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3D–printing of materials with anisotropic heat distribution using conductive polylactic acid composites

Yuan Zhuang[a,b,1], Wentong Song[a,1], Gang Ning[c], Xueyan Sun[a], Zhongzheng Sun[a], Guowei Xu[d], Bo Zhang[d], Yening Chen[a], Shengyang Tao[a,*]

[a] Department of Chemistry, Dalian University of Technology, Dalian 116024, Liaoning, PR China
[b] School of Petroleum and Chemical Engineering, Dalian University of Technology, Panjin 124221, Liaoning, PR China
[c] Department of Architecture, Dalian University of Technology, Dalian 116024, Liaoning, PR China
[d] School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, Liaoning, PR China

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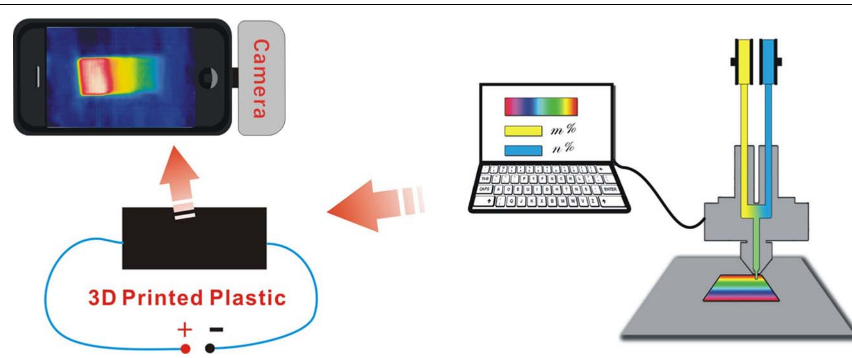
ABSTRACT

A series of plastic items with anisotropic heat and resistance distribution were prepared by 3D printing. Conductive graphene doped polylactic acid (G-PLA) and pure PLA were used as raw materials. The programmed mixing printing method was adopted to construct these objects. The effects of the extrusion ratios of G-PLA and PLA, applied voltage and heat distribution on the printed items were investigated. We observed that the resistance of the printed items was controlled by the extrusion ratio during the 3D printing process. The distribution of the resistance is programmed by the slicing software and the single chip microcomputer in the 3D printer. The temperature of the printed test sheet varied from 20 to 90 °C according to the applied electronic current and voltage. Heterogeneous temperature regions were identified and showed isotropy. The temperature gradient field was constructed by designing and printing items with a quasi-continuously change resistance. The thermal signal was presented in the form of color information through a thermography device. As such, a simple message can be expressed and stored in this printed objects.

GRAPHICAL ABSTRACT



1. Introduction

In crystals, the array and amount of atoms vary for different surfaces. Due to this structural difference, the physical, chemical, and mechanical properties of crystals are usually directionally dependent [1–3]. This phenomenon is referred to as the anisotropy of crystals. The anisotropy

* Corresponding author.
E-mail address: taosy@dlut.edu.cn (S. Tao).
[1] These authors contributed equally to this work.

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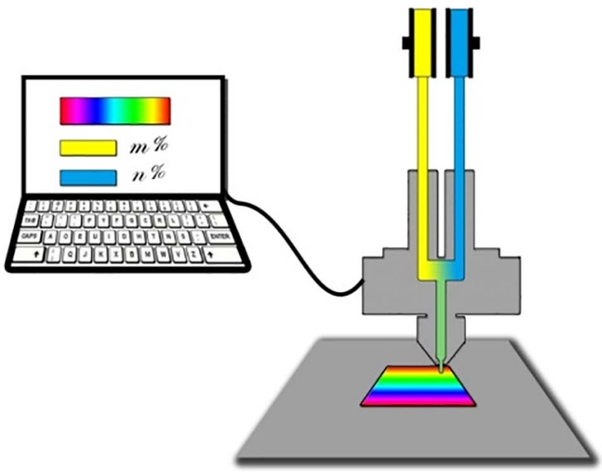

Fig. 1. Schematic representation of the mixed fabrication process of 3D–Printed conductive polylactic acid composites.

of materials affects many of their properties, including absorbance, refractive index, conductivity, and tensile strength and so on [4–8]. Based on anisotropy, researchers have developed many functional materials, such as nonlinear optical materials, magnetostrictive materials, photonic crystals, and piezoelectric materials [9–14]. However, because the microstructure of amorphous materials is homogeneous and disordered, it is difficult to classify these materials as anisotropic. Therefore, it is a significant but challenging project to adjust the distribution of the amorphous materials' components or structure at the micro-level, which may lead to the formation of anisotropic materials.

Recently, three-dimensional printing (3D printing), an additive manufacturing method that creates a physical object from a digital design, has gradually become a remarkable technology for fabricating functional materials and structures. For example, Leroy Cronin et al. successfully used a 3D printer to initiate chemical reactions by printing the reagents directly into a 3D reaction ware matrix, and so put reaction ware design, construction and operation under digital control [15]. Inspired by the botanical systems, Mahadevan et al. successfully printed composite hydrogel architectures that are encoded with localized, anisotropic swelling behaviour controlled by the alignment of cellulose fibrils along prescribed four-dimensional printing pathways [16]. Lewis et al. printed a 3D mesoscale architectures with minimum feature sizes ranging from 100 nm to 100 μm from multiple classes of materials [17]. Folch et al. used a 3D printer to fabricate micro fluidic systems due to its automated, assembly-free 3D fabrication, rapidly decreasing costs, fast-improving resolution and throughput [18]. At the same time, starch/acrylonitrile butadiene styrene copolymers (ABS) biomass alloys was prepared successfully by the 3D printing technology [19]. 3D printing is becoming an attractive research topic for chemical industrial [20,21], material science [22,23] and biomedical applications [24–26] owing to its advantages of easy operation, low cost as well as fast manufacturability.

The key feature of 3D printing is the slicing of the 3D digital model in one direction (usually along the Z-axis) into a series of thin layers by computer software, followed by the construction of each individual layer by the printer [27]. There are many interfaces between layers of the printed objects (PO). Thus, for most 3D printers, the process is not continuous, but rather a step-by-step deposition along the Z-axis [28]. In this way, every layer is a single unit. Based on this understanding, if the specific component distribution in each layer is programmed and deposited on an assigned location in a controlled manner, macroscopic physical properties of materials will exhibit an anisotropic or gradient change [29]. Therefore, lots of functional materials with anisotropic properties can be fabricated by this new 3D printing technology.

As an exploration, herein, we create materials with anisotropic heat distribution by using a 3D printer to mix and print two kinds of filaments: graphene-doped conductive PLA and pure insulated PLA. Through adjusting the extrusion and mix ratios of the two filaments, the resistance of each layer in the printed object could be varied to a default value (Fig. 1). As a result, a plastic object with controllable resistance at different sites was achieved. Under the applied electric field, the printed object, which is composed of an amorphous polymer, exhibited a heterogeneous and anisotropic temperature distribution. The formed anisotropic temperature field may be beneficial for some special chemical reactions, temperature-controlled surface wettability and phase change process. This indicates our ability to successfully fabricate anon-crystalline substance with anisotropy at the macro-level using a cheap desktop 3D printer.

2. Experimental

2.1. 3D Printing of PLA polymer

The 3D printing of PLA was performed using an isun3d 230C 3D Printer (Isun3d Tech Co., Ltd. China). This printer can extrude and melt two kinds of filaments into one nozzle (0.4 mm in diameter) allowing for a passive mixing process in the nozzle. The extrusion ratio (volumetric fraction) of the two different kinds of filaments (pure PLA to G-PLA) can be manually adjusted by the control panel which is connected to a single chip microcomputer. In this paper, the mentioned values of the extrusion ratio all mean the volume fraction of pure PLA to G-PLA. For example, if the extrusion ratio is 3:7, it means the volume fraction of pure PLA is 30%, and the volume fraction of G-PLA is 70%. Pure PLA and conductive graphene-doped PLA (G-PLA) polymer filaments (1.75 mm in diameter), used as the raw printing materials, were purchased from Poly maker Co., Ltd. The G-PLA filament with a volume resistance of 0.8 Ω cm^{-1} was produced from Graphene 3D Lab Inc. All the filaments were used directly, without any further treatment. CAD designs were drawn and visualized using Autodesk 123D Design and transferred to 3D printable formats (G-code) using the cure software. The temperature of the extruder was set at 195 °C, and the 3D printer stage was not heated. The thickness of sliced layers and walls of printed objects was 0.1 mm and 0.8 mm, respectively. The fill rate was 100% and the printing speed was 20 mm s^{-1}. As shown in the Fig. S1, the camera image of the mixed fabrication process as well as the step-by-step workflow for the fabrication of the sheet was given.

2.2. Characterization

The microscopic features of the samples were taken with a QUANTA 450 scanning electron microscope (SEM) at 30 kV. Thermal gravimetric analysis (TGA) was carried out using TGAQ600 ramp 10 °C min^{-1} to 500 °C. Raman spectra were collected using a Nicolet Almega XR

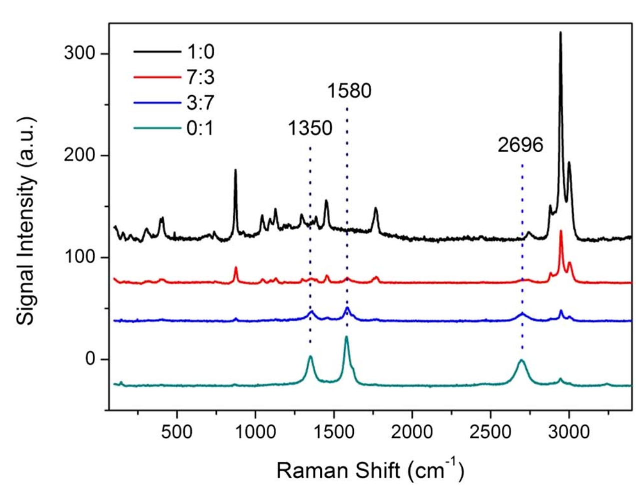

Fig. 2. Raman spectra of objects printed with different extrusion ratios of PLA and G-PLA.