Lifetime Prolongation of Poly (dimethylsiloxane) Surface Modification via 2-Hydroxyethyl Methacrylate Grafting for Electroosmotic Flow

Eun-Soo Choi * and Sang-Sik Yang**

Abstract - To use Poly-dimethylsiloxane (PDMS) for the electrokinetic flow channel, the PDMS surface must be modified to be hydrophilic. With O_2 plasma treatment, it is difficult to maintain hydrophilicity for more than one day. In this paper, we present the chemical modification of the PDMS surface using 2-Hydroxyethyl methacrylate (HEMA) to prolong hydrophilicity lifetime. The oxide radicals generated temporarily on the PDMS surface by O_2 plasma are grafted with HEMA. Once the PDMS samples have been grafted, they demonstrate improved hydrophilicity retainment and electroosmotic flow characteristics compared to the untreated PDMS and the oxidized PDMS following the O_2 plasma process. This phenomenon was verified by the contact angles, Fourier transform infrared (FTIR) spectra and electroosmotic flow rates observed for more than 300 hours.

Keywords: electroosmotic flow, microfluidic, PDMS, surface modification

1. Introduction

Poly-dimethylsiloxane(PDMS)-based microfluidic devices can be fabricated simply and inexpensively by polymer casting using a mold [1], [2]. PDMS devices have rapidly acquired high popularity in the field of bio-chip and Lab-on-a-Chip due to such merits as transparency and biocompatibility. However, PDMS does have certain drawbacks such as extreme hydrophobicity, molecular adsorption onto the PDMS surface and so on [3]. Hydrophilicity is required for the electroosmotic flow (EOF). Including exposure to O_2 plasma, many other methods have been proposed to modify the PDMS surface, for example, other types of gas ($SiCl_4$, CCl_6) plasma, silanization, adsorbed coatings, and protein or lipid coatings. But exposure of the PDMS sample to oxygen plasma provides only a temporary reduction in contact angle. Protein-based coating frequently results in ill-defined patterns and heterogeneous surface properties as proteins are attached in a multiplicity of orientations with some molecules denatured and others folded [3]. Other plasma treatments using $SiCl_4$, CCl_6 and other surface coatings require difficult multistep procedures [4].

Against the recommended coatings above, we propose a new simple grafting method using 2-Hydroxyethyl methacrylate (HEMA). In previous researches related to PDMS, HEMA was generally used to make a copolymer grafted with PDMS and it causes structural changes in the bulk polymer. In this paper, however, only the modification of the surface property is concerned. The oxide radicals even on the surface of PDMS channels generated immediately after the oxygen plasma are bonded with the CH_2 groups in HEMA. In this paper, the modified surface is compared with the untreated surface and the surface after O_2 plasma treatment in terms of the contact angle, FTIR and the electroosmotic flow rate. In most BioMEMS applications, biocompatibility is one of the main requirements for the substrate material. HEMA has the necessary biocompatibility, transparency, and high mechanical strength. Samples or devices treated with HEMA can be applied to many fields including the biomedical area.

2. Sample Fabrication

For the fabrication of PDMS channels and specimens, Sylgard 184 (Dow corning) prepolymer is mixed thoroughly with its cross-linking catalyst and cured at 75°C for 3 hours. PDMS specimens for the contact angle test are immersed in a HEMA (Sigma Aldrich) solution for 6 hours, immediately following the oxygen plasma treatment. This HEMA solution is heated and stirred in a flask at 60°C with nitrogen gas pumped in. The oxide radicals generated temporarily on the PDMS surface during O_2 plasma treatment are grafted with HEMA. Then, the specimens are rinsed in deionized water at 40°C, stirred for 1 hour and dried in an oven. Some specimens were dried at 45°C and others at 80°C. We chose the two temperatures arbitrarily considering the boiling point of HEMA, which is 65°C.

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PDMS structure for the flow test is cured at 75°C for 3 hours on a SU-8 mold and the polymer layer is peeled off. The PDMS structure is bonded with hydrophilic glass following the oxygen plasma treatment. Subsequently, HEMA heated at 60°C is infused into the PDMS channel with a syringe for the modification of the surface structure. After grafting, the PDMS channel is rinsed with deionized water at 40°C and dried in a 45°C oven.

3. Measurement

At room temperature, a droplet of deionized water was placed on the PDMS surface, and the contact angle was measured with a contact angle measurement system. A BRUKER IFS 66/s spectrometer was used for attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. The detector splitter was a DTGR KBr combination providing a spectral range of 5000 - 6000 cm^{-1}. The KRS-5 crystal has the configuration of a trapezoid with two edges at 25°. The PDMS specimen was placed on a clamp and the absorbance spectrum was recorded with the resolution of a 4 cm^{-1} and 2283 scans were collected. A water spectrum in air was also recorded and subtracted from the PDMS spectra to remove the water peaks in the region from 3800 cm^{-1} to 3200 cm^{-1}.

4. Results and Discussion

Fig. 1 shows that oxygen radicals that are generated newly on the PDMS surfaces by O_2 plasma bond with hydrogen in the air. When the treated PDMS is dipped in the heated HEMA, the formed hydroxyl group is broken and the remaining oxygen bonds with CH_2, which is in the HEMA. Finally, the CH_2 group in HEMA is bonded on the PDMS surface. Thus, the hydrophilic groups are fixed on

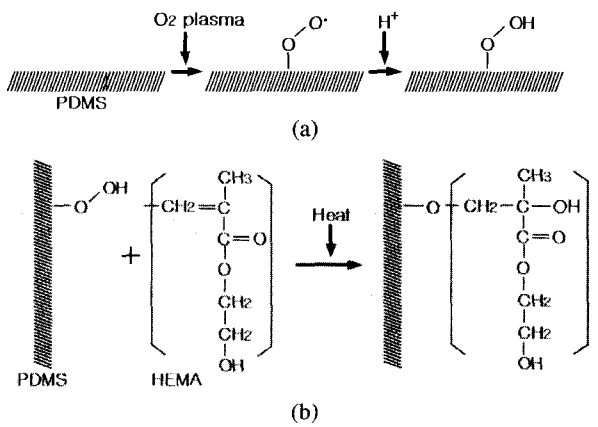

Fig. 1 The surface modification of PDMS surface. (a) O_2 plasma treatment (b) HEMA treatment

the PDMS surface. Fig. 2 shows each spectrum of the absorbance of the untreated PDMS surface and the HEMA-treated PDMS surface. The peak at 1729 cm^{-1} signifies the carbonyl group that is generated by dipping in heated HEMA after being exposed to oxygen plasma. The peak at 2904 cm^{-1} indicates the CH_2 group. The PDMS specimen dried at 45°C shows a larger magnitude of absorption than the one dried at 80°C in both the carbonyl and CH_2 group peaks.

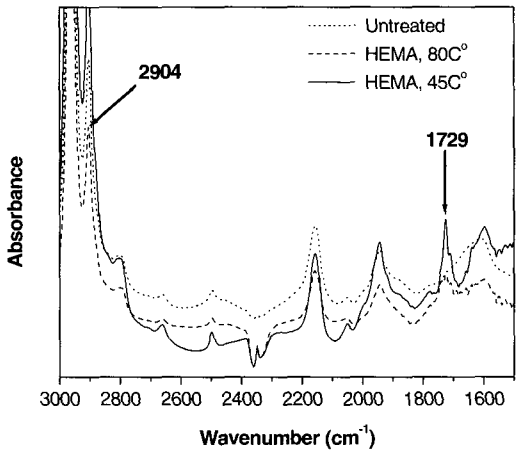

Fig. 2 The absorbance spectra of the untreated PDMS and two PDMS samples treated with HEMA.

Fig. 3 presents the contact angles of four PDMS surfaces treated under different conditions. The untreated PDMS shows high hydrophobicity. The surface of PDMS treated with oxygen plasma resumes hydrophobicity in about 30 hours. The HEMA-treated PDMS dried at 80°C has a larger contact angle than that dried at 45°C. From this phenomenon, it can be inferred that the activation energy is forfeited by drying at a temperature higher than the boiling point of HEMA. The PDMS that was treated with HEMA and dried at 45°C has the lowest contact angle and maintains the hydrophilicity over 300 hours.

Fig. 4 shows the EOF velocity of deionized water in the PDMS channels treated by two methods when 20 V/mm is applied. One method is the O_2 plasma treatment and the other is HEMA treatment at 45°C. After one day elapses, the EOF velocity saturates. This can be explained in terms of the chain mobility of HEMA. HEMA has two groups. The CH_2 group is hydrophobic and the OH group is hydrophilic. If the grafted surface is exposed to air after grafting, the hydrophilicity decreases because the hydrophilic group moves to the surface while the hydrophobic group moves into the air. Once the chain is stabilized, the contact angle and the flow velocity remain constant. The EOF velocity in the HEMA-treated PDMS channel is about three times that of the other one. It was

also confirmed that the treatment with HEMA at 45°C prevents cell adsorption.

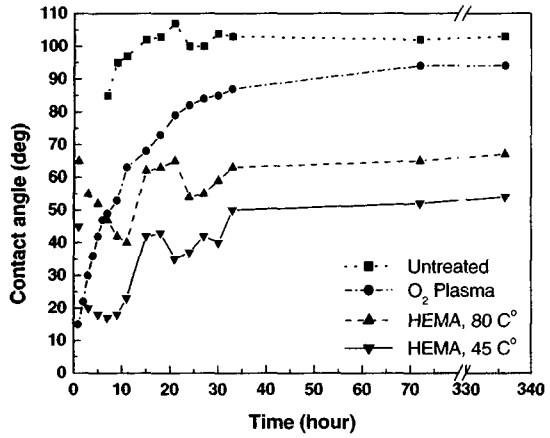

Fig. 3 Contact angles of PDMS surfaces after various treatments.

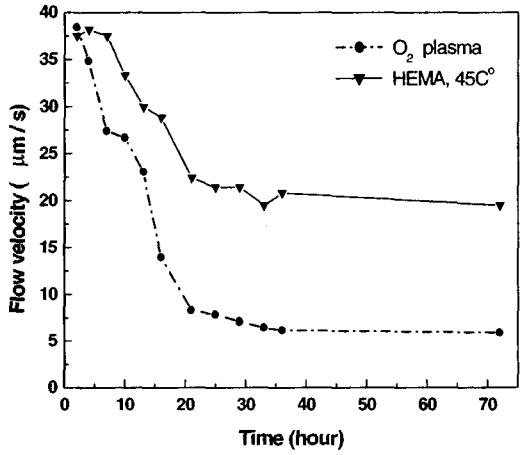

Fig. 4 The electroosmotic flow velocity in the PDMS channel after surface modification.

5. Conclusion

The chemical modification of PDMS with 2-Hydroxyethyl methacrylate achieves a hydrophilic channel surface through a simple procedure. This modification improves the electroosmotic flow characteristic by about three-fold. The acquired surface modification using HEMA is able to remain stable for over 300 hours. Further, the absorbance spectrum illustrates that the wettability of the surface treated with HEMA is mainly attributed to the carbonyl group. This surface modification with HEMA is very useful and yields various applications in the biomaterial field.

Acknowledgements

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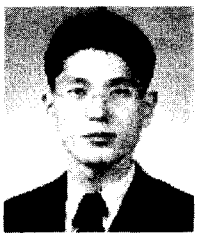
References

[1] Becker. H., Gartner. C., "Polymer Microfabrication Methods for Microfluidic Analytical Applications", *Electrophoresis*, vol.21, pp.12-36, 2000.

[2] Bruin, J. M., "Recent Developments in Electrokinetically Driven Analysis on Microfabricated Devices", *Electrophoresis*, vol.21, pp.3931-3951, 2000.

[3] Shuwen Hu, Xueqin Ren, Mark Bachman, Christopher E. Sims, G. P. Li and Nancy Allbritton, "Surface Modification of Poly (dimethylsiloxane) Microfluidic Devices by Ultraviolet Polymer Grafting", *Anal. Chem.*, vol.74, pp.4117-4123, 2002.

[4] S. D. Gillmor, B. J. Larson, J. M. Braun, C. E. Mason, L. E. Cruz-Barba, F. Denes and M. G. Lagally, "Low-contact-angle Polydimethyl Siloxane (PDMS) Membranes for Fabricating Micro-bio Arrays", *2nd Annual International **IEEE-EMBS** Special Topic Conference on Microtechnologies in Medicine & Biology*, Madison, pp.51-56, 2002.



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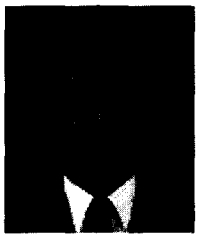

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