



Modification of polycarbonate with hydrophilic/hydrophobic coatings for the fabrication of microdevices



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ARTICLE INFO

Article history:

Received 1 October 2013

Received in revised form

20 November 2013

Accepted 29 November 2013

Available online 7 December 2013

Keywords:

Polycarbonate

Hydrophilic/hydrophobic coating

Urethane linkage

Siloxane bond

Chemical resistance

Valve-free sequential injection

ABSTRACT

In this paper, we introduce a simple strategy for modifying the surface of polycarbonate (PC) to make it either hydrophilic or hydrophobic. The aminosilane, bis[3-(trimethoxysilyl)propyl]amine (bis-TPA), was used to produce the hydrophilic surface via aminolysis of the carbonate backbone to form strong urethane linkages, leaving alkoxy silane parts exposed on the surface. To obtain the hydrophobic surface, PC coated with bis-TPA was further reacted with (tridecafluoro-1,1,2,2-tetrahydrooctyl)-triethoxysilane (FTES), where inorganic moieties of both silanes condensed to realize siloxane (Si–O–Si) bonds. In this way, fluorinated groups were left exposed on the terminal surface of the PC, rendering it hydrophobic. In-depth surface characterizations were performed, including water contact angle measurement and X-ray photoelectron spectroscopy (XPS) analysis, in order to identify the optimum conditions for achieving surface modification without sacrificing substrate transparency. To extend the use of these PC surface treatments to microfluidic applications, the hydrophilic coating was further adopted for use in bonding two PC substrates by forming Si–O–Si bonds at the interface. Using the hydrophilic treatment of PC, we obtained microchannels, which were resistant to organic solvents. Furthermore, by employing subsequent hydrophobic treatment, multiple liquids were successfully injected into microchannels sequentially in a valve-free manner

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1. Introduction

Plastic substrates have attracted a great deal of attention as promising alternatives to glass, silicon, and quartz in the fabrication of microfluidic devices. This is because they have many advantages such as high mechanical strength, optical transparency, low cost, ease of molding, mass production capabilities, and commercialization potential [1]. In particular, their low fabrication cost increases the feasibility of single use devices, which provides practical applications with added cleanliness, and eliminates cross contamination, a common problem that occurs when devices are recycled. Despite the many advantages of plastic substrates, they can be easily damaged by organic solvents, with a tendency to melt, swell, or become opaque. To overcome this limitation, many researchers have strived to coat plastic substrates with sol-gel matrices [1–3]. This process can be conducted under relatively low temperature conditions, enabling desirable functional groups to be incorporated with high uniformity within the sol-gel matrix.

However, the coating requires multiple steps, and control of the density of the formed sol-gel network is difficult to achieve.

Another approach to producing plastics that are resistant to organic solvents is to make the surface hydrophobic [4]. Many commonly used hydrophobic materials such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) are relatively expensive and opaque. For this reason, hydrophobization of the surface of a cheaper plastic would provide a facile alternative for realizing hydrophobic surfaces on a transparent and robust plastic backbone at low cost. Zhao et al. created a hydrophobic polycarbonate (PC) surface by swelling the polymer with acetone and then initiating coagulation with either water or methanol [5]. Hozumi et al. used radio frequency plasma-enhanced chemical vapor deposition with a fluoropolymer or fluoroalkyl silane to create hydrophobic PC [6]. Although promising results have been demonstrated, these methods are not suitable for cases where the inner walls of microchannels need to be hydrophobized after the device has been assembled. In addition, the exact mechanism by which the hydrophobic surface is produced using these methods is not entirely clear.

Among the numerous plastic substrate materials available, PC is known to possess high impact resistance, low moisture absorption, a relatively high glass transition temperature (T_g), and optical transparency, which makes it an appropriate material for low cost

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microdevice fabrication. It has previously been reported that in the presence of aminosilane, PC undergoes aminolysis, which causes scission of the carbonate backbone. This results in the formation of strong urethane linkages between the PC and aminosilane, with the organic moiety exposed on the terminal surface [7–15]. The bonds are formed through the donation of the lone pair of electrons to the carbonyl group [9], which opens the double bond between the carbon and oxygen, followed by chain scission at the carbonate backbone to form a robust urethane bond between the amine functionality of the aminosilane and the PC. This results in the surface hydrophilization of the PC, and provides the possibility to further modify the surface via subsequent chemical treatment.

In our previous study [16], we adopted this concept as a simple and affordable method for bonding two PC substrates for fabricating microdevices, and analyzed the strength of the bonds. Using the proposed method, chemical bonding was realized under relatively mild conditions, with channel profiles well preserved with high resolution, which is not possible when traditional thermal bonding methods are used. The bonding was shown to be sufficiently robust as to endure over 520 kPa without burst or leakage. An aminosilane incorporating a primary amine was adopted for the bonding as these easily undergo hydrolysis. This meant that the innate properties of the PC could be recovered inside the microchannels after the assembly, simply by flushing the channel with water. As a result, the same inner surface as that achieved using thermal bonding was obtained while preserving channel morphology in high fidelity.

In the present study, an aminosilane incorporating a secondary amine rather than a primary was utilized for the hydrophilic/hydrophobic surface modification of PC in order to realize a hydrolytically resistant coating. It is known that secondary amines rapidly react with carbonate groups in solution at room temperature [17]. A homogeneous PC microdevice was constructed by first carrying out surface hydrophilization of two PC substrates using an aminosilane, and then oxidizing and embossing the surface under relatively mild conditions. The assembled PC microdevice was assessed for its resistance to the organic solvent, toluene, in order to evaluate its suitability for facilitating organic solvent-mediated chemical reactions. Furthermore, hydrophobic coating of the PC microchannels was realized by the addition of an extra step, which involved a simple reaction of the hydrophilic surface groups with a fluorinated silane. The assembled PC microdevice containing hydrophobic microchannels was further applied for sequential injection of multiple reagents in a valve-free manner, the injection mode of which was only possible when the microchannels were rendered hydrophobic.

2. Materials and methods

2.1. Materials

Bis[3-(trimethoxysilyl)propyl]amine (bis-TPA), aminopropyltriethoxysilane (APTES), and (tridecafluoro-1,1,2,2-tetrahydrooctyl)-triethoxysilane (FTES) were purchased from Sigma. Ethyl alcohol (94.0%), isopropyl alcohol (99.5%) and toluene (99.5%) were purchased from Daejung. Polycarbonate (PC) ($T = 2$ mm) sheet was purchased from Goodfellow. Polytetrafluoroethylene (PTFE) ($T = 0.3$ mm), a kind of Teflon, was purchased from IXAK.

2.2. Surface hydrophilic/hydrophobic coating

The processes by which the PC was rendered hydrophilic or hydrophobic as well as the process for realizing PC–PC assembly are shown in Fig. 1. Fig. 1(a) shows the chemical structure of PC. The surface of PC was first cleaned with isopropyl alcohol (IPA) by dipping the substrate in IPA and shaking for 5 s at room temperature

and then dried using a compressed air. Bis-TPA was diluted in ethanol to 0.1, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0% (v/v), and reacted with PC at room temperature for 20 min as shown in Fig. 1(b). To realize PC–PC assembly, bis-TPA-treated PC substrates were embossed at 130 °C under a pressure of 0.1 MPa as shown in Fig. 1(c). To make the resulting hydrophilic PC surface hydrophobic, it was further reacted with FTES diluted in ethanol to 0.1, 0.5, 1.0, and 2.0% (v/v) and reacted at room temperature for 15, 30, and 60 min. The resulting alkoxy silane groups from both bis-TPA and FTES underwent hydrolysis and condensed to form siloxane (Si–O–Si) bonds after 1 h of reaction at room temperature [18,19] as shown in Fig. 1(d). For comparison purposes, a different aminosilane, aminopropyltriethoxysilane (APTES), was used in place of the bis-TPA.

2.3. Contact angle measurement

The water contact angles were measured by the sessile drop technique using a Phoenix 300 contact angle measuring system (Surface Electro Optics, Korea), and results were analyzed with Image Pro 300 software. All the measurements were repeated five times.

2.4. XPS analysis

XPS analyses were conducted using an Axis-Hsi (Kratos Analytical, UK) equipped with a magnesium X-ray radiation source of dual gun (1253.6 eV) and pass energy of 20 eV. The pressure in the chamber was below 5×10^{-9} Torr before the data were taken, and the voltage and current of the anode were 15 kV and 10 mA, respectively. The take-off angle was set at 45°. The binding energy of C1s (284.5 eV) was used as the reference. The resolution for the measurement of the binding energy was about 0.1 eV.

2.5. Assembly of two PC substrates

Microchannels were engraved in a piece of PC using a computer numerated control (CNC) milling machine. This microchannel-engraved PC and a flat piece of PC were both treated with a predetermined concentration of bis-TPA in ethanol at room temperature for 20 min and then dried. Afterwards, they were placed in physical contact at 130 °C, which is slightly below the T_g of PC (145 °C), and a pressure of 0.1 MPa was applied for 30 min using a home-built pneumatic press machine. As a control experiment, pristine PC microchannels were fabricated by thermal bonding, which was realized by embossing microchannel-patterned PC and a flat PC substrate at 145 °C under 0.1 MPa for 30 min.

2.6. Chemical resistance to organic solvent

Pristine, bis-TPA-treated, and FTES post-treated PC substrates, all 2×2 cm in size, were immersed in toluene, and any visible change in the color of the surface was recorded at 0.5, 1, 3, 5, 8, 10, 20, 30, 45, 60, and 90 min. The degree of chemical resistance was correlated with the observed color changes from transparent to opaque. Toluene was also introduced into microchannels formed in pristine, bis-TPA-treated, and FTES post-treated PC, and the color change was observed.

2.7. Valve-free sequential injection of multiple liquids

Microchannels with varying dimensions were engraved in PC. The width and depth of the largest, intermediate, and the smallest microchannels were fabricated to be 2.0 and 0.5 mm, 1.0 and 0.3 mm, and 0.5 and 0.2 mm, respectively. After assembly with a flat piece of PC via bis-TPA treatment, the inner microchannels were treated with FTES in order to render the inside of the microchannels

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