Rapid Tooling technologies in the processing of thermoplastic polymers

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Abstract. Thousands of people are affected by the newest achievements of material science and manufacturing technologies each year in the form of biomedical implants. In this field, the aim of developement is to create individual implants to satisfy the geometrical and adapting requirements of the patient. This manufacturing process has been recently improved by shortening the cycle time and using cost effective methods. Biocompatible thermoplastic polymers can be shaped with hot pressing technique. Rapid Tooling was used to create a forming tool for manufacturing process. 3D Printing was used to fabricate the computer generated forming tool. This tool was reinforced by infiltrating it with an epoxy resin. Different epoxy resins were examined to secure the best mechanical properties of this tool. Then the reinforced tool was used for hot pressing of the biocompatible thermoplastic polymer, poly(ε-caprolactone).

Introduction

Bone Tissue Engineering is a frontier field of biology, chemistry, medicine and mechanical engineering. It examines the bone from an engineering viewpoint for a better understanding of the biological processes. Different studies revealed the structure and the mechanical properties of bones that help us to develop and create a more receptible implant for the patient [1, 2]. The ideal material for undertaking cranioplasty should be malleable to fit precisely even complicated cranial defects, strong but lightweight, easily securable to the cranium, biocompatible and chemically inert, radiolucent, non-ferromagnetic, readily available, and inexpensive [3]. One of the most essential properties of an engineered construct used in medical environment is its biocompatibility, or ability not to elicit a significant or prolonged inflammatory response. It is important to know that any injury will elicit some inflammatory state and this is certainly true with the implantation of a manufactured scaffold [4]. In pursue of creating the ideal material the aim of the developers is to achieve as many positive attributes as possible even if this means the relapse of other features. Different materials suit different properties; therefore, developers experiment with several materials for biomedical use. These materials can be divided in four groups: (1) metals, (2) ceramics, (3) polymers and (4) composite materials. Polymeric materials have a wide variety of applications for implantation since they can be easily fabricated into many forms; such as, fibers, textiles, films, rods, and viscous liquids. Polymers show similar properties to natural tissues because collagen is polymeric, too. In some cases it is possible to achieve a bond between synthetic polymers and natural tissue polymers [5]. The major advantage of polymers is that they can be tailored to suit specific functions and thus exhibit controllable properties. Furthermore, since many synthetic polymers undergo hydrolytic degradation, a scaffold's degradation rate should not vary significantly between hosts [6].

Medical implants usually fit individual requirements; such as, their geometrical form. This means that the implant is a result of small-lot or single part production. Rapid Prototyping (RPT) is a technology that supports engineering by creating prototypes in a simple and quick way. Prototypes can be used not only for testing and proofing ideas and concepts relating to the development of the product but also for the production of the individual implant [7].

Rapid Tooling has evolved from RPT. Rapid tooling (RT) is defined by the applications that are aimed at making tools and molds for the production of prototypes and preseries products by using the same processes as those used in rapid prototyping [8]. This concerns both the model (positive) as well as the mold (negative).
There are two methods of achieving Rapid Tooling. Indirect methods use a pattern generated from a rapid prototyping device. The pattern is used to cast or form molds or tools made of a variety of materials, including epoxy, aluminum and metal alloy blends. Direct methods produce tools or tooling inserts from the rapid prototyping device. Materials for direct methods include many metal alloys, alloy blends, ceramics, composite materials, and even rapid prototype plastics [9]. For some applications, RPT processes allow production tooling to be made directly. "Soft" tooling that can only be used for low production volumes allowing up to several hundred shots to be produced. "Hard" or volume production tooling can also be made using relatively new RPT processes.
In the manufacturing process of the medical implant, the soft tool was created by 3D Printing. The 3D printer machine spreads a layer of powder from the feed box to cover the surface from the build piston. The printer then prints binder solution onto the loose powder, forming the first cross section. The powder is glued together at where the binder is printed. The remaining powder remains loose and supports the layers that will be printed above. When the cross section is completed, the build piston is lowered, a new layer of powder is spread over its surface, and the process is repeated. The part grows layer by layer in the build piston until the part is completed. Finally the build piston is raised and the loose powder is vacuumed, revealing the complete part [7].
This paper focuses on demonstrating the forming of a bicompatible thermoplastic polymer with Rapid Tooling applications. We have created the forming tool by applying different printing adjustments. The infiltration resins' properties were examined as they determine the mechanical strength of the hot pressing tool.

Experimental

3D model of the forming tool was created with a SolidWorks CAD Software. The STL file of the cranium was kindly provided by Varinex Zrt. The 3D model of the tool was printed by Z Corporation's Z810 3D Printer. For the printing, we used commercially available ZP102 plaster powder and ZB58 binder from the same manufacturer.
For the infiltration, we used Eporezit AH-12 epoxy resin (Polimerkémia Kft.), We examined the effects of different hardeners; such as T-111, T-58 (Polimerkémia Kft.) and LonzaCure Dedta 80 (Lonza Kereskedelmi Képviselet). The resins were mixed with an Eurostar – Kika Labortechnik mixer at 120 rpm. To ensure the required temperature we used Heraeus Function Line Drying Oven to ensure. The programability of the oven was 0.1°C exact.
The material of the implant is Capa 6250 polycaprolacton (PCL) was provided by Perstorp Caprolactones, Perstorp Ltd. According to the manufacturer's datasheet, the melting point of polycaprolacton is at 58-60°C. The material's mean molecular weight is 25 000 g/mol. Relative density of PCL is 1.1, on the scale where 1 stands for water's density.
For forming the material, we used Collin P200E type hot-press. The maximum hydraulic pressure of the press is 24 MPa, and the maximum temperature can be set for 350°C.
The thermal properties of samples were studied by differential scanning calorimetry (DSC). The non-isothermal curves were measured with a Perkin-Elmer DSC 7 equipped with Perkin-Elmer Intercooler 2 cooling system, the purge gas was nitrogen (20 cm^3/min). Sample weights were between 5 and 10 mg, which were measured using a Sartorius RC 210 analytical balance (accuracy: ±0.01 mg). The measurements were carried out between 0 and 200°C with a heating and cooling rate of 10°C/min. The results were evaluated according to ISO 11357-2 standard.
The hardness measurements were performed by Zwick/Roell H04.3150 durometer and evaluated according to Shore D standard. For each data point 10 measurements were made.

Results and Discussion

The manufactured tool was created with 3D Printing of the model. During the manufacturing, we decided to use two different adjustments. We chose these adjustments according to former researches done in the university [10, 11]. Samples manufactured with these adjustments were easily infiltrated and the porosity of the model guaranteed that the properties of the resin would emerge.

One of the adjustments we used was Basic adjustments (the standard settings of the printer), which generated a core-shell structure. The printed tool was easily treatable and relatively hard on the surface. The tool did not suffer any damage between the printing and the infiltrating phase.

The other adjustment was using 60% saturation. According to previous researches [10, 11], samples with 60% saturation were successfully infiltrated, and after curing they showed the best mechanical performance. However, the printed forming tool showed bad mechanical properties. The forming tool was weak in its structure and had to be handle with care. It was slightly damaged when the unnecessary powder was being removed from the surface. The damage did not affect the cavity but the tool broke during the infiltration.

The glass transition temperature of the used epoxy resin seemed to be adequate to the forming of pure PCL implants. However, the molding of filled/porous samples or other materials (e.g. polylactide) may require higher temperatures, thus we studied the effect of some commercially available curing resins.

We have examined AH-12 epoxy resin with the following additives: T-111, T-58 and Dedta 80. The method of handling the resin is described in Table 1. Number 5-8 and 17 resins were recommended by the trader, 1-4 were references prepared by the original hardener. Number 9-16 data were made by two-level Taguchi factorial design.

Table 1 Methods of preparing epoxy resin

Number of sample	Hardener	Amount of hardener to 100g AH-12	Mixing time	Temperature of polymerization	Duration of polymerization
		[g]	[mins]	[°C]	[h]
1	T-58	40	15	80	6
2	T-58	40	15	100	6
3	T-58	40	15	120	4
4	T-58	40	15	160	0,5
5	Dedta 80	31	15	80	6
6	Dedta 80	31	15	100	6
7	Dedta 80	31	15	120	4
8	Dedta 80	31	15	160	0,5
9	Dedta 80	80	20	80	4
10	Dedta 80	120	20	100	4
11	Dedta 80	80	20	80	5
12	Dedta 80	120	20	100	5
13	Dedta 80	120	20	80	6
14	Dedta 80	80	20	100	6
15	Dedta 80	120	20	80	8
16	Dedta 80	80	20	100	8
17	T-111	80	30	100	0,75

The properties of the polymerized resins were tested. However, some of the mixtures did not polymerized, and some of them could not have been examined with Shore durometer because the resin was boiled during polymerization. These reasons eluded the evaluation of the Taguchi test. The feasible tests are listed in Table 2.

Table 2 Analysis' of epoxy resin samples

Number of sample	Polymerization	DSC test	Shore hardness test	Comment
1	Yes	Yes	Yes	
2	Yes	Yes	No	Resin got boiled during polymerization
3	Yes	Yes	No	
4	Yes	Yes	No	
5	Yes	Yes	Yes	
6	Yes	Yes	Yes	
7	Yes	Yes	Yes	
8	Yes	Yes	Yes	
9	No	No	No	Did not polymerized
10	Yes	Yes	Yes	
11	No	No	No	Did not polymerized
12	Yes	No	Yes	Did not polymerized completely
13	No	No	No	Did not polymerized
14	No	No	No	Did not polymerized
15	Yes	No	Yes	Did not polymerized completely
16	No	No	No	Did not polymerized
17	Yes	Yes	Yes	

Glass transition temperatures of the resins were examined with DSC. The results of the analysis are shown on Figure 1.

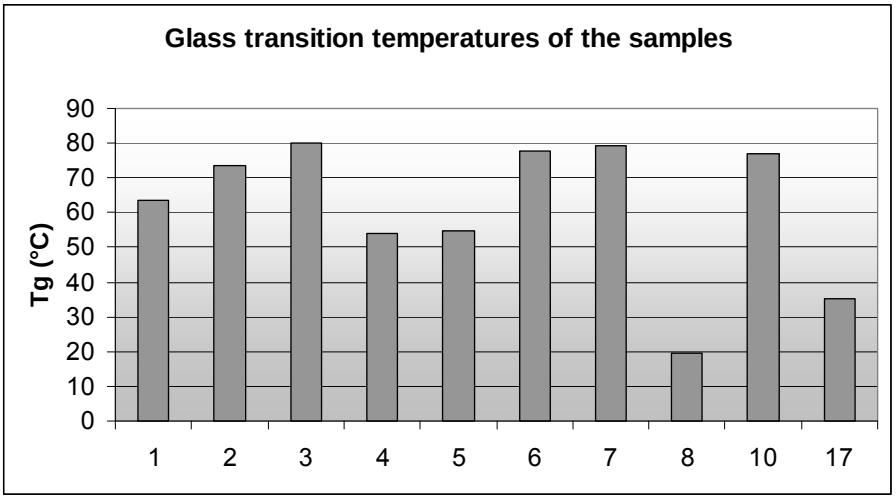

Fig. 1 Glass transition temperatures measured with DSC

The increased curing temperature in the case of T58 hardener enhanced the T_g of the samples except for 160°C, however the resin could not endure the high temperatures because it boiled and degraded. According to the trader, the Lonzacure Dedta 80 hardener increases the T_g to the curing temperature. In this study this result was not attained, although different compositions were examined, too. The results of the Taguchi-design tests could not be evaluated by DSC, since the polymerization was not complete or absolutely did not take place. The use of T111 hardener also resulted in a relatively low T_g.

The mechanical properties of the resins were examined by measuring the materials' Shore D hardness. The hardness of the mold is important during the processing since at low values the mold

wall could be damaged during hot-pressing. The results of the hardness analysis are shown on Figure 2. Except samples 15 and 17, all studied resins showed adequate properties.

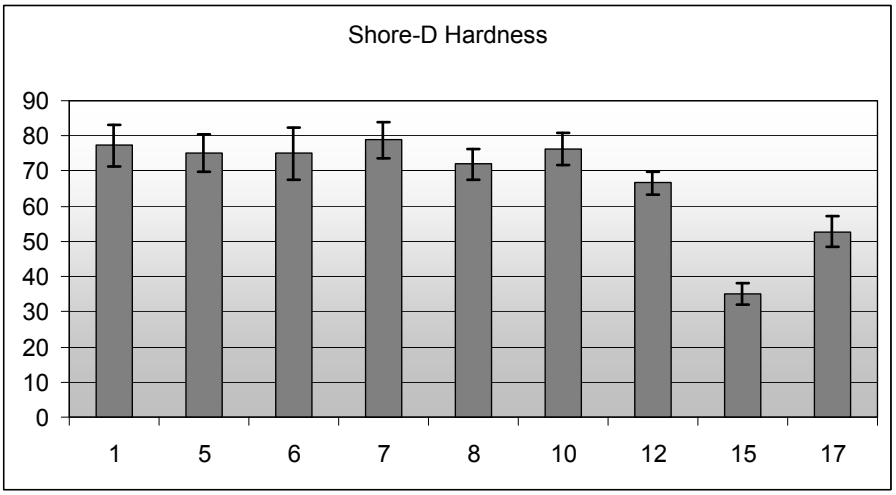

Fig. 2 Shore-D Hardness of examined epoxy resins

The infiltration of the 3D printed forming tool was accomplished in a vacuum chamber. In order to decrease the viscosity of the resin, we heated up the tool to 60°C. Then the tool was placed in to resin bath. For the resin bath, we used the 100:40 mixture of AH-12 and T-58. The tool was kept in the bath for 15 minutes and the bath was vacuumed to 10 mPa. The infiltration lasted 5 minutes and during this time the extent of the vacuum did not change. The tool printed with Basic adjustments was successfully infiltrated. The photo of the infiltrated tool can be seen on Figure 3. The tool was kept in laboratory for one week at 22°C. The infiltrated tool's mass can be seen in Table 4. The glass transition temperature (T_g) of the epoxy resin used during tool infiltration was 64°C.

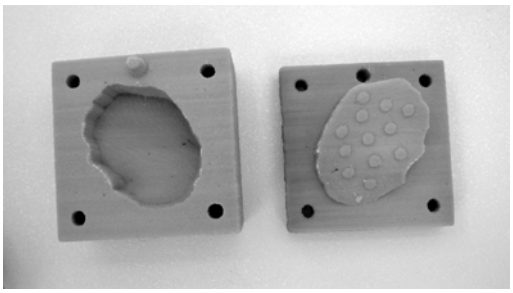

Fig. 3 Successfully infiltrated forming tool

Before the hot pressing, the necessary amount of the thermoplastic polymer was calculated because assuring the necessary polymer film between the tools is a practical need in case of pressing.
The forming tool and the implant material were heated up to 80 °C and were kept in the oven for 30 minutes. The PCL was melted in the forming tool.
When the implant material was completely melted, the forming tool was placed into the press and closed. Then the tool had to be cooled to get back the required mechanical properties because its mechanical strength were naturally lower above glass transition temperature but the implant material still had to stay in melted state. These two conditions created a narrow technological process temperature range. We used the low heat conductivity of ceramics and polymers to achieve the required thermal state. We started to cool the tool and when it was already chilled below T_g, and the implant material was still in melted state, we started the hot pressing technique with increasing pressure. The two sides of the forming tool were finally pressed together with 4 MPa for 30 seconds.
The cooling of the tool and the implant took with water 30 minutes. The forming tool had to be completely destroyed to remove from the product due to the implant's complex geometry. The product did not suffer any damage during the procedure and the necessary polymer film remained

between the two sides of the tool. The mass of the final product weighed 5.8 g. The final product can be seen on Figure 4.

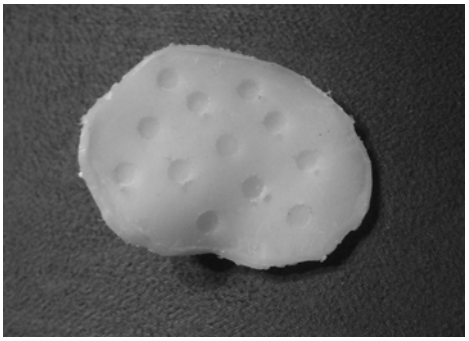

Fig. 4 Cranial implant made of PCL

Summary

Small-lot and single part production is an important opportunity for biomedical engineering. We have introduced a new method of forming thermoplastic polymers, which can be used for creating medical implants. The 3D printed tool was infiltrated with epoxy resin to achieve adequate mechanical performance and then, it was used for hot pressing of poly(ε-caprolactone).
In our work, we have examined several resins which are applicable for infiltration. The samples' glass transition temperatures and their Shore-D hardness were measured. In virtue of our results, we have selected the resin for the infiltration.
However, studies are needed to further improve the mechanical strength of tool and the glass transition temperature of the infiltration resin.

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