Kasuga and colleagues [18]. These cited studies investigated the mechanical properties of the composites without printing them in 3D, and thus the differences are most likely related to the application of the 3D printing technology in our work. The electron microscopy images showed that 3D printing resulted in the appearance of layered structures in PLA and also in the composites. Also, it is important to mention that the particles in the ‘PLA Model’ and ‘PLA Gypsum’ were bigger sized in our case. The microscopy images showed that the structure of the composites become more heterogeneous and porous, with the enhanced concentration of CaCO₃, which helps us to understand the mechanical behaviour of these new materials.

We have also revealed that the thermoforming process are considerably easier with the composites containing CaCO₃. All of the materials are easily produced and printed with desktop machines. It appears that the ‘PLA Gypsum’ and ‘PLA Model’ can be potential substitutes for traditional materials. The limitations for this replacement are the higher prices and slower printing speed compared with other 3D printing technologies, however, there are promising results, which aim to hasten the FFF technology significantly [25]. The time needed for the two different production cycle (2 and 19 h, respectively) seems to be the biggest hurdle at the moment for routine clinical translation, besides the availability of the trained 3D printing specialists in the healthcare system.

As it is unambiguous, in the everyday trauma care waiting 19 h for a cast to be ready is not an option. Using a temporary cast can be a current solution until 3D printing times decrease to an acceptable range, which is anticipated considering the fast paced development of 3D printing technologies—like Fast-FFF [25] - and 3D scanning methods. In our pilot examinations, we involved a healthy volunteer whose arm could be easily scanned without traumatic diversions. In case of a traumatic patient the opposite arm can be the template for mirrored use for scanning. In the stage of the clinical trial, it will be crucial to specify the inclusion criteria deliberately, thus this device is inadequate if the fracture is presented with severely traumatized and distorted limbs, unless the fracture is treated with closed reduction and the limbs could be immobilized in the correct anatomical position.

The static tests and Shore D measurements indicate that the materials can be also used for medical modelling (for example: bone models for IO—intravenous cannulation - trainers, teeth models for skills training, and individualized training of bone synthesis procedures). Our recent study— analysing the thermal behaviour of these materials - have shown that these materials are suitable for disinfection procedures also, which is an important feature in clinical applications [26]. For long-term results, clinical, patient-related studies have to be carried out in the near future, along with detailed market research, focusing on IP (intellectual property) relations also.
Acknowledgments

This research was supported by a grant from the National Research, Development and Innovation Office and the European Union (GINOP 2.3.2-15–2016-00022). The present scientific contribution is dedicated to the 650th anniversary of the foundation of the University of Pécs, Hungary.

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