Short Review of Polymer Composites for 3D Printing

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Abstract

3D printing technology is a rapid prototyping technology, which can use different materials to prepare real objects through layer by layer printing based on three-dimensional digital model. At present, the material with the largest amount of application and the most extensive molding method is polymer material。The research of ABS, PLA, PCL, TPU, photosensitive, resin polymer hydrogel and their composites are reviewed in this paper.

1. Introduction

3D printing technology, also known as additive manufacturing technology, is a new manufacturing technology made by computer-aided design (CAD), which is similar to ordinary printers and directly prints products. The forming process is adopting 3d drawing tools such as UG Pro/E Solid Works to conduct 3d modeling of the products to be printed and export them into STL format firstly. Then, 3d slicing software was used to conduct language segmentation and slicing processing on the established model and generate gcode file which is transferred to the 3D printer. Finally, the 3D printer is used to deposit the material layer upon layer on the working platform and finally print the whole product.

A 3D printing system can realize the printing of different materials. For example, metallic,stone polymer materials can be applied to 3D printing among which the polymer materials have the largest amount of application and the most extensive molding method. Several typical polymer materials for 3D printing including ABS, PLA, PCL and TPU photosensitive resin polymer hydrogel and their composite materials are introduced in this paper firstly. Then the application of materials for 3D printing in biomedical electrical aerospace and other fields was discussed.

2. Typical materials for 3D printing

2.1 ABS resin

ABS resin is a thermoplastic resin composed of three components. ABS material is suitable for 3D printing technology with the following characteristics. The first is the moderate detail performance. The second is the high strength. The third is suitable for product functional verification. However, the unsaturation of butadiene makes ABS have poor heat resistance and ozone resistance and warping deformation and dimensional shrinkage will occur under the action of thermal stress, which limit the development of pure ABS in the field of 3D printing technology.

Quill et al. [1] obtained BN (boron nitride) /ABS composites with thermal conductivity and electrical insulation by FDM and injection molding respectively. The study showed that the thermal conductivity increased significantly and the impact strength of bending strength decreased with the

increase of BN content.Tekinalp et al. [2] applied staple fiber of 0.2 ~ 0.4 mm to reinforce ABS as the raw material for 3D printing. It was found that the tensile strength and modulus of 3D printed samples were improved by 115% and 700% respectively, and the fiber orientation was up to 91.5 than traditional technologies. However, samples prepared by FDM have high porosity. Therefore, improving the adhesion and compatibility of two phases through surface treatment of fibers or using appropriate additives is the main direction of future research.

Nikzad M et al. [3-4] applied iron powder and copper powder particles to modify ABS which was used them in FDM 3D printing. The results show that the thermodynamic and mechanical properties of ABS substrate have been significantly improved. When the iron content of ABS/Fe composite is high, the compression strength and energy storage modulus of FDM products are greatly improved and the rigidity of the composite is significantly enhanced at the same time. In addition, some scholars [5] blended glass fiber and carbon nanofiber with ABS for FDM 3D printing. It was found that the mechanical and machining properties of the printed products have been improved obviously. However, the molten ABS smells bad during the printing process and thus people don't like to use ABS as printing material.

2. 2 PLA

PLA is mainly derived from plant starch which has good biocompatibility and biodegradability. PLA can be used for 3D printing, the main advantages of which are low melting point, low viscosity and excellent mechanical properties, but high brittleness, transparent materials and high gloss.

Qin [6] improved the crystallization rate and toughness of PLA by blending polycarbonate with PLA, and also retained the degradability of PLA. Song [7] prepared WF/PLA wood-plastic composite with eucalyptus powder (WF), which was a degradable environment-friendly plastic. When the content of wood powder was 50% (mass fraction), the tensile strength of composite increased by 10 MPa compared with that of pure PLA. Tekinalp [61] prepared staple fiber reinforced ABS composite through fused deposition molding and die casting molding respectively to study the mechanical properties and structural characteristics of the composites. The results showed that the tensile strength and elastic modulus of FDM products have been improved, and the FDM fibers have a higher orientation in the composites. Although the porosity of FDM printed composites is higher, its tensile strength and tensile modulus are higher than those of traditional die-casting composites, which are determined by the orientation and dispersion of fibers in ABS.

Y Tao [66] prepared 3D printing wire of wood powder reinforced PLA composite and successfully applied it in FDM molding. The tensile properties, thermal properties, crystallinity and surface morphology of composites were tested and characterized by scanning electron microscope (SEM) thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The results showed that the initial bending resistance of the composite was enhanced, the initial thermal degradation temperature of the composite decreased slightly, and the melting temperature was hardly affected. Chizari [10] prepared PLA nanocomposite with 40% (mass fraction) carbon nanotubes (CNT). It was found that the conductivity of the composite was up to 3 800 S /m. Thstudy explored the application of 3D printed conductive composites in smart sensors in textile or electronic fields.

In the field of tissue engineering, Lactic acid produced by degradation of PLA scaffold can cause inflammation and allergic phenomenon. Blending PLA with CS (chitosan) can improve the toughness

of PLA and alleviate the acid produced by the degradation of PLA. The PLA/CS scaffold has been successfully applied in the field of neural tissue engineering as a three-dimensional system to increase the differentiation of neurotic cells. [11]

2. 3 Polycaprolactone (PCL)

PCL is widely used as medical biodegradable materials and drug control release system , with good biodegradability, biocompatibility and non-toxicity. As PCL has the ability to store and restore deformation, it can adapt to the rapid development of 4D printing. At present, researchers mainly improve the mechanical strength of PCL through blending and copolymerization modification.

Visser et al. [12] developed a 3D printing technology, called melt electrospinning writing, which could print a filament with a diameter of 5 microns, which can be blended with methylacrylamide   to prepare high-strength composite scaffold. Lee et al. [13] mixed chitosan (CS) obtained by electrospinning with PCL nanofibers to prepare CS /PCL chains by 3D printing and produced artificial blood vessels successfully. Qu, etc. [14] prepared PCL/nHA nanocomposite scaffolds based on electrohydrodynamic printing. The average diameter of the scaffold is (8. 85±12)μm, which is close to the size of living cells. In addition, scaffolds have good biocompatibility which can realize the multi-scale regulating cell microenvironment and promote tissue regeneration.

2. 4 Thermoplastic polyurethane (TPU)

TPU has excellent wear resistance, corrosion resistance, radiation resistance, oil resistance, oxygen resistance and ozone resistance which is widely used in the field of 3D printing. Akbarian et al. [15] prepared short aramid fiber reinforced polyurethane composite and found that the short fiber had serious axial splitting and fracture fibrification during its blending with the polyurethane.

In recent years, biodegradable natural fibers with low cost have gradually become a research hotspot. El-shekeil et al. [15-16] strengthened thermoplastic polyurethane with Kenaf fiber and Cocoa Pod Husk Fibers. It was found that the tensile and flexural properties of the composites were improved with the load increasing. Polyurethane is widely used in conductor field. Kim et al. [17] invented a 3D multi-axial force sensor manufactured by FDM, whose structure part USES thermoplastic polyurethane (TPU) as filament, and the sensing parts use carbon nanotube (CNT) /TPU nanocomposite filament to realize the customization, rapid manufacturing and economic feasibility of multi-axial sensor. The nano porous PMMA/TPU composite prepared by Wang et al. [18] has higher mechanical properties than ordinary honeycomb materials with a thermal conductivity of 24.8mk/mK, which has potential applications in the field of 3D printing. Chen et al. [19] prepared biocompatible TPU/PLA/GO nanocomposite elastomer, which is a kind of good tissue engineering scaffold material. Its unique shape memory function, antibacterial effect and excellent electro-thermal performance can be applied in advanced scientific and technological fields.

2.5 Light cured solid material

Research on 3D printing of photocurable materials at home and abroad focuses on two aspects. The first is that different prepolymer photoinitiators were used to optimize the parameters to obtain the resin meeting the performance requirements. The second is to optimize the 3D printing equipment. Wang et al. [20] prepared epoxy resin matrix with continuous through-hole by 3D printing technology, and then prepared CNTs/epoxy resin composites with excellent electrical properties and electrical shielding properties by dipping process, which provided necessary reference for the preparation of

composites with electromagnetic shielding properties.

Tumbleston[21] adopts the continuous liquid interface production (CLIP) technology to enable the parts to be formed within 10 minutes, and improves the accuracy and speed of SLA technology, which is 25 ~ 100 times faster than traditional printing technology.

Comptom et al. [22] used epoxy resin and other raw materials to prepare a lightweight honeycomb composite with excellent mechanical properties, which is a 3D printing honeycomb composite.

3. Conclusion

3D printing is a creative technology which are not widely used in industry. There are still some limitations to overcome in the research of polymer materials of 3D printing. Firstly, the orientation and content of fibers are important factors affecting the properties of materials. At present, the nozzle will be blocked obviously when the fiber content is greater than 40% (mass fraction). Therefore, the fiber content should be further improved and the materials should be processable. Secondly, the nanoparticles should be treated with chemical surface treatment or modified by adding compatibilists in order to avoid agglomeration of nanoparticles and ensure a good interface between nanoparticles and polymers. Thirdly, how to eliminate the gap in printing process and ensure the good interface between matrix and reinforcement is the main content of future research.

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