Polymer 50 (2009) 5358–5361

Contents lists available at ScienceDirect

Polymer

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

Polymer Communication

The fabrication of polymer microfluidic devices using a solid-to-solid interfacial polyaddition

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ARTICLE INFO

Article history:
Received 2 July 2009
Received in revised form
11 September 2009
Accepted 18 September 2009
Available online 24 September 2009

Keywords:
Polymers
Microfluidic devices
Fabrication

ABSTRACT

It is hard to permanently seal the microfluidic channels made of thermoset polymers without using conventional adhesives. Here, we reported a polyaddition-based mechanism to solve the problem. The method is based on introducing amine groups onto the surface of one material and epoxy groups on another material and enabling the amine–epoxide polyaddition reaction at their closely contacted solid-to-solid interface to establish a covalent and permanent bonding. It was successfully used to permanently seal polydimethylsiloxane (PDMS) microfluidic channels with glass in a scalable and multifunctional fashion and to seal epoxy (SU-8) microfluidic channels with PDMS. This type of interfacial polyaddition can be easily extended to other materials for microfluidic device fabrication and is expected to find some applications in specialty bonding.

1. Introduction

Polymeric microfluidic devices, especially those made of thermosets, have played an increasing role in the research and commercialization of micro-total analysis systems because of their easy fabrication, low cost, and biological-favored performance [1]. They are usually fabricated by creating open microfluidic channels on a polymer flat substrate and then encapsulating or sealing the channels with a flat polymer or inorganic sheet or film preferably without using any adhesive, which may easily flow into the channels and deteriorate their performance. While a reactive process, such as casting and photolithography, can be conveniently used to fabricate thermal and chemical-resistant thermoset microfluidic channels with a broad range of dimension and precision, there are very limited methods to enclose the obtained channels without using adhesives. Thermosets, in principle, can not be bonded through a molecular diffusion method, such as thermal pressure bonding, solvent bonding, ultrasonic and laser welding [1], because their molecular chains are constrained by the crosslinked network and can not diffuse into a contacted foreign material to get entangled. Instead, they are usually bonded through a chemical reaction occurring at the interface of two solid materials. Silanol condensation [2], is so far the most popular method used to permanently seal microfluidic channels (polydimethylsiloxane (PDMS), particularly), while an unfinished crosslink reaction can be also utilized to seal channels [3]. Unfortunately, the available methods are only applicable to specific materials and are not easy to control. For instance, they cannot be used to seal SU-8 (an epoxy photoresist) microfluidic channels with PDMS. Although SU-8 is an ideal material for the fabrication of various microfluidic devices, a mechanical pressure still has to be applied to seal SU-8 microfluidic channels physically with PDMS [4]. Even for the popular condensation-based encapsulation of PDMS microfluidic channels, the short shelf life and stress sensitivity of oxygen plasma-activated PDMS might still cause a process problem and face a technical challenge in up scaling. Here, we report a method that can be used to easily seal thermoset and even thermoplastic microfluidic channels permanently.

2. Experimental

PDMS sheets with open microfluidic channels, fabricated by casting PDMS mixture (Sylgard 184, Dow Corning) on SU-8 mold masters, were oxidized in a plasma chamber of Harrick Plasma (model PDC-001) and quickly coated with a solution containing 0.1–1.0 wt% 3-aminopropyltrimethoxysilane (APTMS, Simga–Aldrich) in anhydrous toluene (Simga–Aldrich) and dried. Ethanol-cleaned Pyrex glass sheets were coated with a solution containing 0.1–1.0 wt% γ-glycidoxypropyltrimethoxysilane (GOPS, Simga–Aldrich) in anhydrous ethanol (Simga–Aldrich) and dried. The coated PDMS surface was brought into a close contact with the coated glass surface, and heated at 80–100 °C for 30 min to seal the PDMS microfluidic channels. The coated PDMS sheets with or without

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doi:10.1016/j.polymer.2009.09.053

microfluidic channels were also directly attached to the dried SU-8 films with or without microfluidic channels for the same heating process to seal the PDMS or SU-8 microfluidic channels. The SU-8 solid films were fabricated with SU-8 photoresist (SU-8 2015, MicroChem) on silicon wafers through photolithography process by following the manufacturer-recommended procedure but without hard baking.

A XPS of Physics electronics (model XPS 5500) was used to analyze the surfaces of the above APTMS-coated PDMS and GOPS-coated glass after they were exposed to the above heat treatment and thoroughly washed with anhydrous ethanol. A differential scanning calorimeter of TA Instruments (model DSC 2010) was used to analyze the content of unreacted epoxy groups in the SU-8 films, and a FTIR–ATR of Nicolet 550 spectrometer was used to analyze the reaction of epoxy on the nitrogen plasma-excited PDMS.

The bonding of the encapsulated PDMS microfluidic channels and SU-8 microfluidic channels was tested by pumping DI water into the inlet of each of their straight channels using a syringe pump of Harvard apparatus (Model 33) while keeping the outlet open. For each channel, the flow rate was initially kept at a low value for 2 min and then stepwise increased to the value until the channel was fractured to calculate the average maximum holding pressure of the channels.

3. Results and discussion

Fig. 1 illustrates the proposed method for encapsulating or sealing thermoset microfluidic channels. Amino groups and epoxy groups are introduced onto the two involved materials respectively and amine–epoxide reaction is enabled at their closely contacted interface to establish a covalent and permanent bonding. Polyaddition, which is the most commonly used reaction for curing epoxy resins [5], is what happens at such a solid-to-solid interface in dry conditions.

The concept was simply demonstrated in encapsulating PDMS microfluidic channels with glass. In this case, the PDMS surface was amino functionalized after it was oxidized through an oxygen plasma treatment to generate silanol (Si–O–H) groups [2,6] and then coated with a 3-aminopropyltrimethoxysilane (APTMS)/toluene solution. The glass surface was epoxy functionalized using a γ-glycidoxypropyltrimethoxysilane (GOPS)/ethanol solution. Permanent sealing was established by attaching the PDMS to the glass and then heating them to 80–100 °C for 30 min without applying any pressure. Given that silanol groups on the glass surface are generally utilized to covalently capture GOPS and APTMS through silanol condensation reaction for biological applications [7,8], and the silanol groups generated on the PDMS surface are widely used to react with the silanol groups on glass and PDMS for permanent bonding [2,9], chemical coupling is expected to happen between the oxygen plasma-activated PDMS and APTMS, and between glass and GOPS. As confirmed by XPS analysis, APTMS stays on the PDMS surface while GOPS stays on the glass surface as shown in Fig. 2. The covalent attachment of APTMS to PDMS and GOPS to glass, and the inter-polyaddition reaction between the two silanes ultimately form the chemical linkage between the PDMS and glass, resulting in the permanent bonding. This process is suitable for up scaling and precision device alignment because the two coated surfaces can be stored for many hours or can be brought into a close contact and then separated for many cycles without losing their capability for establishing an irreversible bonding. It also simultaneously introduces the bio-application-required amine and epoxy groups onto the channel surface and may be utilized to incorporate channel surface functionalization into the channel sealing process. These are clear advantages over the existing process of sealing PDMS microfluidic channels using glass, which only allows a few minutes to bring the oxygen plasma-activated PDMS and glass together to achieve irreversible bonding, does not allow any chance to rework on their pre-bonding contact without using a solvent to protect the surfaces, and is unable to simultaneously functionalize channel surface with these chemical groups.

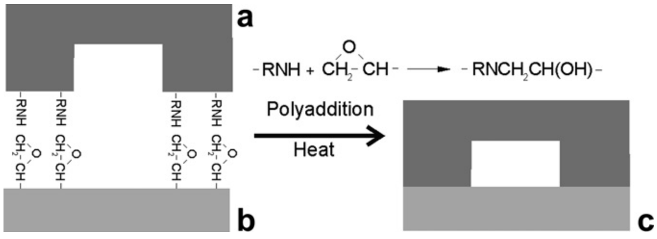

Fig. 1. Schematic illustration of the permanent sealing of microfluidic channels using the interfacial polyaddition between the two functionalized surfaces. (a) Open microfluidic channel with–RNH groups on surface, where R can be H or alkane. (b) Lid with epoxy groups on surface. (c) Sealed microfluidic channel.

Further more, the above described amino functionalization of PDMS can be replaced by simply activating PDMS with nitrogen plasma. A permanent sealing was established between the nitrogen plasma-activated PDMS and the above GOPS-coated glass by bringing them in a close contact and exposing them to the above thermal process. According to literature reports, up to 1.9% nitrogen can be introduced to PDMS surface by nitrogen plasma treatment in the typical form of C–NH_2, C–NRH–, N–C–N and C=N– [6,10]. This effect was also confirmed in our XPS analysis, and the generated amine groups were found sufficient enough to lead to a permanent and tight sealing. Meanwhile, the epoxy surface functionalization can be extended to utilizing the remaining epoxy groups on a solidified epoxy resin. Both the APTMS-coated and nitrogen plasma-activated PDMS were found to be able to bond permanently on SU-8 films when there were sufficient remaining epoxy groups on the SU-8 surface. Our detailed study showed that when SU-8 epoxy photoresist only completed about 57% or less of its total reaction as characterized by its reaction heat using DSC, there were still sufficient unreacted epoxy groups remaining on its surface for the reaction to happen and for the strong bonding to be established. Fortunately, this is the case when SU-8 devices are fabricated with the manufacturer-recommended procedure but without any hard baking or hardening. In other worlds, the post-baked flat SU-8 may be used to seal PDMS microfluidic channels or the developed SU-8

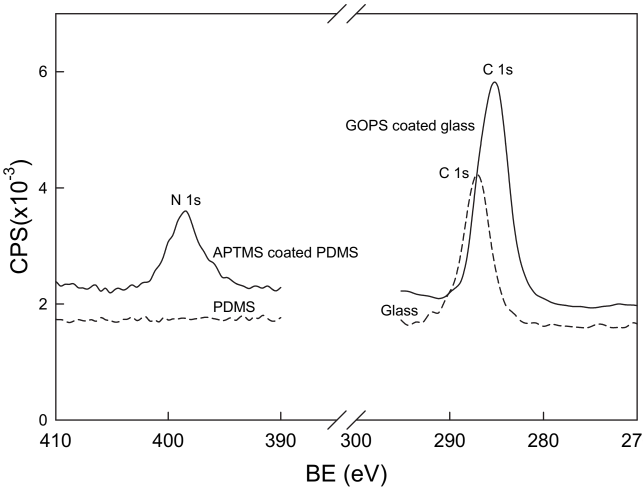

Fig. 2. XPS confirmed the surface attachment of APTMS to PDMS and GOPS to glass. The coated PDMS and glass were exposed to 100 °C for 30 min and then washed with ethanol.

microfluidic channels may be dried and permanently sealed with the PDMS, and then hardened. The evolved process of sealing SU-8 microfluidic channels with PDMS was proved to be simple and robust.

The sealed PDMS and SU-8 microfluidic channels were evaluated with hydraulic testing. Devices with 15 isolated straight channels, 20 μm high, 5 cm long, and ranging from 20 to 160 μm in width (10 μm increment), were fabricated for the testing. When water was pumped into the channels, the fluidic pressure within each channel dropped along the channel and had a maximum value near its inlet. The channel was fractured in the inlet area when the water flow rate was increased to a certain level, at which the local fluidic pressure reached the holding limit, or maximum holding pressure of the channel. This maximum handling pressure is a comprehensive property related to the channel sealing, the mechanical strength of the involved materials, and the external connection of the channels to metal tubings. It was estimated from the corresponding flow rate, channel dimension, and water viscosity using the well-known Hagen–Poiseuille's equation [11]. Table 1 shows the maximum holding pressures of the channels. The values are very high for polymer microfluidic devices. They are close to the maximum holding pressure (0.99 ± 0.12 MPa) of the PDMS microfluidic channels permanently sealed with glass using the standard oxygen plasma-activation process because fracture mostly occurred within PDMS and press fit-based channel-to-tubing connection [12] in the permanently sealed devices. Such a truly permanent and strong sealing qualifies the encapsulated microfluidic channels for various applications, including those encountered with high fluidic pressure, such as flow cytometry [4] and particle classification [11].

Amine–epoxide polyaddition, regardless whether the amine is primary or secondary, is an easy reaction that can be completed rapidly at an evaluated temperature or with the assistance of a catalyst [5]. In addition to its popular application in the curing of epoxy resin, the reaction is also utilized to improve the fiber-matrix bonding of fiber-reinforced epoxy resin. APTMS, for instance, is used as a typical coupling agent to pre-treat glass fibers for the purpose, and the amine–epoxide polyaddition happens on the fiber surface during the curing of liquid epoxy resin [13]. In our study, the reaction of SU-8 on amino-activated PDMS surface was confirmed with FTIR–ATR analysis. As seen in Fig. 3, SU-8-based absorptions at 1495 cm^{-1} and 1603 cm^{-1}, which correspond to the aromatic ring stretching of epoxy resin, are visible on the nitrogen plasma-activated PDMS but not on the untreated PDMS after they were all coated with a commercial SU-8 solution (SU-8 2015), heated at 100 °C for 30 min, and then washed with cyclopentanone and acetone. The reaction is apparently even able to directly happen between the amino-activated PDMS and SU-8 devices or GOPS-coated glass, resulting in the above described permanent channel sealing. The reason is that PMDS is soft enough to conform itself to the rigid surface of SU-8 device or glass to establish a liquid-to-solid equivalent contact in a large area. This type of conform contact-based solid-to-solid bonding is similar to the case of bonding PDMS to glass using silanol condensation [2], and is necessary for the large-area contact of amino with epoxide and thus their polyaddition reaction. It requires one of the materials being in rubbery state at the processing temperature if the method is to be extended to other material systems.

Table 1
Maximum holding pressure of the sealed microfluidic channels.

Channel materials		Lid materials		Maximum holding pressure (MPa)
Materials	Surface	Materials	Surface	
PDMS	O_2 plasma and APTMS coating	Glass	GOPS coating	0.97 ± 0.13
PDMS	N_2 plasma	Glass	GOPS coating	0.99 ± 0.14
SU-8	Dried after the development	PDMS	O_2 plasma and APTMS coating	0.91 ± 0.12
SU-8	Dried after the development	PDMS	N_2 plasma	0.99 ± 0.10

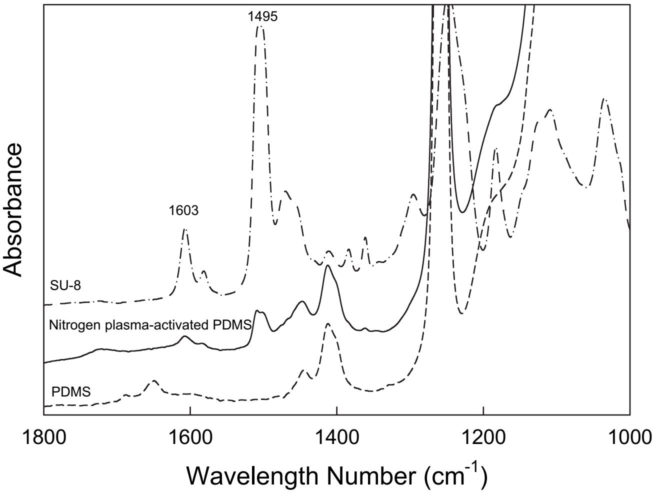

Fig. 3. FTIR–ATR spectra of SU-8 and PDMSs. The PDMSs were coated with the same SU-8 solution, heated at 100 °C for 30 min, and washed with cyclopentanone and then acetone.

While only PDMS, glass and SU-8 were involved in this work due to their popularity in microfluidic applications, the above described method should be applicable to other systems, no matter whether the involved materials are thermosets, thermoplastics or inorganics, and no matter whether the application is in microfluidic channel sealing or other specialty bonding. The reason is that the required surface functionalization can be easily achieved on various materials and the amine–epoxide polyaddition reaction is simple and fast. For instance, N–H bond can be easily introduced onto a thermoset and thermoplastic surfaces by nitrogen or ammonia plasma treatment [14,15], while epoxy groups can be grafted onto a polymer surface through a free radical reaction using glycidyl methacrylate [16,17] or coupled to another metal oxide surface through the similar GOPS deposition process. Given that SU-8 microfluidic channels can be permanently sealed with nitrogen plasma-activated PDMS, it is hard to deny the possibility. As long as the functional groups on the two surfaces are sufficient, and one of the materials is soft enough, a strong bonding should be achieved between two solid materials. Our future research will focus on establishing the quantitative relationship between the surface concentration of the function groups and the associated bonding strength to guide the application.

4. Conclusions

In conclusion, open thermoset polymer microfluidic channels can be easily and permanently encapsulated or sealed by introducing an amine–epoxide polyaddition reaction into their closely contacted solid-to-solid interface with a lid. The reaction is enabled when the two involved solid surfaces are functionalized with amine groups and epoxy groups respectively, and one of the involved material is soft enough to conform itself onto the surface of another materials at an elevated processing temperature. While it was demonstrated in successfully sealing polydimethylsiloxane (PDMS) microfluidic channels with glass in a scalable and multifunctional fashion and sealing epoxy (SU-8) microfluidic channels with PDMS, the method is extendable to other materials and applications.

Acknowledgements

The authors would like to thank Simona Moisa and Zhenhua He for XPS analysis.

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