Polymer composites for obtaining human anatomic structures

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DOI: https://doi.org/10.14314/polimery.2023.6.3

Abstract: Composites based on PLA with the addition of 3, 6 and 10 wt% silica, hydroxyapatite and bentonite were obtained by twin-screw extrusion. Maleic anhydride grafted polyethylene was used to enhance interface interactions. The influence of the fillers used on the Charpy impact strength, Rockwell hardness, tensile properties and processing shrinkage was investigated. Test samples were obtained by 3D printing. The highest impact strength and hardness were obtained for the composite containing 10 wt% hydroxyapatite. PLA with 10 wt% hydroxyapatite and 3 wt% bentonite was used to obtain anatomical structures by 3D printing.

Keywords: polylactide, medicine, hydroxyapatite, bentonite, silica, anatomical structures.

Polymers used in medicine

Polymers are widely used in medicine. Such polymers are called biomedical polymers [1]. They are used in various branches of medicine, such as aesthetic medicine, dentistry, surgery, orthopedics, cardiology, ophthalmology, and many others. Some of them, i.e., polysaccharides, polypeptides, or polynucleotides, are produced by living organisms. They are called biopolymers and perform important biological functions [2].

The breakthrough event that revolutionized the biomedical industry was the appearance of synthetic polymers on the market in 1920. Initially, they were used to close wounds or treat teeth [3]. In recent years, there has been tremendous progress in the field of materials that meet the patient’s body. Currently, polymeric materials can be used to build elements that have direct contact with the internal or external parts of the patient’s body, as well as to build medical apparatus and tools. They have also found application in pharmacy as blood substitutes or substances introducing drugs into the body (drug carriers) [4, 5].

Polymers used in medicine

Polymers in medicine have a very wide range of applications and are used in the production of medical equipment, surgery, and dentistry. The use of polymeric materials accelerates and facilitates the treatment of patients. Polymeric materials are used in the production of implants and limb prostheses, as well as devices for drug administration. In bone implantology, they also occur as materials that crosslink in situ, injected to fill cavities.

The most common polymers used in medicine are:
- polyethylene (PE), used to produce disposable gloves, syringes, containers, plasters, orthopedic external prostheses, and parts of endoprostheses [2].
- polystyrene (PS), used to obtain dressing materials, disposable dishes, Petri dishes, tissue culture containers, pipettes, flasks, and jaw prostheses [6].
– polyesters, which have been used to obtain sterile trays, surgical and dental instruments, scalpel blade holders, syringe components, cannulas, surgical threads, tendon prostheses, artificial bone, and dressing materials [7],
– polyvinyl chloride (PVC), from which blood collection and transfusion sets, drips, blisters, mouthpieces, speculums, fluid transport tubes and oxygen masks are obtained [6],
– polycarbonates (PC), which have been used to obtain medical equipment, glucometers, separators, dialyzer covers, insulin pumps and pens [8],
– poly(methyl methacrylate) (PMMA) is used to obtain dressing materials, contact lenses, and hip joint prostheses [9, 10],
– ultra-high molecular weight polyethylene (UHMWPE) the most used material in tendon and ligament prostheses is ultra-high molecular weight polyethylene [11],
– poly(tetrafluoroethylene) (PTFE), which has been used to obtain cardiac surgical catheters, artificial heart valves, elements of artificial kidneys and vascular prostheses [12]
– polyurethanes (PUR), which have been used to obtain elements of artificial heart valves, surgical threads, drains, elastic and stiffening bands, and urological coils [13],
– polyamides (PA), which are often used to obtain: dental products, sterilization containers and surgical threads [14].

Due to the contact of polymeric materials with the patient’s body, they must meet several requirements: they should retain their physicochemical properties despite the action of high temperature, detergents, X-rays or aseptic. Polymers, like most materials, may degrade after some time of use, which is why it is also important that their decomposition products do not cause inflammation, allergic, immunological reactions, or any other interactions with the body in patients [15]. Figure 1 presents selected areas of application of polymeric materials in relation to the patient’s body.

In recent years, biodegradable polymers have played a key role in medical applications. The most used biodegradable polymers in medicine [16] are:
– poly(lactic acid) (PLA), used to obtain surgical sutures, stents, and vascular grafts as well as plates for craniofacial anastomoses.
– poly(glycolic acid) (PGA), used to produce devices implanted in the body: plates, rods, screws. In tissue engineering, it is used as bone implants and in controlled drug delivery,
– poly-(β-hydroxybutyrate) (PHB), used to obtain surgical sutures, rivets, adhesive barriers, skin substitutes, dressings and surgical meshes.

In recent years, we have seen a dynamic development of the use of polymeric materials in rapid prototyping technologies, in the material extrusion method, where they are introduced into 3D printers in the form of a filament. As mentioned, details made of basic, unmodified materials are most often used as conceptual prototypes, because polymers do not provide adequate functionality, necessary mechanical and usable strength of details. For this reason, it is necessary to intensify research on the modification of polymeric materials used so far. We are seeing great progress in the development of hybrid polymer composites, which, thanks to improved performance properties, can be successfully used to obtain functional models using additive manufacturing techniques. The production of 3D printing fibers is usually done using physical modification. Several types of auxiliary agents are introduced into the polymer matrix, and after the homogenization process, the material is extruded in the form of a filament of a specific diameter. The most used auxiliary agents for thermoplastics are fillers, plasticizers, stabilizers, dyes, pigments, release agents, lubricants, flame retardants, antistatic agents. Occasionally, e.g., fragrances, biostabilizers are used.

Currently, in the rapid prototyping technology, modification of polymers most often leads to the creation of polymer composites or nanocomposites when the introduced dispersed component has at least one dimension in the nanometric scale. Polymer composites are created by introducing inorganic and organic particles or hybrid systems, e.g., inorganic-organic.

Many inexpensive, inorganic fillers are widely used for thermoplastics, including:
– silica, which among the commonly available additives is often used due to many advantages: high chemi-
Keywords: polymeric composites, additive manufacturing, 3D printing, PLA, silica, hydroxyapatite, bentonite

Introduction

The use of polymeric composites in medicine is based on the incorporation of natural and mineral fillers into thermoplastic polymers. The addition of fillers improves the mechanical properties of the composite, such as modulus of elasticity and tensile strength [17]. Clay minerals are used due to their uncomplicated processing. Bentonite is a naturally occurring clay mineral with small particle sizes and a high level of plasticity [18]. Studies have shown that the addition of an additive to the polymer matrix strengthens the thermal and mechanical properties of the composite, such as tensile strength, elongation, and hardness [19, 20]. Hydroxyapatite (HAp) is commonly used in medicine, among others, as a drug carrier for bone tissue to treat inflammation or postoperative complications [21, 22].

In summary, the modification of the properties of thermoplastic polymers for 3D printing applications consists in introducing a single filler into the polymer matrix. The introduction of one type of additive into the polymer matrix does not guarantee the desired results, because it is difficult due to the single function and structure of the fillers when used alone. For this reason, hybrid systems work best, i.e., those built with more than one additive to achieve a more complex filling system. The combination of many advantages of 3D printing with above-average properties of the materials obtained in this way will ensure a completely new quality of additive manufacturing of parts.

The aim of the work was to develop PLA composites with selected fillers (colloidal silica, hydroxyapatite, bentonite) with improved performance properties and good dimensional stability, used to obtain anatomical structures by 3D printing with the use of the molten polymer deposition method.

EXPERIMENTAL PART

Materials

Polylactide (PLA, Natural, ColorFabb, Belfield, Netherlands), colloidal silica (SiO₂, Aerosil COK84, Evonic Industries, Hanau, Germany), hydroxyapatite (Sigma Aldrich, Germany), bentonite “Specjal” (Zakłady Górniczo Metalowe “ZĘBIEC” SA, Starachowice, Poland), polyethylene grafted with maleic anhydride (PE-g-MAH, Fusabond E226, DuPont, Wilmington, DE, USA) were used as raw materials.

Preparation of composites and samples for testing

The compositions of PLA-based composites are listed in Table 1. Before melt mixing PLA, silica, hydroxyapatite, and bentonite were dried in a vacuum dryer at 60°C for 6 hours. Then, all components were homogenized using a Coperion ZSK 18DL (Germany) twin-screw extruder equipped with a granulation line. The process was carried out at a temperature of 180–210°C, with a screw speed of 400 rpm and output of 4 kg/h. The composites were dried in a vacuum drier at 60°C for 4 hours. Filaments with a diameter of approx. 1.75 ± 0.05 cm were made on the Gamart line for obtaining filaments in the temperature range of 175–190°C, screw speed of 120 rpm, extrusion speed of 120 mm/s and winding speed of 85 mm/s.

Samples for testing (Fig. 2) were obtained on a TierTime Up Box+ printer (Beijing, China), working in the technology of extruding polymers from the melt. The process was conducted using a nozzle with a diameter of 0.4 mm at a temperature of 210°C and a printing speed of 60 mm/s. The working table temperature was 60°C.
the layer height was 0.2 mm, the infill was 100%, and the infill pattern was a straight line ± 45°.

**Methods**

Tensile properties were measured using an Instron 5967 universal testing machine (UK) according to ISO 527, at ambient temperature. The crosshead speed was 5 mm/min (to obtain 1% of the tensile stress), and then the speed was increased to 50 mm/min. The gage length was 50 mm. For each series, five measurements were made. Rockwell hardness was measured using a Zwick/Roell hardness tester at ambient temperature. For each batch, ten determinations were conducted in accordance with ISO 6508. Charpy impact tests were determined using the PSW Gehrad Zorn impact tester. All tests were conducted at room temperature in accordance with ISO 179. For each series, five measurements were made.

**Determination of shrinkage of fittings after printing**

The obtained linear shrinkage after printing was determined by measuring the length of the bar 24 hours after printing and calculating according to the formula.

$$S_L = \frac{(L_f - L_w)}{L_f} \cdot 100$$  \hspace{1cm} (1)

Where: $L_f$ – beam length dimension in accordance with the design shown in Fig. 2, $L_w$ – dimension of the molding corresponding to $L_f$ 24 hours after printing and cooling to room temperature.

**RESULTS AND DISCUSSION**

The Rockwell hardness, Charpy impact strength, Young’s modulus, tensile strength, elongation at break and linear shrinkage are listed in Table 2. The addition of selected fillers significantly improves the mechanical properties of the obtained composites. The highest increase in hardness (19%) was observed for composites containing 10 wt% hydroxyapatite. Comparable results can be observed in the literature [23], where Person et al. obtained PLA with 5, 10, 15 and 20 wt% of hydroxyapatites. They also observed the influence of hydroxyapatite content on the increase in the hardness of the tested composites. However, in the case of PLA composites containing 10 wt% hydroxyapatite and 3 wt% bentonite, this parameter increased by 22% compared to unfilled PLA (Table 2). Such a significant increase in hardness is caused by the appropriate dispersion of the layered aluminosilicate (bentonite), which, as is known from the literature, improves the examined feature [24, 25].

In the case of Charpy impact tests, the best results were obtained for a composite containing 10 wt% silica, where the impact strength increased by 22% compared to PLA. These observations are consistent with other studies [26]. In the case of hybrid composites, the best results were obtained for the PLA with 10 wt% hydroxyapatite and 3 wt% bentonite, where the impact strength increased by 32% (Table 2). This effect can also be explained by the appropriate dispersion of bentonite plates, which, as mentioned, was also observed by other researchers [24, 25].

The highest value of Young’s modulus was obtained for composites containing hydroxyapatite, both in hybrid composites and in composites containing only this filler. The increase in this parameter ranged from 6 to 12% compared to unfilled PLA (Table 2). Other researchers obtained similar observations [27]. The best results of tensile strength were obtained for composites containing one filler (hydroxyapatite or bentonite), where the improvement of this parameter is by 19 and 20%, respectively. In the case of hybrid composites, the best results were obtained for K11 and K12 composites (K11 by 37% and K12 by 32%).

Moreover, it was observed that the addition of all fillers resulted in a decrease in elongation at break from 4.8% for PLA to even 2.4% for K11 (Table 2). This phenomenon can be explained by the decrease in PLA flexibility with increasing filler content [28].

The calculated and determined linear shrinkage for printed moldings in the form of bars significantly depends on the type of filler and its concentration in the composite (Table 2). The most favorable results were obtained for the hybrid composites K11, K13. Significant reduction of shrinkage will allow for better accuracy of printed human anatomy models.

**Anatomical structures obtained by 3D printing**

The anatomical structures were made using a developed modular manufacturing system based on the creation of a virtual model using CAD programs based on
Table 2. Mechanical properties of PLA-based composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rockwell hardness N/mm²</th>
<th>Charpy impact strength kJ/m²</th>
<th>Young’s modulus MPa</th>
<th>Tensile strength MPa</th>
<th>Elongation at break %</th>
<th>Linear shrinkage %</th>
</tr>
</thead>
<tbody>
<tr>
<td>K0</td>
<td>33.9 ± 1.1</td>
<td>6.6 ± 0.4</td>
<td>1459 ± 21</td>
<td>32.3 ± 1.8</td>
<td>4.8 ± 0.3</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>K1</td>
<td>35.2 ± 1.2</td>
<td>7.1 ± 0.3</td>
<td>1483 ± 20</td>
<td>34.1 ± 1.4</td>
<td>3.4 ± 0.2</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>K2</td>
<td>36.8 ± 0.9</td>
<td>7.7 ± 0.4</td>
<td>1494 ± 18</td>
<td>36.4 ± 1.1</td>
<td>3.1 ± 0.3</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>K3</td>
<td>37.4 ± 1.1</td>
<td>8.1 ± 0.4</td>
<td>1532 ± 22</td>
<td>37.9 ± 1.2</td>
<td>2.5 ± 0.3</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>K4</td>
<td>37.1 ± 0.6</td>
<td>7.3 ± 0.3</td>
<td>1486 ± 23</td>
<td>34.3 ± 1.9</td>
<td>2.9 ± 0.3</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>K5</td>
<td>39.4 ± 0.7</td>
<td>7.8 ± 0.3</td>
<td>1495 ± 22</td>
<td>37.1 ± 1.6</td>
<td>2.4 ± 0.1</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>K6</td>
<td>40.3 ± 1.3</td>
<td>8.2 ± 0.2</td>
<td>1542 ± 22</td>
<td>38.6 ± 1.1</td>
<td>2.7 ± 0.2</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>K7</td>
<td>34.8 ± 0.9</td>
<td>7.6 ± 0.5</td>
<td>1487 ± 18</td>
<td>34.6 ± 0.9</td>
<td>3.5 ± 0.1</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>K8</td>
<td>36.2 ± 1.2</td>
<td>7.9 ± 0.3</td>
<td>1501 ± 19</td>
<td>37.5 ± 1.1</td>
<td>3.1 ± 0.3</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>K9</td>
<td>37.7 ± 0.8</td>
<td>8.0 ± 0.4</td>
<td>1533 ± 16</td>
<td>39.0 ± 1.0</td>
<td>3.1 ± 0.4</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>K10</td>
<td>40.9 ± 0.8</td>
<td>8.1 ± 0.4</td>
<td>1562 ± 19</td>
<td>42.9 ± 0.8</td>
<td>2.7 ± 0.1</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>K11</td>
<td>40.7 ± 0.6</td>
<td>8.7 ± 0.6</td>
<td>1634 ± 19</td>
<td>44.4 ± 1.6</td>
<td>2.4 ± 0.3</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>K12</td>
<td>41.6 ± 0.9</td>
<td>8.2 ± 0.4</td>
<td>1602 ± 17</td>
<td>42.6 ± 1.7</td>
<td>2.7 ± 0.2</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>K13</td>
<td>38.9 ± 0.8</td>
<td>8.1 ± 0.3</td>
<td>1592 ± 18</td>
<td>41.9 ± 1.4</td>
<td>2.4 ± 0.2</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>K14</td>
<td>37.8 ± 1.1</td>
<td>8.2 ± 0.5</td>
<td>1598 ± 17</td>
<td>42.1 ± 1.6</td>
<td>2.5 ± 0.3</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>K15</td>
<td>38.2 ± 0.8</td>
<td>8.1 ± 0.4</td>
<td>1595 ± 18</td>
<td>42.1 ± 1.8</td>
<td>2.5 ± 0.3</td>
<td>0.7 ± 0.1</td>
</tr>
</tbody>
</table>

Fig. 3. View of the CAD model developed based on a computed tomography (CT) study

Fig. 4. STL model of the anatomical structure

Fig. 5. Printed models of anatomical structures: a) structure with supports, b) structure with removed supports and other artifacts
computed tomography (CT) studies (Fig. 3). As a result, the developed system increases the precision and accuracy of obtaining the STL model of the anatomical structure, which fully reproduces the copied human anatomical structure (Fig. 4).

The obtained models of anatomical structures using the 3D printing method (Fig. 5) can be used for didactic classes for medical students, as well as for preoperative training by the surgeon, which will not only increase the precision of the procedure, but also the doctor’s comfort.

CONCLUSIONS

Currently, rapid prototyping techniques are used in many fields, e.g., in the aviation and automotive industries. In recent years, polymeric materials and 3D printing are also very often used in medicine, e.g., in the process of visualizing the geometry of anatomical structures and in the process of making surgical templates or implants [29]. Thanks to the homogenization process using a twin-screw extruder, a good dispersion of the fillers used in the polymer matrix was obtained. As a result of these treatments, composites in the form of filaments were obtained without any technological complications. The introduction of selected fillers into the PLA polymer matrix resulted in an increase in the Rockwell hardness of the composites obtained by 3D printing. The best results were obtained for composites containing 10 wt% hydroxyapatite.

The improvement in Young’s modulus and breaking stress was observed for K11 composite shapes containing a hybrid system of fillers (10 wt% hydroxyapatite and 3 wt% bentonite). The development of new polymer materials based on PLA containing a hybrid addition of fillers (hydroxyapatite, bentonite, and silica) used for 3D printing allowed for more accurate shaping of the structure and better dimensional stability of the printed anatomical models and avoiding adverse phenomena resulting from the physicochemical properties of polymers, such as warping and shrinkage. Such properties of polymer composites will allow for better precision of the 3D printing technology used and the quality of the obtained anatomical structure.

ACKNOWLEDGMENT

Many thanks to the Dean of the Faculty of Chemistry, Prof. dr hab. Eng. Dorota Antos for making it possible to complete a scientific internship at the Department of Polymer Composite.

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https://doi.org/10.1016/j.jare.2018.05.001


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