OPTICAL 3D μ-PRINTING OF POLYTETRAFLUOROETHYLENE (PTFE) MICROSTRUCTURES

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ABSTRACT

This paper reports a novel 3D micro-printing (μ-printing) method for polytetrafluoroethylene (PTFE) microstructures by using optical maskless exposure and thermal decomposition technologies. PTFE nanoparticles were mixed with polymer monomer to form a UV curable colloidal mixture, which can be cured layer-by-layer to form 3D microstructures by using an optical maskless exposure system. The microstructures were dried and sintered to remove solvent and other polymer except PTFE. 3D PTFE microstructures with nanopores ranging from tens to hundreds of nanometers were fabricated for the first time. Based on its super-hydrophobic property, PTFE bionic insect was fabricated to demonstrate the super weight-carrying ability on the water surface. The printable PTFE microstructures have great potential in medical implants, chemically inert micro reactors/filters, and microfluidics control applications.

INTRODUCTION

Polytetrafluoroethylene (PTFE) is a fluoropolymer with many unique properties, such as excellent chemical inertness and thermal stability, anti-solvent, hydrophobicity, low surface energy and low friction coefficient [1, 2]. Those attractive properties render PTFE plenty of important applications, such as non-stick hydrophobic coating, chemically inert containers and filters, waterproof breathable fabric, biocompatibility implants, and dielectric materials [2-6]. However, the fabrication of PTFE microstructures and microdevices is usually difficult because of its insolubility, high melt point and high melt viscosity [7, 8]. As PTFE is poorly soluble in almost all solvents, it is unrealistic to cast PTFE solution in mould. As the melted PTFE does not flow but behaves like a gel, injection molding, which is commonly used in fabrication of complex polymer structure, is also very difficult to implement for PTFE. Some PTFE derivatives can provide better manufacturability. For example, perfluoroalkoxy alkane (PFA) and fluorinated ethylene propylene (FEP) allow melting and injection molding process; some amorphous fluoroplastics like CYTOP® and Teflon™ AF can dissolve in special perfluorinated solvents for spin coating [1]. However, those derivatives partially sacrifice chemical inertness and thermal stability, and thus cannot totally take the place of pure PTFE in many applications.

Because of their appealing applications, the fabrication of pure-PTFE microstructures has attracted remarkable attention. Traditional methods like cold-moulding and hot embossing have been demonstrated to imprint microstructures on PTFE films [9] and mechanical extension has been applied to produce large-area porous PTFE structures for filters, fabric, and implants [4, 10]. Micromachining methods like cryogenically assisted abrasive jet and sanding with sandpaper have been demonstrated to fabricate microstructures on bulk PTFE [11, 12]. Duo to the high stability of fluorocarbon bond, PTFE can totally depolymerize to monomer by using appropriate external energy. Therefore, high-energy beams like synchrotron radiation [13, 14], laser-plasma X-ray [15], femtosecond laser [16], and focused ion beam [17, 18] have been studied to directly pattern pure PTFE. Those methods can fabricate some good 2D and 2.5D microstructures through tilt or grayscale etching process. However, the fabrication of 3D PTFE microstructures still remains challenges.

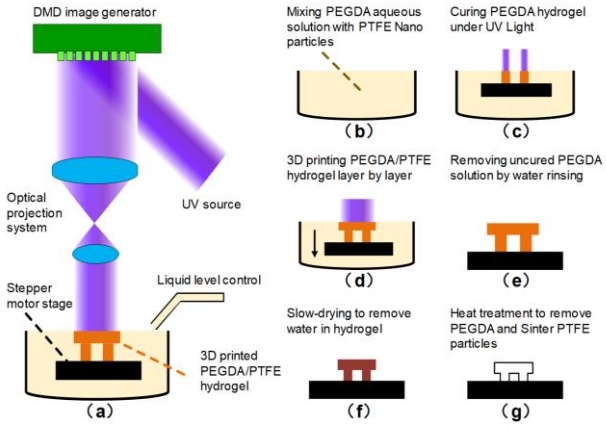

Figure 1: Schematic diagram of the optical 3D μ-printing of PTFE microstructures (a) and the process flow (b~g).

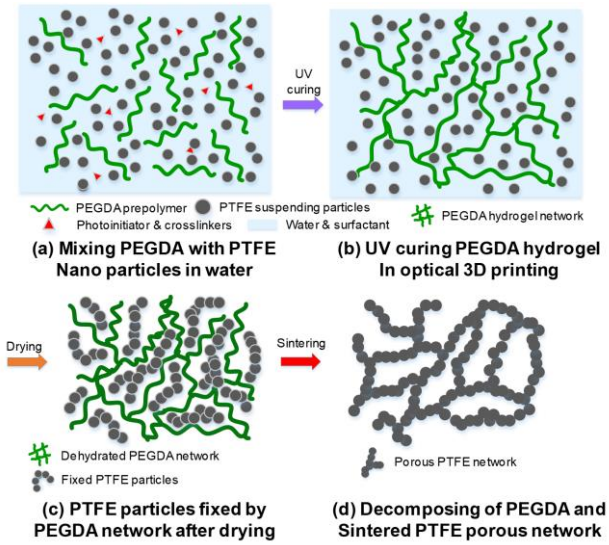

Figure 2: Transformation from PEGDA/PTFE-nanoparticle dispersion to PEGDA/PTFE composite hydrogel followed by pure PTFE.

To overcome those difficulties, we present a flexible fabrication method for 3D PTFE microstructures without using mold or related machining/etching processes in this

paper. With optical 3D micro-printing technology, PTFE microstructures can be fabricated by using low-power UV light source instead of high-energy beams. The additive manufacturing nature of the method allows highly flexible design and manufacturing of complex PTFE microstructures, which are difficult to be implemented by using other microfabrication methods. Moreover, the processing method can provide nanopores ranging from tens to hundreds of nanometers in PTFE microstructures, which can further enhance the hydrophobic property of the PTFE microstructures.

METHODOLOGY

In order to use optical 3D micro-printing, a photocurable mixture with PTFE component need prepared. In our experiments, an aqueous emulsion polymerized PTFE nanoparticle dispersion was used, in which PTFE nanoparticles are dispersed in water with the aid of surfactant. A water-soluble poly(ethylene glycol) diacrylate (PEGDA) photopolymerization system was chosen for photo-curing process. As the common pre-polymer for hydrogels and biomaterials [19-21], PEGDA and the photoinitiator Irgacure 2959 have good water solubility and thus can be mixed well with PTFE nanoparticle dispersion. Such a PEDGA/PTFE -nanoparticle dispersion can be photocured to form hydrogel. As only a small amount of PEGDA is needed to cure the entire dispersion, it is thus not difficult to totally remove PEDGA in subsequent sintering. The polymerized PEGDA will depolymerize in the temperature range of 360-400℃ [22], which is slightly above the melting point of PTFE, but below its thermal decomposition temperature. Therefore, PEGDA is an ideal interim polymer material to bind PTFE nanoparticles to form microstructures and then be removed via thermal decomposition without causing severe influence on the PTFE microstructures.

In the experiments, PTFE emulsion Teflon DISP30 from DuPont Co. was chosen, which contains 60 wt% suspended nanoparticles (~220nm size). The emulsion is mixed with PEGDA pre-polymer (average Mn 700), photoinitiator (Irgacure 2959), ultraviolet absorber (HMBS, CAS 4065-45-6), polymerization inhibitor (TEMPO, CAS 2564-83-2), and fluorocarbon surfactant (3M FC4432) to prepare the photocurable nanocomposite. The final composite contains 50 wt% PTFE, 15 wt% PEGDA, 34 wt% water, and a small amount of other additives.

The schematic of the optical 3D μ-printing of PTFE microstructures is shown in Figure 1. An in-house optical maskless exposure system with ultraviolet light source (with the wavelength of 365 nm) is used to cure the mixture layer by layer [23]. The ultraviolet light is transmitted and collimated to the digital micromirror device (DMD). A control software makes DMD generate UV pattern which will be projected onto the target substrate through a reduction projection optics. A controlled stepper motor stage and a liquid-level control device are used to adjust the height of each layer in 3D printing process.

The transformation from photocurable dispersion to PEGDA/PTFE composite hydrogel and then pure PTFE is shown in Figure 2. With the UV exposure, the PEGDA pre-polymer was polymerized to form a network embedded with PTFE nanoparticles. The cured PEGDA/PTFE hydrogel microstructure is developed by using DI water to remove uncured nanocomposite and then baked in an oven to remove water. Finally, the microstructure is heated up to 400 ℃ for sintering, at which temperature PEGDA will decompose and evaporate totally. Meanwhile, the PTFE nanoparticles are melted and sintered to form a microstructure with porous network. Due to the high melting point and high melt viscosity, partially melted PTFE nanoparticles exhibit gel-like behavior and can sustain the 3D structural geometry of the original design after sintering.

RESULTS

Figure 3 shows the printed 3D PTFE microstructures, i.e. a cubic frame and a double propeller.

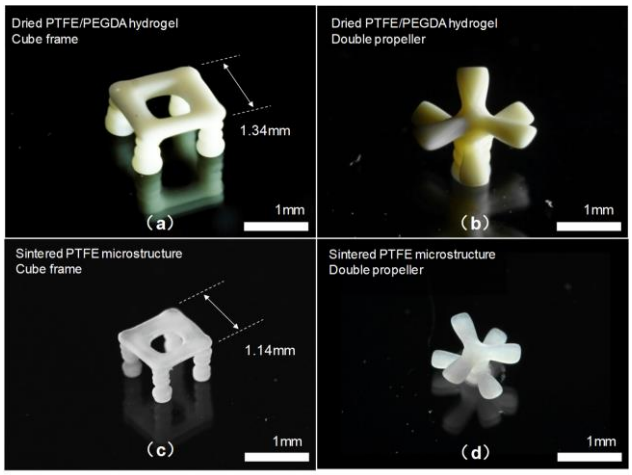

Figure 3: 3D micro-printed PEGDA/PTFE structures before sintering (a, b), and PTFE microstructures after sintering (c, d).

Before drying, the hydrogel contains about one third of water and thus is translucent white and soft. After drying, the most of water is removed. Then, the hydrogel shrinks and changes from a translucent hydrogel to an opaque white, hard and crisp object, as shown in Figure 3(a) and (b). In the experiment, the width of the printed structure shrunk 19.8% after drying process. The ratio of the pre-polymer and solvent in the mixture plays an important role for the printing process. A larger proportion of pre-polymer can improve the mechanical properties of the printed PTFE/PEGDA structure, but is unfavourable for the subsequent sintering process.

After sintering, the 3D structure became white translucent and tough, indicating that the PTFE nanoparticles are welded to each other, see Figure 3(c) and (d). During the process, the width of the structure shrinks 14.7%. The reasons for the shrinkage include the removing of PEDGA, the welding of PTFE nanoparticles and the volatilization of low-molecular-weight PTFE.

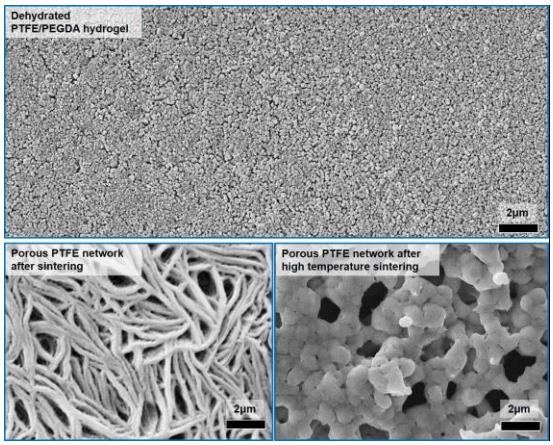

Figure 4: SEM images show the change of the surface morphology before and after sintering process.

The microcosmic changes of the polymer surface during the printing and sintering processes are shown in Figure 4. UV curing forms a PEGDA network so as to build PEGDA/PTFE microstructure during the printing process. In the sintering process, PEGDA volatilized (gas generated by the decomposition of internal PEGDA escapes) and left nanopores on the PTFE microstructures. The sintering time and temperature affect the welding of PTFE particles and thus determine the porosity and shrinkage degree of the final PTFE structure. From the scanning electron microscope (SEM) images, porous nanostructures with the size ranging from tens to hundreds of nanometers were observed on the fabricated PTFE microstructures.

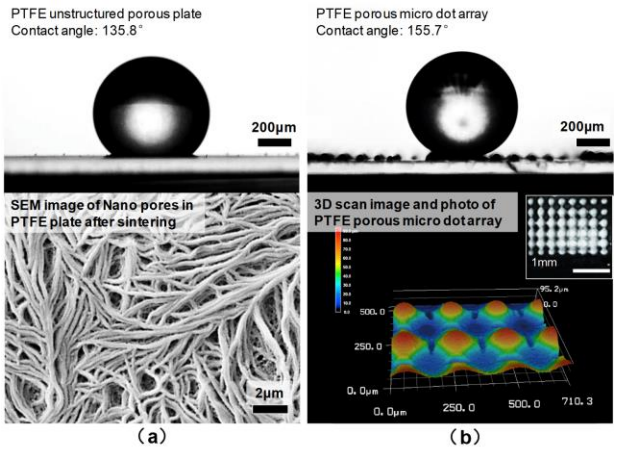

Figure 5: Measurement of the contact angles of water on porous PTFE surfaces without (a) and with (b) micro-dot array.

As a fluoropolymer, PTFE is known with good hydrophobic property. With the compound micro-/nano-structures, its hydrophobic property can be further enhanced because of the increased effective surface area. Figure 5 shows the super-hydrophobic performance of a nanoporous PTFE surface and another PTFE surface with compound micro-/nano-structure. The nanoporous PTFE surface (without microstructure) revealed 135.8 ° contact angle of water, which is larger than that of normal bulk PTFE, i.e. 120 ° contact angle. If further print microstructures on the surface, the hydrophobic property of the PTFE surface can be further significantly improved. In the experiments, a 2D array of microdots with the size of ~150 μm has been printed to achieve a super-hydrophobic surface whose contact angle of water is 155.7 °.

To further demonstrate the super-hydrophobic performance of the printed PTFE microstructures, a bionic insect with microvilli legs was designed and fabricated, see Figure 6. Inspired from gerridae, an insect that can walk on water surface with its super-hydrophobic legs, a bionic insect with six legs was designed and printed by using the established micro-printing technology. For such a super-hydrophobic microstructure, surface tension rather than buoyancy can provide extra load-bearing capacity. In the experiment, a bionic insect of 1.7-millimeter long and 0.5-mg weight was demonstrated to support 4 tin balls with a total weight of 6.7 mg on water surface, see Figure 6(d). The load is more than thirteen times of the weight of the bionic insect itself. This result renders microstructured PTFE very appealing for hydrophobic devices and applications.

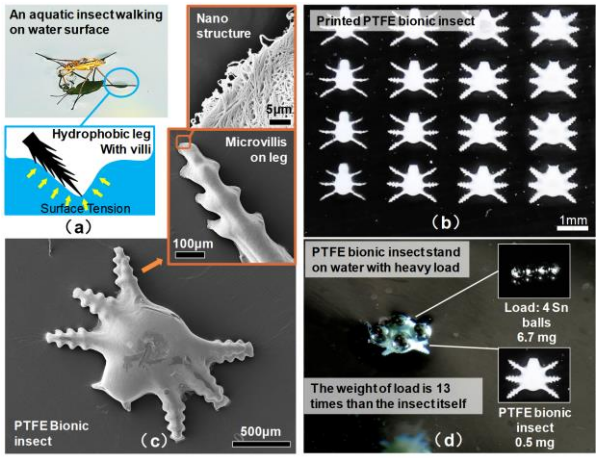

Figure 6: Biological prototype (a) and the printed PTFE bionic insect with super-hydrophobic nanopored PTFE microvilli legs (b~c). The fabricated PTFE bionic insect can support a weight load 13 times of its own weight on the water surface (d).

CONCLUTIONS

In this paper, a novel optical 3D micro-printing method has been presented to fabricate PTFE microstructure. 3D PTFE microstructures with nanopores ranging from tens to hundreds of nanometers have been demonstrated for the first time. Experiments have been carried out to reveal the super hydrophobic property of such compound micro-/nano-structures. It is believed that the printed PTFE microstructures have great potential in medical implants, chemically inert micro reactors/filters, and microfluidics control applications.

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