Applied Surface Science 329 (2015) 58–64

Contents lists available at ScienceDirect

Applied Surface Science

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

Selective three-dimensional hydrophilization of microstructured polymer surfaces through confined photocatalytic oxidation

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ARTICLE INFO

Article history:
Received 22 October 2014
Received in revised form
19 December 2014
Accepted 20 December 2014
Available online 26 December 2014

Keywords:
Polymer
Surface
Microstructure
Modification
Wettability
Pattern

ABSTRACT

While the conventional photomask technique gives only two-dimensional anisotropies, in this study we fabricated microstructured polymer surfaces with a selective three-dimensional anisotropy. With the applied removable mesh, we were able to confine the contacting area between the surface and photoinitiator and provide three-dimensional wettability anisotropies. Different types of meshes were used depending on the desired micropatterns shape, size and substrate material. The results revealed the three-dimensional anisotropic micropits pattern with depth profiles, which would be applicable for the confinement and patterning of cells and biomolecules. In addition, the proposed method is applicable for creating selectively activated polymer surface as a substrate for further atomic layer deposition. Moreover, we demonstrate a low cost and fast mass productive method for patterning a viscous polymer liquid in a micro-sized scale.

1. Introduction

Polymeric materials are the most utilized commercial products nowadays with their low cost and versatile properties. The tailoring of the monomer chemical structure has inspired researchers to synthesize new polymeric materials with enhanced properties. However, for many applications, advanced surface properties, such as wettability [1], adhesion [2], permeability [3], are needed in addition to the special bulk properties. The microfluidic devices demand wettability control [1], cell culturing needs exceptional cell adherence with the surface [2], and drug delivery systems require permeability of the biomolecules within the body [3]. Therefore, the polymer surface modification attracts great interest of researchers. For example, it was found that a nanostructured thin film on contact with the epithelial tissue increases permeability of the proteins [3].

The polymer surfaces can be modified both chemically and topographically. The chemical modification increases the surface energy and activates the surface. The activated smooth polymer surfaces with the enhanced adhesion and biocompatibility are utilized in coating [4], pharmaceutical industry [5], and other biochemical applications [6]. The commonly used chemical modification methods include UV irradiation [7], plasma treatment [8] and monolayer self-assembly [9].

The topographically patterned surfaces, containing pillars, pits or other complicated structure shapes are widely applicable in self-cleaning [10], microdevices [11], and nanomedicines [12]. It was found that cells differentiate and localize on the topographically patterned surfaces in a more controlled way than on the smooth ones [13]. However, for chondrocyte cells cultured on polymer surfaces with pillar-shaped structures, the original phenotype tends to adopt a fibroblast-looking morphology during de-differentiation, decreasing the primary usability [14]. Thus, a three-dimensional confinement of the chondrocytes' morphology is of great importance. In this sense, pit-shaped geometries on surfaces with adjustable size and shape matching the cells would be useful. For that, a precise size control is required in the pattern fabrication process. The commonly used photolithography method satisfies the precision demand [15]. As a clean room technique, the performance is restricted in a special environment. On the contrast, the patterning method with a microworking robot [16] has no special environmental needs. The microstructuring is performed with a computer controlled microneedle, therefore the patterns with size precision are achievable on solid substrates. In addition, with the needle as a transfer tip, patterning and depositing of viscous liquid is also possible. Moreover, the robot technique provides a quicker and microscaled liquid patterning alternative to the slow nanoscaled dip-pen lithography with the AFM tip [17,18].

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http://dx.doi.org/10.1016/j.apsusc.2014.12.147
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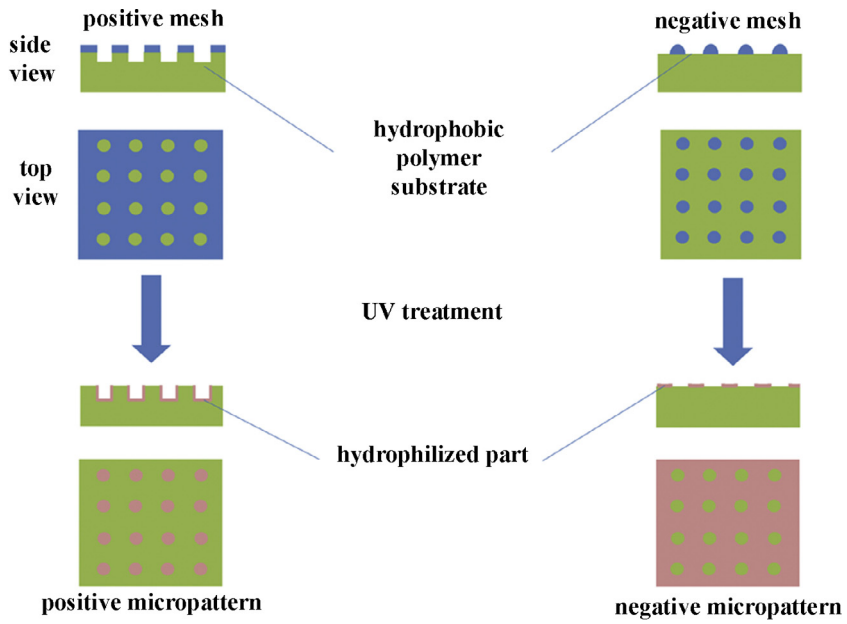

Fig. 1. Schematic representation of the positive and negative meshes, and the hydrophilized positive and negative micropatterns. The scheme is not drawn to scale.

The topographical structuring of the polymer surfaces increases the surface area, which in turn improves the surface adherence properties [19]. However, considering the hydrophobic nature of the structured surfaces the complete penetration of target cells or other materials inside the structure may be difficult. For example, with polar cell culture media and hydrophobic structured polymer surfaces, the chondrocyte cells prefer to attach only on top of the pillars forming roof-like extracellular matrix [14]. Fortunately, Myllymaa et al. [20] has shown that a hydrophilic coating on structurally modified polymer surfaces significantly improved the adhesion, spreading, and contact guidance of osteoblast typed cells. Therefore, combining the surface topography with selective hydrophilization may be one possible solution. Selective chemical modification inside the structures creates the affinity differences on the surface due to selective wettability changes [21]. The hydrophobic nature of the chemically unmodified part will repulse the polar solvent, preventing the cell adhesion. The hydrophilic part gives a driving force to embed cell culture medium. Meanwhile the surface structures provide the shape confinement for the cells.

The selectivity of the chemical surface modification can be controlled with an applied photomask [22]. With the aid of the photomask, selective confined photocatalytic oxidation (CPO) reaction between the polymer surface and photoinitiator was performed through UV treatment [23]. The CPO reaction activates and oxidizes the inert C—H bonds and, finally, hydroxyl bonds are formed after further hydrolysis. On the hydroxyl activated sites, Yang et al. [24] successfully deposited the metal oxide layer. Moreover, with the selectively activated polymer substrate further atomic layer deposition (ALD) can be performed. However, the selective modification is mostly performed onto the smooth surface. The two-dimensional anisotropies might create difficulties to regulate the size and shape of the immobilized biomolecules.

While the conventional CPO method utilizing photomasks to regulate the UV irradiation gives a two-dimensional anisotropic pattern, in this study, we explore the possibility of creating wettability anisotropies with depth profiles on microstructured polymer surfaces. The key issue is to have a removable protecting mesh to restrict the contact area between the photoinitiator and the polymer surface. The use of different mesh materials, and the microscale patterning of both solid substrate and viscous prepolymer mixture will be shown to facilitate selective three-dimensional hydrophilization processes.

2. Materials and methods

2.1. Materials

The polypropylene (PP) homopolymer (HD 120 MO) and high density polyethylene (HDPE) (MI 7.5 C68410) were purchased from Borealis Polymer Ltd. Polydimethylsiloxane (PDMS) prepolymer mixture was prepared from Sylgard 186 (Dow Corning, USA). Ammonium persulfate (CAS: 71310-21-9) and acetone (CAS: 67-64-1) were obtained from Sigma–Aldrich and were used as received. Sodium chloride crystals were purchased from J.T. Baker (Deventer, Netherlands).

2.2. Methods

The irradiated areas of the polymer substrate were controlled by the applied meshes. The schematic representation of the meshes and hydrophilized micropatterns is shown in Fig. 1. With applied positive mesh, the whole substrate was covered except the micropits. Thus, only the micropits are hydrophilized. The resulting hydrophilized micropattern is positive. On the contrary, the negative mesh is the deposited microdots on the smooth polymer substrate, and the rest of the surface area is hydrophilized. Correspondingly, the hydrophilized micropattern is negative.

2.3. Surface structuration and mesh preparation

2.3.1. Surface structuration

A schematic representation of the surface structuration and mesh preparation is shown in Fig. 2(step1). Flat PP and HDPE samples with thickness of 1500 μm were prepared by injection molding with a DSM Midi 2000 melt compounder and a DSM microinjection molding machine. With or without the meshes, the microstructuration of the sample was done by a RP-1AH microworking robot from Mitsubishi Electric, with a CR1 control and a feedback unit from Delta Enterprise Ltd. The tungsten carbide based working needles of different sizes were supplied by Gritech Ltd.