One-step surface modification of poly(dimethylsiloxane) by undecylenic acid

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ABSTRACT

Poly(dimethylsiloxane) (PDMS) is a popular material for microfluidic devices due to its relatively low cost, ease of fabrication, oxygen permeability and optical transmission characteristics. However, its highly hydrophobic surface is still the main factor limiting its wide application, in particular as a material for biointerfaces. A simple and rapid method to form a relatively stable hydrophilised PDMS surface is reported in this paper. The PDMS surface was treated with pure undecylenic acid (UDA) for 10 min, 1 h and 1 day at 80 ºC in a sealed container. The effects of the surface modification were investigated using water contact angle (WCA) measurements, Fourier transform infrared spectroscopy in attenuated total reflection mode (FTIR-ATR), and streaming zeta-potential analysis. The water contact angle of 1 day UDA-modified PDMS was found to decrease from that of native PDMS (110 º) to 75 º, demonstrating an increase in wettability of the surface. A distinctive peak at 1715 cm^{-1} in the FTIR-ATR spectra after UDA treatment was representative of carboxylation of the PDMS surface. The measured zeta-potential (ζ) at pH 4 changed from -27 mV for pure PDMS to -19 mV after UDA treatment. In order to confirm carboxylation of the surface visually, Lucifer Yellow CH fluorescence dye was reacted via a condensation reaction to the 1 day UDA modified PDMS surface. Fluorescent microscopy showed Lucifer Yellow CH fluorescence on the carboxylated surface, but not on the pure PDMS surface. Stability experiments were also performed showing that 1 day modified UDA samples were stable in both MilliQ water at 50 ºC for 17 h, and in a desiccator at room temperature for 19.5 h.

Keywords: Poly(dimethylsiloxane) (PDMS); microfluidic devices; biointerfaces; surface wettability; zeta-potential analysis; fluorescence dye.

1. INTRODUCTION

Silicon, glass and polymers are the mainstream substrates used for microfluidic devices. Both Henares et al.[1] and Zhang et al.[2] reviewed the advantages and disadvantages of these three materials. The two biggest advantages of silicon are its superior thermal conductivity and the availability of advanced fabrication technology for microstructures adopted from the electronics and semiconductor industry. However, silicon is not optically transparent, which prevents simple transmission optical detection in silicon channels. Alternatively, glass substrates possess well-defined surface chemistries, good electroosmotic flow (EOF) characteristics and superior optical transparency. However, the costly fabrication facilities for silicon and glass limit their commercialisation potential. Considering cost, time and labor, polymers appear more attractive for microfluidic devices. Poly(dimethylsiloxane) (PDMS) is a moldable silicon-based rubber and has various advantages over other polymeric systems, including biocompatibility, gas permeability, optical transparency, ease of molding into (sub)micrometer features and bonding, relative chemical inertness, and low manufacturing costs which allows the material to be disposable.[3, 4] The biggest problem with pure PDMS surfaces is that they are hydrophobic, which causes other hydrophobic species to be adsorbed onto its surface. This is a problem which is exacerbated by the high-surface-to-volume ratio of the microchannel. This inhibits EOF and hence surface modifications must be carried out to inhibit non-specific adsorption of proteins and improve EOF in PDMS microfluidics. Makamba et al.[5] provided a comprehensive review on PDMS surface modification while Abbasi et al.[6] have reviewed the modification of PDMS for biomedical applications.

There are various surface modification techniques available to render the PDMS surface more hydrophilic, including physical and chemical techniques. The most common physical methods are plasma and laser treatment, such as UV/ozone treatment[7, 8] and oxygen plasma.[9] However the hydrophilic surfaces formed by exposure to the oxygen

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plasma are short-lived. In order to control this, many researchers reported placing the modified surfaces into water or polar solvents to maintain the hydrophilicity. [10, 11] A two-step plasma modification using O_2 and C_2F_2[9] was also reported to increase the lifetime of the hydrophilic surface. With the exception of surface modification by physical technologies, chemical techniques are also widely used to modify PDMS surfaces. Hong et al.[12] filled a PDMS microchannel with concentrated HCl solution at 25 ºC for 4 h to create a hydrophilic surface. Subsequently, 150 μg/mL bovine serum albumin (BSA) was introduced to prevent non-specific adsorption. Fukuba et al.[13] introduced a 2-methacryloyloxyethyl phosphorylcholine (MPC)-based polymer with a silane coupler into microchannels and thermally polymerised the MPC-based polymer onto the PDMS surface. Sibarani et al.[14] used two phospholipid polymers, poly(2-methacryloyloxylethyl phosphorylcholine (MPC)-co-n-butyl methacrylate) (PMB) and poly(MPC-co-2-ethylhexyl methacrylate-co-2-(N,N-dimethylamino)ethyl methacrylate) (PMED) to coat PDMS surfaces by a solvent evaporation method. The above modifications were all carried out before operation of the respective microfluidic devices. However Kim et al.[15] added 2.5 % polyvinylpyrrolidone (PVP) to a polymerase chain reaction mixture as a dynamic coating material to achieve modification during the device operation. Similarly, Garcia et al.[16] added three different anionic surfactants, sodium dodecylsulphate (SDS), sodium deoxycholate (DOCh) and phosphatidic acid (PA) into the EOF running buffer for dynamic surface modification of PDMS and found a significant increase in the EOF.

In order to obtain a more effective and stable hydrophilic PDMS surface, many researchers have combined physical and chemical techniques together. Khorasani et al.[17] modified a PDMS surface by CO_2-pulsed laser induced graft polymerisation of 2-hydroxyethyl methacrylate (HEMA). Bodas et al.[18] spin coated HEMA onto a O_2 plasma pretreated PDMS surface and applied another O_2 plasma treatment after coating. In this case the contact angle of the modified PDMS still increased after treatment from 7 º to 49 º after 2 weeks, however this is still more hydrophilic than pure PDMS. Xiao et al.[19] exposed a PDMS surface to acrylamide by atom-transfer radical polymerisation (ATRP) after the treatment of PDMS with UV/ozone. The modified surface was stable for up to 4 weeks. Lee et al.[20] and Wu et al. [21] reported similar methods to modify PDMS surfaces where poly(L-lysine)-graft-poly(ethylene glycol) (PLL-g-PEG) and three epoxy-modified polymer, including poly(dimethylacrylamide-co-glycidyl methacrylate) (PDMA-co-GMA), poly(vinyl pyrrolidone)-g-glycidyl methacrylate (PVP-g-GMA) and poly(vinyl alcohol)-g-glycidyl methacrylate (PVA-g-GMA) were absorbed from aqueous solution onto O_2 plasma pretreated PDMS surfaces.

In recent years, it has been demonstrated that PDMS surfaces can be hydrophilised by some metals and metal oxides.[22-24] Niu et al.[22] coated titanium dioxide (TiO_2) onto a PDMS surface and showed that the contact angle changed from 105 º to 25 º and that protein adsorption was greatly reduced. Feng et al.[23] reported that sputtering gold onto a PDMS surface resulted in a water contact angle decrease of approximately 25 º. Zhang et al.[24] synthesised PDMS-gold nanoparticle composite films for biochemical analysis on microchips. These approaches turn the modified PDMS opaque which is a disadvantage for applications in microfluidic devices.

Aside from surface modification, some research groups[25, 26] have carried out work on bulk modification, which is also aimed at obtaining a hydrophilic surface. Seo et al.[25] have added a nonionic surfactant (TX-100) to PDMS prepolymer and found water wettability was enhanced and that the wettability could be easily controlled by changing the initial concentration of TX-100. Xiao et al.[26] used the amphiphilic biocompatible copolymer poly(lactic acid)-poly(ethylene glycol) (PLA-PEG) as an additive to modify bulk PDMS and successfully suppressed the adsorption of myoglobin onto the PDMS surface. Luo et al.[27] added 0.5 wt% undecylenic acid (UDA) to PDMS prepolymer before curing and also used n-dodecyl β-D-maltoside (DDM) as a dynamic coating to improve EOF.

In this work, we present a cheap, easy and highly repeatable surface modification for PDMS which involves coating pre-cured PDMS with a thin film of UDA with subsequent heat treatment to induce hydrosilylation. UDA-modified surfaces were characterised by means of water contact angle (WCA) measurements, Fourier transform infrared spectroscopy in attenuated total reflection mode (FTIR-ATR) and zeta-potential analysis. Fluorescence labeling and stability experiments were also performed. The results showed that modified PDMS surfaces became more hydrophilic compared to pure PDMS and that carboxylation of the PDMS surface was achieved.

2. EXPERIMENTAL SECTION

2.1 Material

PDMS Sylgard 184 (Dow Corning Corporation, USA) was purchased as a two-component kit, including pre-polymer (base agent) and cross-linker (curing agent) components. Lucifer Yellow CH dipotassium salt was purchased from Invitrogen, USA. All other chemicals were purchased from Sigma-Aldrich, USA.

2.2 Surface modification

In this study, the two components of Sylgard 184, base and curing agent (10:1 weight ratio) were thoroughly mixed and degassed by applying a gentle vacuum to remove air bubbles. The mixture was then poured onto a clean microscope slide and cured at 80 ºC for 3 h. After curing and immersing in MilliQ water for 2 h, the pure PDMS was peeled off the slide. The pure PDMS was rinsed with MilliQ water, then ethanol and dried under a stream of nitrogen. This cleaned PDMS was then placed in a sealed glass container with enough undecylenic acid (UDA) to thinly coat the bottom surface of each sample. The UDA coated PDMS was kept in an oven at 80 ºC for 10 min, 1 h and 1 day, respectively. After modification, the samples were cleaned by ultrasonication for 10 min in MilliQ water, 20 min in 50 % ethanol and then a further 10 min in MilliQ water. Finally, the modified samples were dried under a stream of nitrogen. Samples were stored in either air or MilliQ water from 0 to 30 days.

2.3 Surface characterisation of the modified PDMS

WCA: The static WCA was measured using the sessile drop method by placing a small drop (2 μL) of MilliQ water onto the sample surface via a syringe, a digital image of which was taken by a Panasonic SuperDynamic WV-BP550/G camera with a macrolens. The image was processed by ImageJ software V1.34. All reported water contact angles are the average value of five measurements on different parts of the sample.

FTIR-ATR: FTIR-ATR was carried out on a Thermo-Nicolet Nexus 870. 64 scans were taken at room temperature and atmospheric pressure with a resolution of 4 cm^{-1}. The data was collected from 625 to 4500 cm^{-1}, and analysed using OMNIC version 7.0 software.

Streaming zeta-potential analysis: Zeta potential data were obtained using a ZetaCAD instrument equipped with an RS232C bi-directional interface as well as a programmable in/out board for automation of the measurements with the aid of a Keithley 2400 high accuracy multimeter. The approach by Mizadeh et al.[28] was adapted where 1 mM potassium chloride was used as a background electrolyte in all experiments. 0.1 M potassium hydroxide and 0.1 M hydrochloric acid was used for pH adjustment. The pure PDMS and 1 d modified samples were immersed in the electrolyte solution overnight to equilibrate the samples. The measurements were carried out at pH 4 and pH 12 at room temperature. The measurements were repeated three times and the results were averaged.

Fluorescence labeling study: 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDAC) and Lucifer Yellow CH dipotassium salt dye were dissolved in MilliQ water (0.4 M EDAC and 1 mg/mL dye). Pure PDMS and modified PDMS samples were immersed into the EDAC/dye solution for 4 h at room temperature after which time they were removed and rinsed with MilliQ water, then ethanol and dried under a stream of nitrogen. The reacted samples were investigated under a fluorescence microscope (Leitz Laborlux fluorescence microscope).

Stability experiment: Modified PDMS samples were kept in MilliQ water at 50 ºC and in PBS buffer (50 mM phosphate, 10 mM EDTA, 0.15 M of NaCl, pH 7.2) at room temperature, respectively to investigate the stability of the surface modification. FTIR-ATR spectra were obtained after 3 h and 17 h to analyse the carboxyl group peak on the modified PDMS surface. Samples were also characterised by FTIR-ATR after storing in a desiccator for 5.5 h and 19.5 h, respectively.

3. RESULT AND DISCUSSION

3.1 WCA results

Fig.1 shows contact angles of the pure PDMS, 10 min, 1 h and 1 d UDA-modified PDMS, which were kept in air or MilliQ water. Pure PDMS shows a WCA of ~110 º in both air and MilliQ water, which remains constant even when the surface is aged for up to 30 days in both media. After 10 min, 1 h and 1 d UDA-modification, the WCA decreased to ~93 º, ~86 º and ~77 º, respectively. The WCA of every sample was measured after 5 d, 10 d, 20 d, 25 d, and 30 d of storage in air and MilliQ water. Over this timeframe, the WCA stayed relatively constant. Whilst not as hydrophilic as a PDMS modified by oxygen plasma,[9] the UDA-modified PDMS surface was significantly more stable in both air and MilliQ water. This implies that in all cases there is little surface rearrangement taking place.

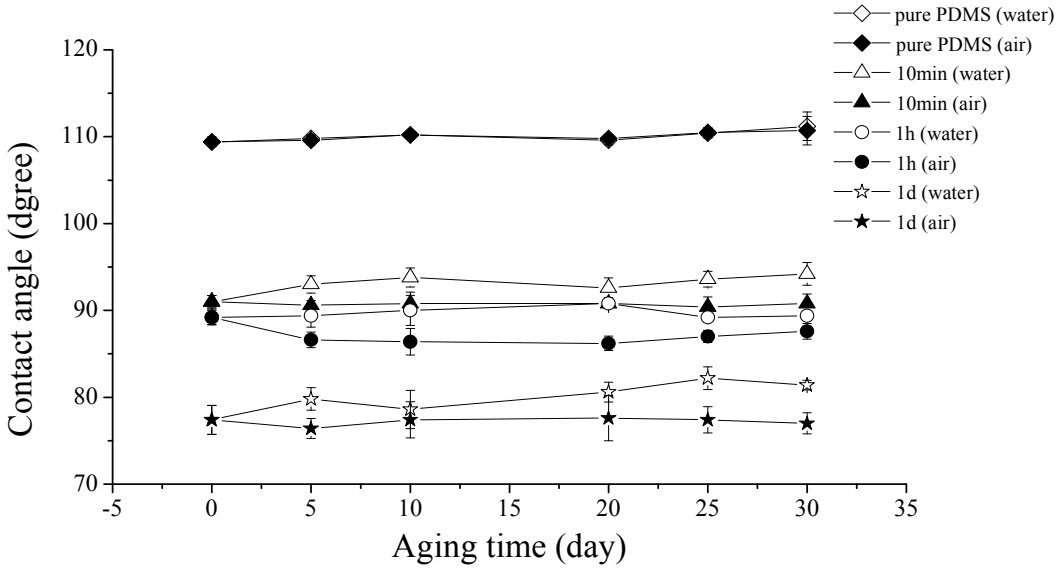


Fig.1. WCA vs. aging time for pure PDMS and UDA-modified PDMS. The samples were stored in air (filled symbols) and in MilliQ water (empty symbols). Diamond: pure PDMS; triangle: 10 min UDA-modified PDMS; circle: 1 h UDA-modified PDMS; pentagram: 1 d UDA-modified PDMS.

3.2 FTIR-ATR

FTIR-ATR was carried out to confirm the functionalisation of the PDMS surface with UDA. Fig.2. shows the spectra of pure PDMS, 10 min, 1 h and 1 d modified PDMS. The spectrum of pure PDMS (Fig.2a) is in accordance with previous publications.[8, 9] From Fig.2, it is very clear that pure PDMS and UDA-modified PDMS have different spectral features in the region 1600-1800 cm^{-1}. A characteristic peak at 1715 cm^{-1} corresponding to carboxyl group is observed in the spectrum of UDA-modified PDMS, and the intensity of the peak increased with the treatment time (see Fig.2 inset).

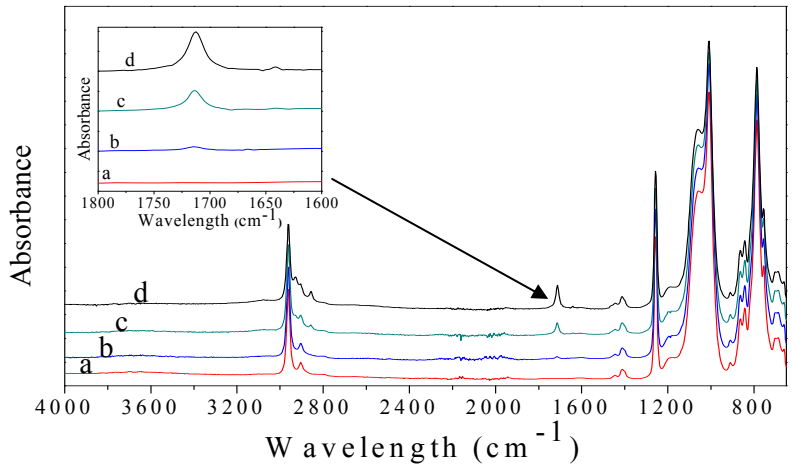


Fig.2. FTIR-ATR spectra of (a) Pure PDMS, (b) 10 min UDA-modified PDMS, (c) 1 h UDA-modified PDMS, and (d) 1 d UDA-modified PDMS.

3.3 Streaming zeta-potential analysis

Fig.3 shows the results of the average zeta potential at pH 4 and pH 12 for pure PDMS, and 1 d UDA-modified PDMS. For pure PDMS, the zeta potential changed from -26.70±0.43 mV at pH 4 to -38.30±1.35 mV at pH 12. This change may

be due to deprotonation of the surface Si-OH groups on the pure PDMS surface at high pH and/or physisorbed cations within the Stern layer.[29] For 1 d UDA-modified PDMS, the zeta potential at pH 4 was -18.88±1.35 mV, compared to -26.70±0.43 mV for pure PDMS at the same pH. This difference was caused by the presence of the protonated carboxyl-terminal moieties from the UDA which are now present on the hydrosilated PDMS surface. Fig.4 (a and b) shows the FTIR-ATR spectra of the 1 d UDA-modified PDMS before and after zeta potential analysis, respectively. The surface appears to be stable at pH 4 with the carboxyl groups clearly remaining (see Fig.4 (a and b) inset). At higher pH, that is pH 12, Fig.3 shows that the zeta potential becomes more negative than at pH 4, changing from -18.88±1.35 mV to -34.24±1.42 mV. This value is very close to that of native PDMS (-38.30±1.35 mV) at pH 12, indicating that the carboxyl groups are no longer present at this pH. It would be expected that the carboxyl groups still remaining are deprotonated at high pH which would result in a far more negative zeta potential than native PDMS. To verify the presence of carboxyl groups at pH 12 Fig.4 (c) shows the FTIR-ATR spectrum. Fig.4 (c) clearly shows the disappearance of the COOH stretching peak at pH 12, strongly suggesting that the surface modification is unstable at highly alkaline pH.

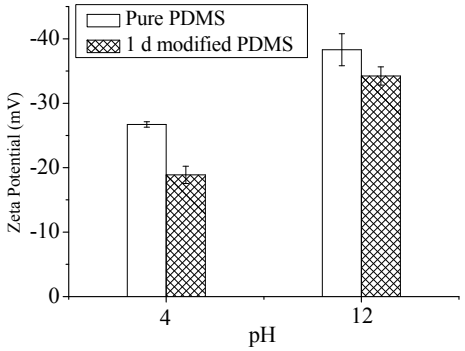


Fig.3. Zeta potential measurements of pure PDMS and 1 d UDA-modified PDMS at pH 4 and pH 12. (n=3).

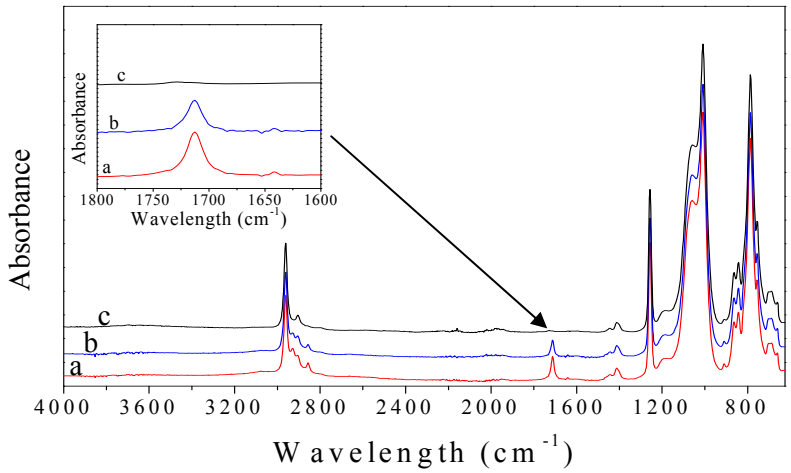
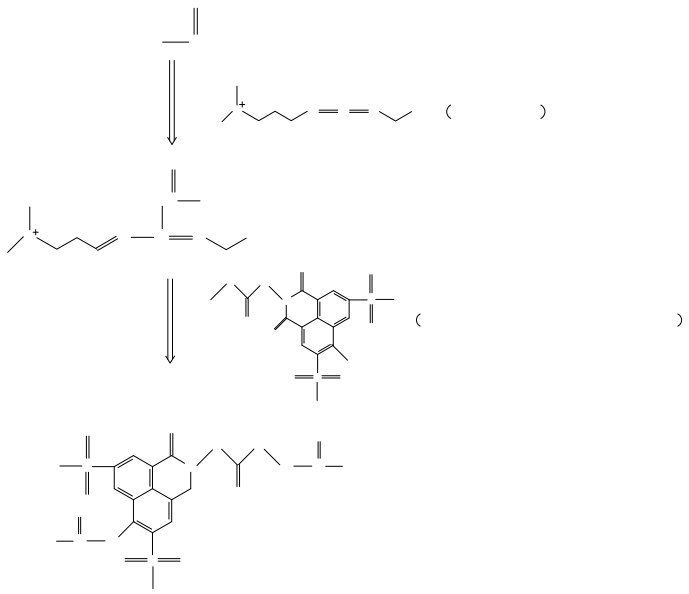
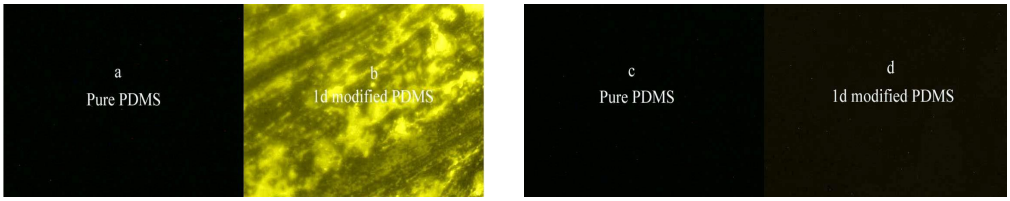


Fig.4. FTIR-ATR spectra of (a) 1 d UDA-modified PDMS before zeta potential analysis, (b) 1 d UDA-modified PDMS after zeta potential analysis at pH 4, and (c) 1 d UDA-modified PDMS after zeta potential analysis at pH 12.

3.4 Fluorescence labeling study

To demonstrate the presence of reactive carboxyl functional groups on the PDMS, Lucifer Yellow CH was coupled to the carboxyl groups on the UDA-modified PDMS using EDAC. Fig.5 shows the reaction scheme. Carboxyl groups on the 1 d UDA-modified PDMS surface were reacted with amino groups on Lucifer Yellow CH dipotassium salt via a condensation reaction.





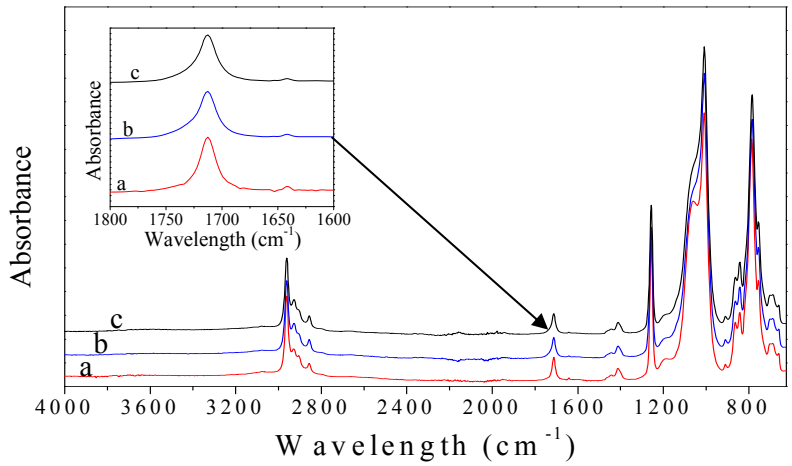


Fig.7. FTIR-ATR spectra of (a) 1 d UDA-modified PDMS before treatment, (b) 1 d UDA-modified PDMS after immersion in MilliQ water for 3 h at 50 ºC, and (c) 1 d UDA-modified PDMS after immersion in MilliQ water for 17 h at 50 ºC.

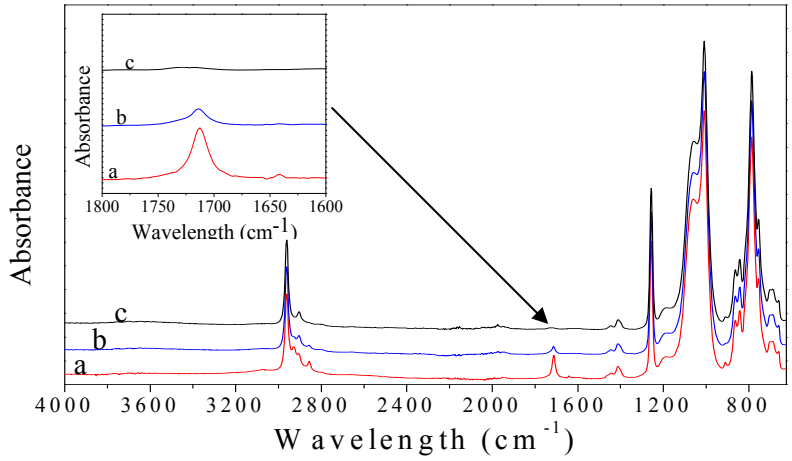


Fig.8. FTIR-ATR spectra of (a) 1 d UDA-modified PDMS before treatment, (b) 1 d UDA-modified PDMS after immersion in PBS buffer (pH 7.2) for 3 h at 50 ºC, and (c) 1 d UDA-modified PDMS after immersion in PBS buffer (pH 7.2) for 17 h at 50 ºC.

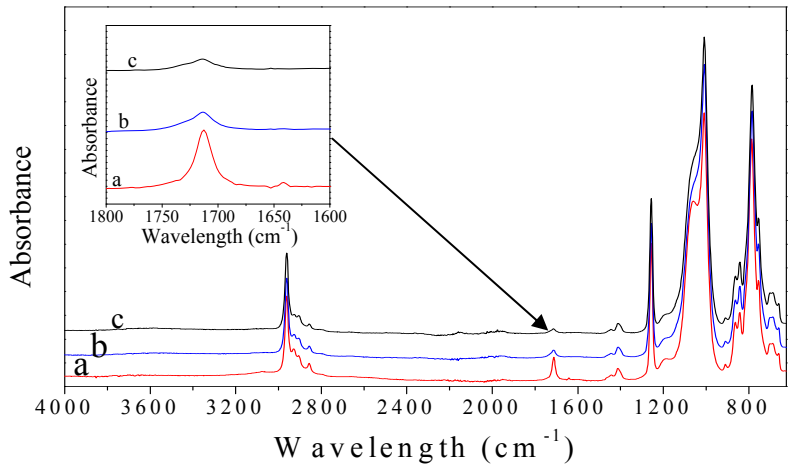


Fig.9. FTIR-ATR spectra of (a) 1 d UDA-modified PDMS before treatment, (b) 1 d UDA-modified PDMS after immersion in PBS buffer (pH 7.2) for 3 h at room temperature; (c) 1 d UDA-modified PDMS after immersion in PBS buffer (pH 7.2) for 17 h at room temperature.

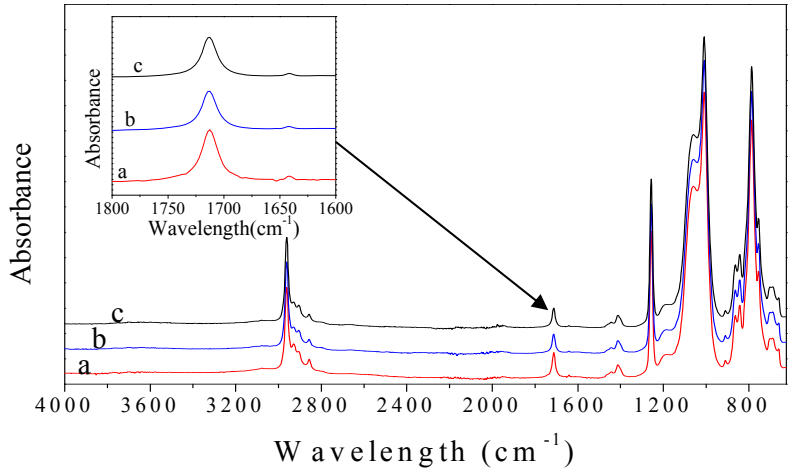


Fig.10. FTIR-ATR spectra of (a) 1 d UDA-modified PDMS before treatment, (b) 1 d UDA-modified PDMS stored in a desiccator for 5.5 h; (c) 1 d UDA-modified PDMS stored in a desiccator for 19.5 h.

4. CONCLUSION

In this study, a simple one-step surface modification of PDMS was demonstrated. The increase in hydrophilicity of the UDA-modified PDMS was confirmed by water contact angle data. The characteristic vibrational band corresponding to the carboxyl stretch of carboxylic acids at 1715 cm^{-1} was found in the FTIR-ATR spectrum of the UDA-modified PDMS. The difference in the streaming zeta potential at pH 4 between pure PDMS and 1 d UDA-modified PDMS further confirmed UDA attachment to the PDMS surface. The fluorescence labeling via a condensation mechanism with Lucifer Yellow CH further demonstrated carboxyl-modified PDMS, however this attachment was unstable in ethanol. The surface was shown to be stable for up to 30 days in MilliQ water but not appropriate for PBS buffer based systems or high pH's. While the results show carboxyl modification of a PDMS surface, further improvement on the method is required in order to enhance the stability of the surface for applications in microfluidic devices.

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