Journal of the Mechanical Behavior of Biomedical Materials 78 (2018) 395–403

Contents lists available at ScienceDirect

Journal of the Mechanical Behavior of Biomedical Materials

journal homepage: www.elsevier.com/locate/jmbbm

Study on temperature and near-infrared driving characteristics of hydrogel actuator fabricated via molding and 3D printing

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ARTICLE INFO

Keywords:
Hydrogel
Layered structure
Intelligent responses
Molding
3D printing

ABSTRACT

A hydrogel material system which was fit for molding and 3D printing was developed to fabricate bilayer hydrogel actuators with controllable temperature and near infrared laser responses. Polymerization on interface boundary of layered structure enhanced the bonding strength of hydrogel actuators. By utilizing anisotropic of microstructure along with thickness direction, bilayer hydrogel actuators fabricated via molding realized intelligent bending/shrinking responses, which guided the preparation of hydrogel ink for 3D printing. In-situ free radical polymerization under vacuum realized the solidification of printed hydrogel actuators with graphene oxide. Based on anisotropic swelling/deswelling behaviors of precise structure fabricated via 3D printing, the printed bilayer hydrogel actuators achieved temperature and near infrared laser responsive deformation. Changes of programmable printing path effectively resulted in corresponding deformation patterns. Combination of advantages of molding and 3D printing can promote the design and fabrication of hydrogel actuators with high mechanical strength, response speed and deformation ability.

1. Introduction

Based on the reversible water swelling/deswelling polymer networks, hydrogel actuators achieve variation of shape dimensions which resulted from local or global change in network structure under the stimulations of temperature (Ma et al., 2016; Drozdov and Christiansen, 2017), light (Wu et al., 2011; Feng et al., 2013), electric field (Liang et al., 2011; O'Grady et al., 2010) and so on. The bending, shrinking and movement of hydrogel actuators expand the applications in various fields including medicine (Markert et al., 2013), biology (Pelah et al., 2007) and bionic robot (Ma et al., 2013; Bassik et al., 2010).

Due to the advantages of remote and non-contact control, light-driven hydrogel actuators are easily controlled with higher spatial and temporal resolution than other stimuli (Wang et al., 2013; Luo et al., 2016) and attract many attentions to design and fabricate novel light-driven soft actuators. Photoreactions play the main role in light-driving behaviors including photoisomerization/ionization of chromophores and photothermal heating of nanoparticles in thermoresponsive matrices (Tomatsu et al., 2011; Shi et al., 2015; Lo et al., 2011). Attributed to the restriction of solution condition and destructiveness of ultraviolet light (Tomatsu et al., 2011; Takashima et al., 2012), model of photoisomerization/ionization of chromophores is limited. But, the near infrared laser with permeation ability (Robinson et al., 2011) can be treated as the stimulation source of photothermal heating. Therefore, more and more attentions have been paid to near infrared laser-driving hydrogel actuators. In order to complete photothermal conversion, many kinds of near infrared laser absorbents have been developed, such as gold nanorods and carbon nanotubes (Fujigaya et al., 2008; Lu and Panchapakesan, 2007). Among near infrared laser absorbents, graphene oxide (GO) with extraordinary photothermal energy transformation ability (Acik et al., 2010) has been widely used in near infrared laser-driving actuators (Jiang et al., 2015; Wang et al., 2015). Based on poly (N-isopropylacrylamide) (PNIPAm) hydrogel, photoresponse functional hydrogels were fabricated in our previous study (Zhao et al., 2017a), which exhibited high detachment property under stimulation of near infrared laser. Therefore, in this paper, we adopt GO as the photothermal conversion absorbent.

Up to now, several kinds of temperature or near infrared laser response hydrogels with bending/unbending properties have been developed via molding. Intelligent response hydrogels with inhomogeneous structures are assigned along with the thickness direction, forming the asymmetrical distribution of crosslinking

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https://doi.org/10.1016/j.jmbbm.2017.11.043
Received 4 September 2017; Received in revised form 24 November 2017; Accepted 27 November 2017
Available online 02 December 2017
1751-6161/

density. The anisotropy of microstructure is the bending/unbending mechanism of bilayer hydrogels. In-situ free radical polymerization and ultraviolet light polymerization are the main methods to realize polymerization of hydrogels. Yao et al. (2015) fabricated a kind of temperature-controlled hydrogel actuator via a two-step photo polymerization. The asymmetrical distribution of nanoclays across the hydrogel thickness led to high responsive bending and elastic properties. Zhang et al. (2014) fabricated a near infrared-driving bilayer hydrogel by stepwise in situ polymerization. The bilayer hydrogel with GO absorbed near infrared irradiation and efficiently transformed it into thermal energy, which changed the isotropic volume contraction into an anisotropic deformation. Even though layered structure of hydrogels can be fabricated successfully, the simple structure restricts the applications. 3D printing can be used for solving fabrication problems of hydrogel actuators with complex structure. Inspired by tendrils, bracts, leaves and flowers respond to environmental stimuli, Sydney et al. (2016) printed hydrogel architectures via ultraviolet light polymerization encoded with localized and anisotropic swelling behavior, which fabricated plant-inspired architectures that changed shape on immersion in water. The corresponding investigation opens a new method for hydrogel actuators via 3D printing. Peng et al. (2017) used a commercial inkjet printer printed a bilayer hydrogel system consisted of poly (sodium acrylate) and an aqueous ferric solution. The fabricated complex 3D shapes underwent shape deformation upon swelling/deswelling. Combined with the investigations of hydrogel actuators fabricated by molding and 3D printing, it can be found that methods of molding and 3D printing own the corresponding advantages and disadvantages, respectively. 3D printing can fabricate complex shapes, but sample size, mechanical strength improvement and cost of different material systems restrict the application. Moreover, the addition of GO in photoresponse functional hydrogel actuators forbids the solidification of printed structures. Therefore, how to develop a hydrogel material system which can be used for molding and 3D printing, and resolve the polymerization problem of printed photoresponse hydrogel actuators with GO are necessary investigations to extend the practical application of hydrogel actuators.

In this study, we developed a hydrogel material system which was fit for fabricating bilayer hydrogel actuators with temperature and near infrared laser responses via molding and 3D printing. The in-situ free radical polymerization under vacuum was adopted to realize the polymerization of the printed photoresponse hydrogels with GO. The molding with one-step polymerization and 3D printing with in-situ free radical polymerization under vacuum provided a simple and efficient method to fabricate different parts of soft actuators. Considering economy and efficiency, the developed material system and fabrication methods promote the development and practical application of hydrogel actuators.

2. Experimental section

2.1. Material

Monomer N-isopropylacrylamide (NIPAAm, $C_6H_{11}NO$, Aladdin, Shanghai, China, 2% stabilizer) was recrystallized from toluene/n-hexane mixture and dried in vacuum at room temperature for 48 h. Nanosized synthetic hectorite clay (Laponite XLG, $Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4$) was purchased from Rockwood, Ltd., (Moosburg, Germany) and used after drying at 125 °C for 2 h. Initiator potassium peroxydisulfate (KPS, $K_2S_2O_8$, Shanghai Aibi Chemical Reagent Co., Ltd., Shanghai, China, Analytical reagent AR), catalyst N,N,N',N'-tetramethylethylenediamine (TEMED, Tianjin Weiyi Chemical Technology Co., Ltd., Tianjin, China, 98%), graphene oxide (GO, Suzhou Hengqiu Graphene Technology Co., Ltd., Suzhou, China, 95%), Nanofibrillated cellulose (NFC, Guilin Qihong Technology Co., Ltd., Guilin, China, 1342 nm) and methyl blue (Shanghai Aibi Chemical Reagent Co., Ltd., Analytical reagent AR) were used as received. Pure water was obtained by deionization and filtration with a Millipore purification apparatus (resistivity ≥ 18.2 MΩ cm).

2.2. Synthesis of PNIPAm-GO bilayer hydrogel via molding

The PNIPAm-GO hydrogel was synthesized via in-situ free radical polymerization of NIPAm in the nanosized clay suspension with GO and NFC. Before the fabrication of PNIPAm-GO hydrogel, the pure water was degassed in the continuous nitrogen-saturated atmosphere for 2 h. 0.5 mL methyl blue solution with concentration of 40 mg/mL was stirred for 0.5 h in 19 mL pure water for the fabrication of the hydrogel without GO. The graphene oxide was first dispersed in 19.5 mL pure water by ultrasonic radiation for 30 min and stirred for 1 h via a magnetic stirrer (Model DF-101S, Changchun Jiyu Technology Equipment Co., Ltd., China). The XLG clay was added into GO suspension, which was stirred for 1 h and ultrasonically radiated for 30 min. Then the reinforcement of NFC with different weights was added and stirred for 1 h in an ice-water bath. The monomer NIPAm was added into miscible liquids of GO, XLG and NFC under nitrogen-saturated atmosphere in an ice-water bath for another 2 h. Finally, 0.5 mL KPS solution with concentration of 40 mg/mL and 27 μL catalyst of TEMED was added under stirring. The solution was rapidly dumped into a laboratory-made rubber mold of 70 mm × 20 mm × 2 mm (Length × Width × Thickness). The polymerization was conducted at 25 °C for 24 h. The mole ratio of NIPAm monomer, initiator, and catalyst in all suspensions was kept at 100: 0.370: 0.638. In order to investigate the effect of GO content on the temperature and near infrared response characteristics of bilayer hydrogels, 0 mg/mL, 1 mg/mL, 2 mg/mL and 3 mg/mL GO was adopted, respectively. PNIPAm-GO hydrogels were defined as PNIPAm-GO0, PNIPAm-GO1, PNIPAm-GO2 and PNIPAm-GO3, where 0, 1, 2, 3 represented the concentration of GO. The compositions of the PNIPAm-GO hydrogels are listed in Table 1.

Fig. 1 shows the fabrication process of bilayer hydrogel. In the bilayer structure, GO contents of GO layers were 1 mg/mL, 2 mg/mL and 3 mg/mL, respectively. Because of the variation of NFC, the two layers exhibited different densities, which provided a fabrication method for bilayer hydrogel effectively via density difference in one-step in-situ free radical polymerization. The GO0 layer was injected first in the laboratory-made rubber mold. After the superimposition of GO hydrogel layer, the laboratory-made mold was sealed tightly. The polymerization of bilayer hydrogel system was also carried out at 25 °C for 24 h.

Table 1
Compositions of hydrogels for molding.

Sample	NIPAm (g)	GO (mg)	NFC (mg)	XLG (g)	KPS (mg)	TEMED (μL)	Methyl blue (mg)	H_2O (mL)
PNIPAm-GO0	2.26	0	40	0.691	20	30	20	20
PNIPAm-GO1	2.26	20	20	0.692	20	30	0	20
PNIPAm-GO2	2.26	40	20	0.692	20	30	0	20
PNIPAm-GO3	2.26	60	20	0.692	20	30	0	20