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Thermoplastic elastomer filaments and their application in 3D printing

The paper provides an overview on the materials used in the 3D printing technology (the Polish and foreign market) with a particular focus on flexible filaments and their possible application in the industry. There are described the techniques of 3D printing and modern filaments available on the market. There is observed the increase of interest in the production of products from filaments based on thermoplastic elastomers (TPE), including the applications in the electronics and medicine, especially in tissue engineering. Ability to modify the physical and mechanical properties of thermoplastic elastomers, combined with their unique elastic and processability properties, opens new possibilities for engineers, designers and bio-engineers. The possibility to use new materials in 3D printing can contribute to faster development of research and accelerates implementation of innovative products.
Keywords: 3D printing, flexible filaments, thermoplastic elastomers (TPE), thermoplastic polyurethanes (TPU).

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Termoplastyczne włókna elastomerowe i ich zastosowanie w druku 3D

Praca stanowi przegląd dostępnych na rynku krajowym i zagranicznym materiałów używanych w technologii druku 3D. Szczególną uwagę poświęcono elastycznym włóknom (ang. *flexible filaments*) oraz ich potencjalnemu zastosowaniu w przemyśle. Przedstawiono i oceniono stosowane technologie druku 3D. Scharakteryzowano nowoczesne włókna kompozytowe, ich właściwości i zastosowanie. Opisano także najnowsze doniesienia literaturowe związane z otrzymywaniem nowoczesnych termoplastycznych elastomerów (TPE) do wykorzystania w technologii druku 3D. Na podstawie przeanalizowanych publikacji zauważono ogromny wzrost zainteresowania wykorzystaniem termoplastycznych poliuretanów (TPU) w przemyśle elektronicznym, medycznym oraz obuwniczym. Dostępne na rynku nowoczesne produkty wykonane przy użyciu drukarek 3D z wykorzystaniem TPU, potwierdzają te doniesienia. Interesujące jest wykorzystanie wodnych dyspersji TPU z możliwą kontrolą bioaktywności do zastosowań w inżynierii tkankowej. Dodatek do wodnych dyspersji TPU, biopolimerów lub poli(tlenku etylenu) (PEO) powoduje znaczny wzrost ich lepkości. Pozwala to na użycie tego materiału w drukarkach 3D w technologii niskotemperaturowego drukowania (LFDM). Możliwość kontrolowanej zmiany właściwości fizycznych i mechanicznych, wyjątkowa elastyczność, trwałość oraz łatwość przetwórstwa termoplastycznych elastomerów otwierają nowe możliwości wykorzystania druku 3D. Dzięki temu technologia ta przestaje być narzędziem jedynie do prototypowania – umożliwia ona drukowanie materiałów gotowych do użytku na skalę przemysłową.
Słowa kluczowe: druk 3D, włókna elastyczne, elastomery termoplastyczne (TPE), termoplastyczne poliuretany (TPU).

1. Introduction

3D printing is a process that has revolutionized the manufacturing industry. This technology is available at our fingertips. It has been using not only by the military, research units or technology advanced companies but people at school or home as well. It is fascinating that nowadays with the only help of a computer and a printer you can quickly create your own idea, project in three dimensions. This technology has opened a new way for scientists, but also gave a tool to develop imagination and creative thinking for children and people who have not yet been involved in the field of science and technology.

The most important properties of 3D printing is its precision – it is possible to manufacture a whole new range of complicated objects using materials with the most diverse properties. Freedom of design, print speed, without wasting materials and the possibility of household makes this technology very welcome by all types of industries.

The main use of 3D printing in most types of industry appears to be a rapid prototyping (RP). There are several technologies using RP for various industrial applications. The major prototyping techniques are summarized in Table 1 [1, 2, 3]. Selective Laser Sintering (SLS) is based on a laser as the power source to sinter powders (thermoplastics, metal, ceramic, glass, alloys). Laser moves automatically sintering the points in space defined by software to form a solid three-dimensional model. Stereolithography (SLA) is based on curing by UV of photosensitive polymeric resins. Fused Deposition Modeling (FDM) machines work owing to a thin filament made from special thermoplastic polymers: through a heated nozzle layer by layer deposition of material creates a 3D object. In Laminated Object Manufacturing (LOM) the layered material (coated an adhesive layer) is rolled on the building platform. The feeding roller heats in order to melt the adhesive. Laser is used to draw the geometry of the object. Three-dimensional printing (3DP) is based on layered powder materials. The process begins with a specific application of the powder layer from the tray. This layer is aligned on the work surface platform using the roller. On the thus prepared powder layer, adhesive is applied, according to a predetermined cross-sectional block. PolyJet (JS) technology is similar to FDM, except that the head is sprayed on the worktable liquid photopolymer that is curable with UV lamps. According to [1], 3D printing processes may be divided into three stages: "Image acquisition", "Image post-processing" and described above "3D printing". In our opinion it should be add a stage of "Material selection".

This paper provides an overview of available filaments on the Polish and foreign markets, as well as an overview of the latest reports associated with the flexible filaments.

Table 1. Overview of chosen rapid prototyping techniques
Tabela 1. Przegląd wybranych technik szybkiego prototypowania

RP technology	Accuracy print/ price	Recommended filaments type	Advantages	Disadvantages	Application
SLS (Selective Laser Sintering)	++	thermoplastic elastomers, composite, glass, metals, alloys – powders	dimensional accuracy, surface finish, variety of materials, large workspace	price, speed, surface roughness	architecture, medicine, automotive, aerospace, mechanical engineering, castings, military,
SLA (Stereolithography)	+++	photocurable resin	high dimensional accuracy, very good surface finish, large workspace,high repeatability of products	price, not so resistant to UV	architecture, medicine, archeology, aerospace, automotive, mechanical engineering
LOM (Laminated Object Manufacturing)	+	adhesive-coated polymer, paper, cellulose, metal sheets	price, speed, dimensional accuracy	a small amount of material available, surface roughness	castings, mechanical parts prototypes
3DP (Three Dimensional Printing)	++	elastomers, composites, metals, ceramics – powders	speed, colour, price	average surface quality	finite element analysis, architecture, castings
JS (PolyJet)	+++	photocurable resin	high accuracy and dimensional tolerance, speed	a small amount of material available	electrical engineering, automotive, aerospace
FDM (Fused Deposition Modeling)	++	thermoplastic, elastomers, composite	price, a large number of filaments available	speed, average surface quality	architecture, domestics use products, (tools, toys, jewelry), medicine, automotive, electronics

(+) – rating of rapid prototyping techniques

2. Filament materials

Material (filament) selection defines not only the properties or the use of printed detail, but also points to the possible use of 3D printing technology. Therefore, the selection of suitable material into the prepared project seems so important. The most common filament dimensions are 1.75 mm and 3.0 mm. Less commonly available filaments are sized as 2.85 or 2.9 mm. In recent years, the number of filament manufacturers in Poland and in the world has increased enormously. Examples of polymer filaments currently produced by Polish companies, are shown in Table 2.

As we can see from the Table 2 thermoplastic elastomers find their place as well in this modern material processing. 3D printing technology with the largest number of available materials is definitely FDM. This is due to the relatively lowest price of the printers based on FDM technology and the possibility of use the thermoplastic polymer or thermoplastic elastomers. They are inexpensive, easy to process and could serve as matrix enabling creation of diverse composites. In Poland, the vast majority of 3D printing materials manufacturers dedicates their products to FDM technology. Standard filaments are mostly thermoplastics. Support filaments are present in the market as well. They are applied in case to obtain very complicated shapes after dissolving support material (e.g. PVA) in water or mechanically removing support made of HIPS. Behind the filament type specified as flexible lies a group of thermoplastic elastomers (TPE). TPE include the entire mass of the block copolymers or mixtures of rubbers with thermoplastics. Manufacturers reserve the information on the composition of the various flexible blends. Flexible filaments are commercially available under the trade names: Poro-Lay series, NinjaFlex, UniFlex, FlexiFil. The most extensive group for 3D printing are composite filaments. Due to the simplicity of preparation of the new blends based on a polymeric matrix, day by day increases number of new composite filaments. By making new polymer composite filaments we can print the products imitating wood or metal alloys, conductive products, materials having antibacterial properties, or being biodegradable. Table 3 provides an overview along with a description of available modern composite filaments.

From Table 3 it is clear that it is still an open market for over working polymer composites with thermoplastic elastomers.

Table 2. Examples of polymer filaments currently produced by Polish companies
Tabela 2. Przykłady włókien polimerowych do druku 3D produkowanych przez polskie firmy

Type of filaments	Material	Recommended extrusion temperatures [°C]	Polish producers	Available diameters [mm]
Standard filaments	Acrylonitrile-butadiene-styrene copolymer (ABS)	200–245	3D Universal	1.75
		235–255	Devil Design	1.75
		220–240	Rico-3D	1.75
		220–250	Spectrum Filaments	1.75, 3.00
		230–270	Plast-Spaw Wolfix	1.75
		no information	3D Vario	1.75, 3.00
		200–240	GumaPlast	1.75
	Poly(lactic acid) (PLA)	200–220	Fiberology	1.75
		190–205	Devil Design	1.75
		190–210	Rico-3D	1.75
		190–210	Spectrum Filaments	1.75, 3.00
		190–230	GumaPlast	1.75, 3.00
		200–220	Noctuo	1.75
		190–210	3D-Vario	1.75
		185–225	Plast-Spraw Wolfix	1.75
	Polyethylene terephthalate (PET)	220–260	GumaPlast	1.75
		200–220	3D Universal	1.75
		220–240	Rico-3D	1.75
		230–255	Spectrum Filaments	1.75
		230–240	Devil Design	1.75
	Polyamide (PA)	240–270	3D Universal	1.75
		245–255	Noctuo	1.75
Flexible filaments	Thermoplastic elastomers (TPE*)	220–250	3D Universal	1.75
		225–255	Spectrum Filaments	1.75
	Thermoplastic polyurethane (TPU)	190–205	Devil Design	1.75
Support filaments	Poly(vinyl alcohol) (PVA)	200–230	Spectrum Filaments	1.75
	High Impact polystyrene (HIPS)	200–230	3D Universal	1.75
		235–250	Devil Design	1.75
		200–235	Spectrum Filaments	1.75
Other filaments	Polycarbonate - acrylonitrile-butadiene-styrene copolymer (PC-ABS)	230–245	3D Universal	1.75
	Poly(methyl methacrylate) (PMMA)	240–255	Spectrum Filaments	1.75
	Poly(lactic acid) (PLA)	200–220	Fiberology	1.75

* no particular information from the producer

Table 3. Chosen examples of modern composite filaments
Tabela 3. Wybrane przykłady nowoczesnych włókien (filamentów) kompozytowych

Type of filaments	Material	Trade name	Country	Manufacturers	Properties (draw from data sheets)	Application
Composite filaments	PLA + carbon fiber	Carbon Fiber Reinforced PLA	USA	Proto-pasta	The addition of carbon fibers to PLA results in an increased stiffness and strength. The carbon fiber in the filament is specifically designed to be small enough to fit through the nozzles, but long enough to provide the extra values.	tools, toys, mechanical parts prototype
	PLA + graphene	Conductive Graphene Filament	USA	Graphene 3D Lab	It is a compound of PLA-based and graphene-enhanced. It has similar properties to normal PLA filament but it also has high electrical conductivity.	capacitive touch sensors, conductive paths
	PLA + PHA + bronze/ cooper/brass powder	Fill Series	The Netherlands	ColorFabb	The materials are combined with PLA and other materials (usually in powder form). The metal such as cooper is able to be polished to give it a nice, realistic looking shine.	jewelry, artistic pieces
	PLA + antimicrobial agent	Purement	Korea	BnK	Antibacterial filament. According to company studies, Purement has been proven to eliminate 99% of staphylococcus aureus and colon bacillus bacteria in laboratory tests. BnK took standard PLA and blended it with “inorganic antibacterial ingredients”. Processing properties are very similar to PLA filament.	kitchen tools, education materials, toys, medical equipment
	PLA + carbon black	Conductive PLA	USA	Proto-pasta	It is consists of Natureworks 4043D PLA and carbon black. Properties similar to PLA filaments (including more flexible and less layer adhesion than PLA). Volume resistivity of 3D printed parts: perpendicular to layers 30 [Ω·cm], along Z axis 115 [Ω·cm].	low-voltage circuitry touch sensor projects,
	ABS + bio-add	Enviro	USA	3D PrintLife	It is a blend of PLA and bio-additive which enhances interaction with ABS. Filament is biodegradable, but only surrounded by high concentration of bacteria and suitable temperature (compostable conditions).	packaging industry

3. Commercial products based on thermoplastics elastomer and 3D printing techniques

Relatively recently there has been interest in thermoplastic elastomers as materials for filaments in the 3D printing technology. World leaders producing filaments churn out more and more of the filaments described as flexible, rubbers, elastomer, and so on. Most of them belong to the group of TPU (thermoplastic polyurethane). Table 4 describes a review of selected commercially available flexible filaments. All available filaments are characterized by similar properties: high flexibility, elongation, durability, strong layer bonding, chemical resistance. There is observed the high industry interest to use those types of filaments. Described below are examples of the systems for dry EEG electrodes – made by Cognionics and the design of modern New Balance sports shoes. Cognionics (USA), a developer of wireless brain scanning systems is manufacturing flexible dry EEG electrodes (Fig. 1). Dry ECG and EEG systems have been long an area of active research and development. EEG usually is based on conductive gels and adhesives that is connected with a whole range of sensors which are attached to the human head [4]. Filaments based on thermoplastic elastomer, and nylon, allow to obtain a product with the desired conductivity, flexibility and complex-cut shape by using 3D printing technology.

By using powder of DuraForm Flex TPU (which is a thermoplastic polyurethane), New Balance corporation created hight-flexible and durable new shoes (Fig. 2). 3D printing technology (SLS) helped designing a new type of midsole. There was thus obtained organically geometric midsole, designed by bio-mechanical engineers. The porous structure of midsole allows to use the minimal amount of raw material to prepare super light product, while properties of thermoplastic polyurethanes offer high flexibility, strength and resistance to abrasion. As a result it was created the innovative product with incredibly unique look, and high performance applications. Moreover, this concept allows to adapt the structure of the pores and their distribution to specific user profiles.

Table 4. A review of selected flexible filaments commercially available
Tabela 4. Przegląd wybranych elastycznych włókien do druku 3D dostępnych na rynku

Type of filaments	Material	Trade name	Recommended extrusion temperatures [°C]	Recommended 3D printing technology	Country	Manufacturers	Available diameters [mm]	Description
Flexible filaments	TPE+PVA	Poro-Lay series	220–240	FDM	Germany	Kai Parthy (inventor)	1.75, 3.00	It is a blend of two main components (elastomer+PVA); PVA as a water soluble polymer in contact with water disappear. The result is a new flexible micro-porous material.
	TPU	NINJA-FLEX	225–235	FDM, 3DP, SLS	USA	NinjaTek	1.75, 3.00	Made from a specially formulated thermoplastic polyurethane (TPU) material, this patented technology boasts a low-tack, easy-to-feed texture.
	TPU	Ultimaker TPU 95A	245–260	FDM,	The Netherlands	Ultimaker	2.90	Semi-flexible and chemical resistant filament with strong layer bonding
	TPU	TPU 92A-1	–	SLS	Belgium	Materialise	–	Thermoplastic polyurethane –strong, high-flexible and durable, sandy, granular look
	TPE+ nylon	PCTPE	230	FDM	USA	Taulman 3D	1.75, 2.85	Flexibility TPE with durability of nylon
	TPU	Dura-Form Flex TPU	–	SLS	USA	3D Systems	–	An elastomeric, thermoplastic polyurethane with high elongation and enhanced durability

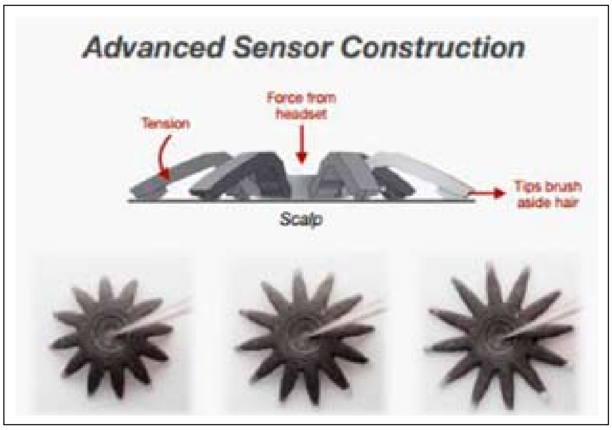

Fig. 1. Flexible dry EEG electrode made by Cognionics –[http://www.cognionics.com/index.php/products/sensors/flex]
Rys. 1. Elastyczne suche elektrody EEG wykonane przez Cognionics –[http://www.cognionics.com/index.php/products/sensors/flex]

Fig. 2. Midsole printed by New Balance (3D SLS technology) [https://www.newbalance.com/article?id=4041]
Rys. 2. Podeszwa wydrukowana przez firmę New Balance (technologia 3D SLS) [https://www.newbalance.com/article?id=4041]

4. Thermoplastic elastomers in 3D printing science world

Nowadays, subject "printing organs" like soft tissue [5], blood vessels [6]) is not shocking. A huge impact on the development of three-dimension printing biotechnology we owe to pharmaceutical companies and their search for new effective methods of testing drugs and the desire to reduce testing carried out on animals. As a result, 3D printing technology has also become a tool for orthopedics, dentistry, transplantology – not only for rapid prototyping, but as a method for producing ready-made implants, scaffolds or living tissues. Thermoplastic elastomers perfectly found their application in bioengineering and 3D printing industry. Conventional synthetic biodegradable polymers such as poly(glycolic acid) (PGA), poly(ε--caprolactone) (PCL), poly(lactic acid) (PLA) and natural polymers, for example: collagen, gelatin, alginate, hyaluronate, have been popular in biomedical industries [7]. It is because of their properties like: biodegradability, non-toxicity, bioactivity, durability or biocompatibility. While, the elastic properties of these materials are insufficient. So far the elastomers have not found particular use in tissue engineering – due to their long time biodegradibility and poor long-term biocompatibility [8]. However, their exceptional durability, thermal stability and suitable elastic property that perfectly matches tissue engineering, has prompted scientists to work on the modifications of that group of polymer materials.

One simple example of elastomers for medical use may be polyurethanes. Polyurethanes (PUs) are a large family of polymers with different chemistry [7] with a structure composed of hard and soft segments. Many publications and press reports [7, 8, 9, 10] indicate PU as the most popular synthetic biomedical polymers because of the excellent biocompatibility, tunable chemical structures, and good mechanical properties [9]. Unfortunately, use of PU in 3D printing technology is very limited and difficult. Currently on the market there are no PU filaments for use in tissue engineering. 3D printing technology is associated with a number of technological procedures which are exposed to the materials used. These processes could involve the use of heat, organic solvent, or cross-linkers that reduce the bioactivity of the ingredients. Therefore now the scientists are looking for new solutions that combine technology of 3D printing with modern materials having application in medicine and tissue engineering. The topic is still open for science.

Hung et al. [11] in their work has received dispersion of biodegradable PU elastomer for use in 3D printer to obtain compliant scaffold. The synthetic processes included mixed soft segments of poly-(ε-caprolactone) diol (PCL diol) and polyethylene butylene adipate diol (PEBA diol). The hard segment was created by isophoronediisocyanate (IPDI) and two chain extenders 2,2-bis(hydroxymethyl) propionic acid (DMPA) and ethylenediamine (EDA). They used thus obtained material for 3D printing technology with low-temperature fused deposition manufacturing (LFDM). This techniques include freeze drying (at –20; –30 °C). To allow printing of PU it was prepared aqueous solution of PU with sodium hyaluronate (HA). As a result they found that PU/HA scaffolds showed high flexibility and excellent recovery capacity after compression. They also examined the application of obtained flexible scaffolds for cartilage regeneration [11].

The same research team under the leadership of Hung [12] has synthesized another flexible material based on polyurethane. Using similar technology like in [11], they obtained water-based elastic and biodegradable PU nanoparticles which were used to fabricate scaffolds by 3D printing. To enable the printing they used poly(ethylene oxide) (PEO) as a viscosity enhancer. The scaffolds were seeded with chondrocytes. Chondrocytes in 3D-printed PU scaffolds had excellent seeding efficiency, proliferation and matrix production.

These studies confirm that the use of modern polyurethane elastomer (PU/HA) or (PU/PEO) and 3D printing technology (FLDM) has the real potential for use in customized tissue engineering. The enormous advantages of the applied technology are primarily:

- dimensional accuracy,
- printing of high viscosity materials,
- speed process,
- the ability to print a single item at a reasonable price, without the need to run specialized production line,
- ability to control changes of print parameters at any point in the process.

Thermoplastic elastomers with 3D printing, may also find application to print electronic devices. Li et al. [13] has considered the use of PU as electrically conductive adhesives (ECA) in next-generation flexible electronics. These devices need to have excellent mechanical robustness and electrical interconnectivity during mechanical deformation. Their application involves flexible displays, conformal antennas, thin-film transistors, sensors arrays, electronic solar-cell arrays, and flexible energy-storage devices [13]. PU-based flexible ECA demonstrates many advantages like: simple and cost-effective processing, eliminating the use of any expensive silver nanoparticles or additives, high electrical conductivity and environmental friendliness. The material obtained had resistivity about $1.0 \cdot 10^{-5}$ Ω·cm. Material having such properties may be used to construct and combine very flexible, efficient, with a complicated shapes and build LED chips, sensors and other electronics, which are obtained by 3D Injet printing.

The invention of Jinneng X. and Jun Z., [14] confirms the special properties of the elastomer filaments and the possibility of their use in 3D printing technology FDM. They patented filament consisting of: 10–90% of TPE (thermoplastic polyurethane elastomer), 3–10% of TPU (thermoplastic polyurethane), 10–90% of PLA – poly(lactic acid), 2–10% of PHA (polyhydroxybutyric acid) and 1–2% of compatibilizer. Material (soft-elastics elastomer) has high elasticity, strength, is environmental-friendly and non-toxic, has excellent processability and does not need vulcanization. The filament could be applied as a novel material for home-use in FDM 3D printing technology.

5. Summary

In these article we showed that, there is a lot of possible application for details made with thermoplastic elastomers and 3D printers. Flexible filaments (soft-elastics elastomers), in conjunction with the FDM 3D printing technique, become a tool for home use: products for baby, clothes accessories, bathroom accessories, handle encapsulation, or rapid prototyping [15]. Moreover, flexible composition based on thermoplastic polyurethane TPU), has found their applications in medicine or electronics. The possibility of a controlled material properties of TPU as well as adapting to the various techniques of 3D printing (SLS, FLDM, SLA, LOM, InJet, etc.) is a very important factor [16] for farther development.

The offer in Polish market is based on standard filaments and is rather poor in comparison to the world market. But, it should be noted a huge increase in the number of Polish producers of filaments and printers in recent years (3D Universal, Devil Desing, Zortax, ZMorph, etc.) This allows to look with optimism to the future and wait for news in the world of filaments and 3D printing technology including those coming from Poland.

References

1. Rengier F., Mehndiratta A., Tengg-Kobligk H., Zechmann C.M., Unterhinninghofen R., Kauczor H.U., Giesel F.L., *Int. J. Comput. Ass.* 2010, **5**, 335–341.
2. Kun K., *Procedia Engineering*, 2016, **149**, 203–211.
3. Leigh S., Bradley R., Purssell C., Billson D., Hutchins D., *PLoS ONE*, 2012, **7**, 11.
4. Yu W., Kai G., Wei-Hua P., Gui Q., Li Q.X., Chen H.D., Yand JH., *Chin. Phys. Lett.,* 2011, **28**, 1.
5. Patra S., Young V., *Cell Biochemistry and Biophysics*, 2016, **74**, 93–98.
6. Pinnock C.B., Meier E.M., Joshi N.N., et al., *Methods*, 2016, **99**, 20–27.
7. Chen Q., Liang S., Thouas G*., Progress in Polymer Science*, 2013, **38**, 584–671.
8. Hsu S., Hung K., Lin Y., Su C., Yeh H., Jeng Y., Lu Ch., Dai S., et al*., J. Mater. Chem. B*, 2014, **2**, 5083–5092.
9. Sartori S., Chiono V., Tonda-Turo C., Mattu C., Gianluca C., *J. Mater. Chem. B*, 2014, **2**, 5128–5144.
10. Janik H., Marzec M*., Przemysł Chemiczny*, 2015, **94/2**, 182–185.
11. Hung K.C., Tseng C.S., Dai L., Hsu S., *Biomaterials*, 2016, **83**, 156–168.
12. Hung K.C., Tseng C.S., Hsu S., *Advanced healthcare materials*, 2014, **3**, 1578–1587.
13. Li Z., Zhang R., Moon KS., Liu Y., Hansen K., Le T., Wong C.P*., Adv. Funct. Mater.*, 2013, **23**, 1459–1465.
14. China CN104004377 (A) – (2014).
15. China CN104292850 (A) – (2014).
16. China CN103756236 (A) – (2014).