3D PRINTING AND BIODEGRADABLE POLYMERS

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ABSTRACT

3D printing technology has a wide range of applications in many industries, including automotive, aerospace, biomedical, electronics and packaging, requiring different types of filaments to be used in producing 3D printed objects. The most commonly used materials are metals, ceramics, composites and plastics of which the latter are most available. Since it is necessary to reduce pollution caused by waste from conventional petroleum-based plastics, biodegradable polymers made from renewable resources or produced synthetically have gained in importance recently. Polylactic acid, poly(butylene succinate), thermoplastic starch, poly(butylene adipate co-terephthalate) and polycaprolactone are well-known representatives of this group of materials. They possess desirable properties for 3D printing which make them promising materials in many areas of applications.

Keywords: *biodegradable polymers, 3D printing, filaments, 3D printer*

1. INTRODUCTION

In recent decades, there has been significant development in various technologies which have become a very important part of everyday life. They can make our lives more comfortable, help greatly in various kinds of jobs or even save human lives. Additive manufacturing better known as 3D printing, belongs among these technologies [1].

Nowadays, a 3D printer is a common item of equipment in the majority of laboratories and companies involved in research and development of new technologies. They are used to produce components for various products [2] as well as for medical applications [3]. 3D printers are easy to control, and their price is relatively low so even small labs can afford to buy them.

This paper briefly describes 3D printing techniques, the most commonly used biodegradable polymers for 3D printing filaments and 3D printed electronics are presented, and the prospects for future research and development in this area are mentioned.

2. 3D PRINTING

The first concept of 3D printing was born in 1974. Ten years later, Charles W. Hull was granted a patent for the invention of a 3D printer [1]. In this printing process, 3D objects are created from digital files by printing layer upon layer. Nowadays, 3D printing is used in a wide range of applications, e.g. for producing artificial human body parts, making lightweight components in the aerospace and automotive industries, shaping foods in the food industry, creating clothes and shoes in the fashion industry and producing complicated structures in the electronic industries [1].

In general, a 3D printer consists of four fundamental parts: print bed, extruder, controller board and filament. The print bed is usually a plain, smooth surface on which the extruder arranges the filament to form layers and creates objects. The choice of print bed material depends on the used filament material. The most commonly used materials for the print bed are aluminium and glass. The role of the extruder is to heat the filament and when it is melted to deposit the melted material on the print bed through the extruder nozzle. The filament is of cylindrical shape with diameter 1.75 mm or 3 mm and consists of the material required for printing the 3D objects. The printing process is controlled by the controller board [2].

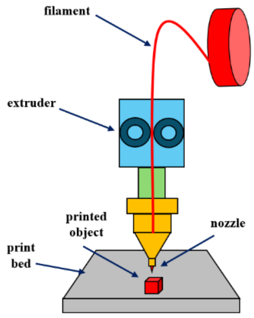


Fig. 1 Scheme of 3D printer [4]

2.1. Materials for 3D printing

Since 3D printing is used in many different applications, materials for filaments also differ and they include metals, ceramics, polymers, composites and special materials like foods or textiles.

2.1.1. Metal 3D printing filaments

Metal 3D printed objects are used in the manufacturing, automobile and aerospace industries, and in medical applications. Metal materials have excellent physical properties which are required for aerospace parts as well as in biomedical applications. Gold, copper, niobium, tantalum and titanium are used in their pure form. Metal alloys are used more frequently than pure metals, because of their enhanced properties. The most frequently used materials are aluminium, titanium, nickel, and cobalt-based alloys, as well as stainless steel. Cobalt-based alloys are suitable for dental applications due to their high malleability, high specific stiffness, ductility and conditions of thermal treatment. Titanium alloys have been used in biomedical applications for 80 years, so using these materials for 3D printing can enhance their utilization. Nickel-based alloys have high corrosion resistance and are temperature resistant up to 1200 °C. These extreme properties are ideal for using them in 3D printed objects (sheets, tools etc.) for aerospace applications [2, 5].

2.1.2. Ceramic 3D printing filaments

Ceramic 3D printing is very popular in the energy, biomedical, automotive, aerospace and electronics industries. Ceramic materials consist of inorganic, non-metallic substances. Typical properties of ceramic materials are heat resistance, hardness, chemical inertness and wear resistance. For this reason they are used for 3D printing of components for thermal insulation, electronics and biomedical implants [4].

2.1.3. Composite 3D printing filaments

Composite materials for 3D printing are usually used in applications which require special properties like high strength, stiffness, durability and heat resistance. In general, composite material consists of at least two materials with significantly different chemical or physical properties. The resulting materials have different properties compared to their components. The composite matrix forms a continuous phase in which reinforcement is dispersed. The most commonly used material for the matrix is poly(acrylonitrile-butadiene-styrene) (ABS) and carbon fibres, fiberglass and Kevlar are often used as reinforcement. Nowadays, composite 3D printing materials are widely used in the automobile industry, because their specific mass (weight) can be lower than that of aluminium or its alloys and they can have higher tensile strength [6].

2.1.4. Polymer 3D printing filaments

Polymers are the most widely used materials for 3D printing, because of their adaptability, durability and low price. Polymers are organic materials with an almost unlimited range of applications, which makes them an inherent part of our lives. They are used in producing a large variety of everyday products. The availability of polymers makes them great materials for 3D printing. Commercially available polymers for 3D printing are e.g. ABS, polycarbonate (PC), Nylon, poly (ether ester ketone) (PEEK) and polyetherimide (ULTEM). In biomedical engineering, polymer filaments are used in 3D printing to fabricate substitutes for e.g. bones, teeth, cartilage, organs and skin. For regenerative medicine, 3D printed prostheses and scaffolds with specific geometry are very important. These scaffolds are implanted into the patient’s body, and they serve as a basis for tissue to regenerate. During regeneration these scaffolds degrade, and they are absorbed by the patient’s body. 3D printing is often used in dental medicine. Dentists can print dental implants, crowns, braces, or aligners and easily replace a missing tooth. The most frequently used filaments are made of polylactic acid (PLA), polyglycolide, polycaprolactone and acrylates. The electronics industry forms another vast field of applications for polymer 3D printing. Polymer filaments are used to print e.g. keyboards, electronic skin patches, antennas, biochips, and other components for flexible electronics. ABS and PLA are the most typically used materials in electronics [3, 8-10].

3. BIODEGRADABLE POLYMERS

Conventional plastic materials produced from oil have numerous advantageous properties; however, their big disadvantage is environmental pollution. There is an effort to use recycled materials for 3D printing, e.g. polyethylene terephthalate (PET) [11]; however, in general only a small percentage of plastic waste is recycled in this way. The solution may lie in using biodegradable polymers for 3D printing in a larger extent.

Polymers are macromolecules consisting of repeating units called monomers. They can be found in living organisms (human, animal bodies and plants) as well as in the plastic products we use every day (e.g. packaging foils, components of vehicles and buildings, electronic devices). After their lifetime these products became plastic waste with degradation taking hundreds of years, which makes sustainable development of society rather difficult [12].

In contrast, biodegradable polymers are environmentally friendly since they decompose into natural byproducts (organic and inorganic) in a relatively short time. Applications of these polymers include three major areas: medicine (surgical implants, implantable matrices for controlled drug release, and adsorbable surgical sutures), agriculture (mulch foils, which can serve as fertiliser at the end of their life), and goods packaging [13].

3.1. Origin of biodegradable polymers

According to their origin, biodegradable polymers can be divided into two categories: natural polymers and synthetic polymers. Natural polymers are obtained from natural renewable resources. Synthetic polymers are usually made from oil [14].

3.1.1. Natural biodegradable polymers

Typical natural biodegradable polymers are collagen, chitosan, gelatine, alginate, lactose, starch, cellulose and pectin. They are components of animal and plant cells. Collagen is a protein which can be found in mammals. Chitosan is a polysaccharide which forms part of the hard exoskeletons of crabs and shrimps. Gelatine is a denaturized protein. Another polysaccharide is alginate, which is derived from brown seaweed. Lactose can be found in milk and is otherwise known as milk sugar. Starch can be obtained from a wide range of crops like potatoes, cereals, corn and fruits. Cellulose is water-insoluble polymer which is a part of herbivores food. Pectin obtained from fruit is used to form gels [14].

3.1.2. Synthetic biodegradable polymers

Synthetic biodegradable polymers include poly (glycolic acid) (PGA), PLA and poly(lactide-co-glycolide) (PLG), which belong in the polyester group. The other groups are polyanhydrides and polyorthoesters (POE). PGA is mostly used in resorbable sutures because its degradation product glycolic acid is a natural metabolite. PLA is used in orthopaedic fixation and sutures. PLG is currently used in the production of resorbable fixation devices. Polyanhydrides and POE are suitable for orthopaedic applications [15].

3.2. Biodegradation of polymers

Biodegradation is a chemical process, in which material degrades through the action of bacteria, algae or fungi. Natural polymers degrade by oxidation and hydrolysis in nature. In the case of synthetic polymers, the action of microorganisms is required. Depending on the absence or presence of oxygen, the biodegradation process can be considered as anaerobic or aerobic degradation respectively. In the case of aerobic degradation, the products of the reaction between polymer and oxygen are carbon dioxide, water, biomass, and some residues. The products of anaerobic degradation include carbon dioxide, methane, water, biomass, and some residues. Biodegradation of polymers is affected by their chemical structure, molecular weight, porosity and morphology [16].

3.3. Biodegradable polymers for 3D Printing

Efforts are being made to replace conventional plastics with biodegradable polymers in all areas of their application, even in 3D printing filaments. Biodegradable polymers for 3D printing involve PLA, poly (butylene succinate) (PBS), thermoplastic starch (TPS), poly (butylene adipate co-terephthalate) (PBAT), polycaprolactone (PCL) and poly lactic-co-glycolic acid (PLGA). Their properties and applications are listed in Tab.1.

4. BIODEGRADABLE 3D PRINTED ELECTRONICS

With increasing demand for electronics, there has been an effort to speed-up production of electronic devices. Typical materials used for printed electronics are metals possessing good electrical conductivity. The main disadvantage of using metals for printed electronics is the increase in production of electronic waste or e-waste. For this reason, there is a need to develop and produce environmentally friendly electronics. One of the possible solutions lies in using biodegradable materials [25].

Printed electronics is a printing technology used to produce electronic devices. Production processes include 3D printing on substrate materials, which are plastic-based or organic. The most commonly used filaments consist of carbon-based compounds. In recent years, printed electronics includes sensors, thin film microstrips, actuators, biochips, electronic skin patches, antennas, electronic components, embedded circuits and keyboards. Producing electronics using 3D printing technology has a lot of advantages, e.g. less waste, lower startup costs, shorter lead times, flexibility in design and lower costs [26].

4.1. Printing technologies

Printing technologies used in the production of electronics can be divided into two main categories: contact and non-contact printing technologies. Contact printing techniques include screen, flexography and gravure printing. Screen printing is commonly used for high-volume production. Flexographic printing employs a polymer-based plate with raised surface patterns. Gravure printing can be used to produce high-quality electronic structures at lower speeds. Non-contact printing techniques include inkjet, aerosol jet printing and laser direct writing. Inkjet printing involves liquid materials or solid suspensions being used at lower pressures and temperatures. Aerosol jet printing is used to produce tiny features, e.g. sensors and antennas. Laser direct writing is used to make basic linear and complex electronic structures on a substrate [26].

4.2. Biodegradable printing materials

The main challenge currently is the development of biodegradable printed electronics. Printed electronic devices generally consist of a substrate and an ink. PLA, cellulose paper or silk belong among the materials suitable for biodegradable substrates. In general, an ink consists of four components: functional material dispersed in solvent (water, ethyl lactate, gellan, xantana), polymeric resin (e.g. cellulose acetate or shellac), and additives. The role of polymeric resin is to bind the ink. Additives are added to the ink to improve its properties. Based on the functional materials, inks for printed electronics can be divided into conductive, dielectric and piezoelectric inks. [25].

Conductive inks can be based on conductive biodegradable polymer. There have been some research projects in which a low quantity poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate) (PEDOT: PSS) was used to produce biodegradable ink using appropriate biodegradable polymer resin [27]. Inks based on PEDOT:biopolymer exhibit conductivities up to 700 S/m [28].

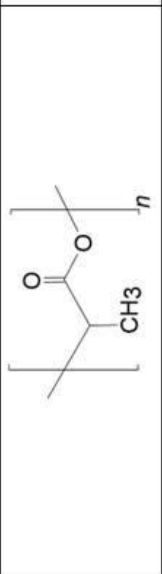
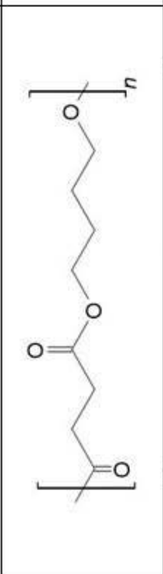
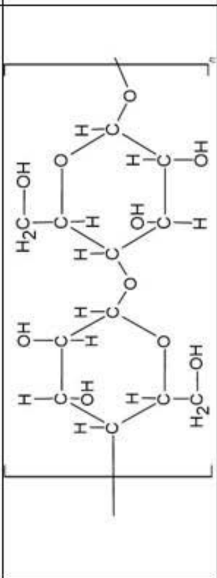
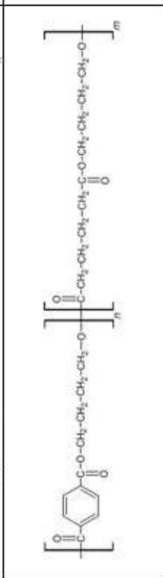
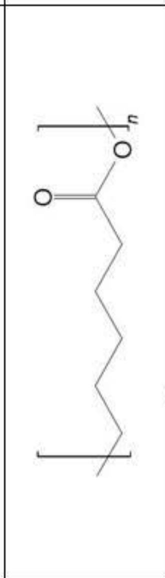
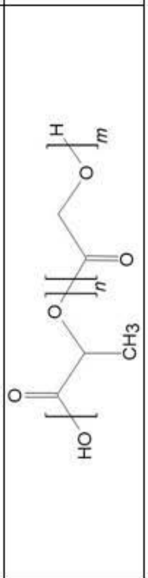
A wide range of biodegradable polymers can be used for dielectric inks from both natural and synthetically made polymers. Glucose, cellulose, lactose and adenine are good candidates for these inks because of their high voltage breakdown and low dielectric loss. PLA, polyvinyl alcohol (PVA), poly (dimethyl siloxane) (PDMS) and polyurethane (PU) have also been used in dielectric inks [25].

There is only a small number of natural biodegradable polymers with piezoelectric properties. The most important among them are chitosan, silk and collagen with sensibility of 4 pC/N, 1 pC/N and 2.64 pC/N respectively. PVA and amino acids also possess piezoelectric properties [25].

4.3. 3D printed electronic devices

Development of biodegradable 3D printing materials is still a challenge. However, scientists from Switzerland have successfully made the first 3D printed supercapacitor from biodegradable materials [29]. Nanocellulose, glycerol and water were used as substrate, plasticizer and solvent respectively. The resulting device was folded from two parts each consisting of electrode, current collector and electrolyte layers. Its final thickness was 1.5 mm and footprint area were 2.25 cm^2. The ink used to print the current collector was made from shellac with dispersed carbon-black particles, while the electrode ink consisted of nanocellulose, water, graphite and activated carbon. The electrolyte ink was made from NaCl, glycerol and nanocellulose. This 3D printed supercapacitor exhibited cycle stability and could operate in a wide range of temperatures. Its working voltage was 1.2 V and it was resistant to large mechanical stresses. This device is proof that biodegradable 3D printed electronics is not only wishful thinking but already reality even if it requires a lot of additional research and effort to replace traditional electronics with the biodegradable type [29].

Table 1 Biodegradable polymers for 3D printing, their chemical structure, properties and applications

	Category	Chemical structure	Properties	Applications	References
PLA	aliphatic polyester		melting point = 180 °C glass transition temperature = 55 °C high strength good biocompatibility non-toxic	scaffolds, membranes, implants packaging materials clothing water bottles, containers electrical, electronic and automotive industry	[17]
PBS	aliphatic polyester		semi-crystalline thermoplastic chemically resistant thermally stabile very good processability in melted state low melting point (less than 120 °C)	scaffolds packaging	[18, 19]
TPS	natural polymer		embrittlement weak hydrophobicity poor mechanical properties low price	blended filaments with PLA matrix for composite filaments	[20]
PBAT	aromatic-aliphatic polyester		high molecular weight branched molecular structure good thermal stability high price mechanical properties like low density polyethylene	packing bags for organic waste compost bags mulch films	[21]
PCL	polyester		semicrystalline structure melting point about 60 °C good mechanical properties great elongation at break high flexibility antimicrobial properties	scaffolds for bone repair drug delivery	[22, 23]
PLGA	polyester		crystalline structure hydrophilic biocompatibility	scaffolds dentistry injectable microsphere	[24]

5. FUTURE OF 3D PRINTING

Nowadays, the ecological aspects of using everyday products are increasingly important, and environmentally friendly materials are desirable for their production. For this reason, biodegradable polymers are promising materials for a wide range of applications. Research of biodegradable materials is still very topical and the efforts to develop materials with even better properties persist. Preparation of nanocomposites with matrices made from biodegradable polymers enables even better properties of the resulting materials to be achieved. The other possibility is blending two or more biodegradable polymers [24].

Biodegradable polymers from renewable resources (e.g. gelatine, chitin, chitosan, and starch) are prospective materials in 3D printing due to their biodegradability and relatively low price. In future it is expected that filaments with tailor-made properties could be prepared from composite materials with matrices made from biodegradable polymers and various types of nanofillers [24, 30, 31].

Low price, wide availability, biodegradability, biocompatibility and the possibility of adjusting material properties are only a few of the advantages of biodegradable polymer materials which make them prospective materials for 3D printing filaments.

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Received June 3, 2024, accepted July 8, 2024

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Mária Kovaľaková graduated from the Faculty of Science, University of Pavol Jozef Šafárik in Košice in 1982. She defended her PhD in the field of physics in 1999 at the Katholieke Universiteit in Leuven, Belgium. Since 1982 she has been working at the Department of Physics, Faculty of Electrical Engineering and Informatics, Technical University of Košice, since 2013 as an associate professor. At present her scientific research is focused on the study of biodegradable polymer materials using techniques of nuclear magnetic resonance spectroscopy and other complementary methods.