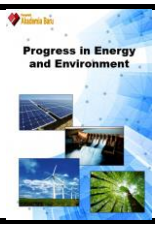
Penerbit Akademia Baru

Progress in Energy and Environment

Journal homepage: http://www.akademiabaru.com/progee.html
ISSN: 2600-7762



Wettability Study of Chitosan Droplet on Surface-Modified PDMS for Microfluidics Application

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ARTICLE INFO

Article history:
Received 24 February 2020
Received in revised form 21 April 2020
Accepted 21 April 2020
Available online 23 April 2020

ABSTRACT

Polydimethylsiloxane (PDMS) is a common polymer used in microfluidics application due to its flexibility and ease in fabrication. Chitosan coated on the inner wall of photocatalytic microfluidic device works as a strong adsorbent in wastewater pollution remediation process. However, there was a problem with its native hydrophobicity of the polymer, which prevents the microchannel from having a high wettability surface property for a material coating. To modify the hydrophobic PDMS surface to hydrophilic characteristic, many researchers would use oxygen plasma technique which requires costly equipment in the treatment process. This current work uses a two-step chemical treatment, piranha solution and potassium hydroxide solution, to modify the hydrophobic native PDMS surface to hydrophilic surface-modified PDMS. In corresponding to the hydrophilicity analysis, the wettability of chitosan droplet on the surface-modified PDMS was studied by conducting sessile drop technique and compared the wettability of chitosan droplet on the surface-modified PDMS against the native PDMS. The chitosan pH value is a significant effect on its adsorption property. Thus, chitosan droplet at various pH value (pH 4.0, pH 4.5, pH 5.0, pH 5.5, and pH 6.0) had been used to test the wettability of the surface-modified PDMS. The contact angle of more than 90° is known to be hydrophobic, and contact angle less than 90°, is known to be hydrophilic. Results obtained the best wettability property was shown at 15 minutes of curing time (compared to treatment time of 1 minute, 5 minutes, 10 minutes, and 20 minutes). The surface-modified PDMS was proven to be hydrophilic, hence, showing it to be a great choice when chitosan is to be coated on the inner wall of the microchannel surface.

Keywords:
Polydimethylsiloxane, Wettability study, Chitosan droplet, Microfluidics application

1. Introduction

Over a few decades ago, numerous studies were conducted on microfluidics, where glass and silicon were the first commonly used based materials [1]. However, through the years, scientists have discovered that the use of glass and silicon in the production of microfluidics devices caused them time, money, and inconvenience due to the photolithography process, where a cleanroom facility is

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needed. Moreover, the use of glass and silicon in microfluidics was incomparable to the use of polymers as glass and silicon have limitations such as limited biocompatibility, natural stiffness, fragility, and inflexibility. Therefore, the focus has turned to the use of polymeric substrates such as polymethylmethacrylate (PMMA), polyvinylchloride (PVC), polycarbonate (PC), polystyrene, polyurethane, and polydimethylsiloxane (PDMS) in the production of the microfluidic device [2].

Polydimethylsiloxane (PDMS) is a member of the siloxane family, derived mainly from silicon, oxygen, and alkane. PDMS generally has a carbon and silicon structure that makes it a mineral-organic polymer [3]. With its ease of fabrication through soft lithography technique, and its numerous advantages such as elasticity, non-toxicity, and optical clarity of up to 280 nm [1,2,4,5], it becomes a very common elastomer used in microfluidics application. During the fabrication of PDMS, the polymers become highly cross-linked and transform into a hydrophobic elastomer, causing a struggle for polar solvents to spread and wet the surface of PDMS. In return, water beads will be forms and adsorption of hydrophobic components will occur on the surface of PDMS. This condition would result in fouling of PDMS in microfluidics application, decreasing the output efficiency of PDMS systems in microfluidics application, causing sample loss and disrupting the experimental outcomes [6,7].

Currently, oxygen plasma treatment is a common technique used by many researchers to convert PDMS properties from hydrophobic to hydrophilic. However, this technique only renders the surface-modified PDMS hydrophilic for a few hours, and the sample had to be used immediately after the treatment [4]. Apart from plasma treatment, corona discharger, "grafted-to", and "grafted-from" methods were also used to treat the PDMS samples [6-10]. Unfortunately, most of it requires either costly equipment or costly chemicals. Therefore, in this project, the surface-modification of PDMS was aimed to be accomplished by using basic chemicals and equipment which are readily available in the laboratory. Hence, a two-step chemical treatment was used to treat the PDMS sample, which is a piranha solution (a mixture of sulphuric acid and hydrogen peroxide) and a potassium hydroxide solution. When sulphuric acid is mixed with hydrogen peroxide; it produces a reactive oxygen atom that reacts with the methyl group in the siloxane polymer. Hence, giving a vacant area for the hydroxyl ions to be attached to the production of silanol groups. Potassium hydroxide solution then spreads the hydroxyl ions over the surface of the PDMS sample to create an even hydrophilic PDMS modified surface [11,12].

Chitosan is a nitrogenous polysaccharide which is produced in large quantities by N-deacetylation of chitin. Chitosan is a promising material because of its biocompatibility, low cost, biodegradability and high adsorption capability [13-15]. Numerous papers have been published regarding the use of chitosan as biocompatible polymer and coatings in microfluidic application [16-19]. The chitosan pH value is significant in its adsorption capability; chitosan adsorbed mass is low at pH under 6.0 [20]. Chitosan has excellent film-forming properties, but its hydrophilic nature limits some of its applications. Therefore, some research works have been performed to modify the chitosan from hydrophilic to hydrophobic [21]. Further studies were needed to investigate the effect of chitosan pH value towards its wettability over PDMS surface.

To observe the hydrophilicity of the surface-modified PDMS, the PDMS was treated at various times, chitosan droplet of different pH was used, and contact angle analysis was conducted. The wettability property was then compared between surface-modified PMDS with the native PDMS.

2. Methodology and Experimental Setup

2.1 *Materials*

Sylgard 184 PDMS base elastomer and curing agent was purchased from Dow Corning Corporation. Chemicals such as sulphuric acid (H_2SO_4, 95% - 97% Grade AR) and potassium hydroxide pellets (KOH) were purchased from Friendemann Schmidt Chemicals. Hydrogen peroxide (H_2O_2, 30% purified) was purchased from R&M Chemicals. Chitosan of medium molecular weight

was used as a solution droplet for contact angle analysis, and it was purchased from Sigma-Aldrich. Pure acetic acid was used to dilute the chitosan powder, and it was purchased form Friendemann Schmidt Chemicals.

2.2 *Preparation of Chitosan Solution*

Acetic acid 0.1 M was prepared by mixing 100% of acetic acid with distilled water. The chitosan powder at 0.3 g was then mixed with acetic acid in a 250 mL beaker, using a magnetic stirrer bar and a digital stirrer hot plate for 30 minutes. Once it was utterly homogenized, dilute water was added into the mixture to adjust at desired pH value, which is pH 4.0, pH 4.5, pH 5.0, pH 5.5, and pH 6.0.

2.3 *Fabrication of PMDS Samples*

PDMS liquid mixture was prepared by mixing the Sylgard 184 elastomer base with curing agent using the ratio of 10:1 (w/w), thoroughly in a stainless-steel cup for 10 minutes. The liquid mixture was then transferred into a petri dish and placed into the desiccator for 15 minutes to eliminate any bubbles formed during the mixing process. Before putting it into the convection oven at 65°C for 16 hours, the desiccated PDMS liquid mixture in the petri dish was rotated manually to ensure even surfaces were obtained. As for surface-modified PDMS, the petri dish was coated and dried with piranha solution first before PDMS liquid mixture was placed into it for fabrication purposes.

2.4 *Piranha Solution and Potassium Hydroxide Solution Treatment*

The sulphuric acid (H_2SO_4) was mixed with the hydrogen peroxide (H_2O_2) in the ratio of 3:2 to produce piranha solution. 30 mL of the sulphuric acid was poured into a beaker placed onto a hot plate stirrer and stirred for 400 rpm. The remaining 20 mL of hydrogen peroxide was then added into the beaker containing sulphuric acid, slowly to avoid any sudden introduction of the two chemicals. 1M of potassium hydroxide (KOH) solutions was prepared by taking 14.02 grams of KOH pellets and mixing it with distilled water in a 250 mL volumetric flask. The treatment started with PDMS samples soaking in the beaker containing piranha solution, followed by a rinse with distilled water, before dipping it into the KOH solution with the equal amount of time immersed in the piranha solution. The treatment time varied from 1 minute, 5 minutes, 10 minutes, 15 minutes, and 20 minutes.

2.5 *Surface Wettability Study*

Sessile drop experiment was conducted using the SEO Phoenix 300 Touch Manual Contact Angle Analyzer that equipped with the Surfaceware 8 software to observe the resultant contact angle of the chitosan droplet onto the surface-modified PDMS samples. The PDMS samples were sized at 2.5 cm × 2.5 cm (± 0.3 cm). Chitosan droplets were obtained by using a 5 mL syringe with a 0.5 mm diameter needle. The PDMS samples were placed on a cleaned glass microscope slide, and the camera attached to SEO Phoenix 300 Touch Manual Contact Angle Analyzer was adjusted to focus on the surface of the sample until a drop of chitosan was obtained, by manually pressing on the syringe. Three drops of chitosan solution were randomly placed on the PDMS samples, and the average contact angle reading was calculated out.

3. Results and Discussion

3.1 *Piranha Solution and Potassium Hydroxide Solution Treatment*

When the piranha solution was prepared, hydrogen peroxide was added into the sulphuric acid solution and never vice versa. It is due to the solution concentration variations, where a small amount of concentrated sulphuric acid will induce a vigorous reaction in a beaker of active hydrogen peroxide. Hence, to prevent any excess vapour from forming and explosive reaction, hydrogen peroxide is always added into the beaker of sulphuric acid. Besides, the rate of adding hydrogen peroxide to sulphuric acid should be slow. If both were introduced with a short amount of time, the reaction would be vigorous.

The PDMS samples were cut into 2.5 cm × 2.5 cm (± 0.3 cm), before treatment in the piranha solution. This cut sample ensures even surface modification of the whole PMDS. However, there was still uneven treatment on the PDMS surface due to hydrophilic modification occurring in the middle of the treatment procedure. This condition then leads the PDMS surface to bind to each other, causing the surface to be unmodified. Potassium hydroxide solution acts as a surfactant in this treatment, where the hydroxyl ions are spread evenly across the entire PDMS surface. The potassium hydroxide solution contributes to the hydrophilicity of the PDMS samples, which benefits in the contact angle analysis.

3.2 *Surface Wettability Study*

Figure 1(a) to 1(f) show the graph of contact angle versus pH of chitosan droplet on native PDMS and on surface-modified PDMS at 1 minute, 5 minutes, 10 minutes and 20 minutes respectively. Three readings of contact angle were recorded later the average value of the contact angle for each treatment time was calculated. Different PDMS samples were used per pH of chitosan droplets, as repetitive usage of PDMS samples with different pH of chitosan droplet can cause a formation of an external hydrophilic layer on top of PDMS samples itself. This alternate the results obtain which can be a false result, as the property tested was merely based on the external hydrophilic chitosan droplet formed instead of the surface property of PDMS samples. The average values of contact angle were summarized in Table 1.

Figure 2 shows the graph of contact angle versus treatment time according to chitosan droplet pH value. When the contact angle obtained is greater than 90°, it is known to be hydrophobic, and when the contact angle attained is less than 90°, it is known to be hydrophilic [8,22]. Hence, the optimal result of contact angle was obtained by surface-modified PDMS when it was treated for 15 minutes, as all pH of chitosan droplet were below 90°. Therefore, rendering the entire PDMS surface to be hydrophilic.

The average contact angle of chitosan droplet on the native PDMS is used as a control in this experiment. Based on the average contact angle results of the control, it was shown that the pH 4.5 and pH 5.0 solution of chitosan showed a hydrophilic characteristic of the native PDMS. Using this observation in the field of microfluidics, it will have a high wettability in the microchannel, either in creating microbeads or having to coat the microchannel and treat it as an anchor layer to attach more hydrophilic solution. Meanwhile, for pH 4.0, pH 5.5, and pH 6.0 of chitosan droplet solutions, each of it showed hydrophobic contact angle results (more than 90°) that are common in native PDMS. However, the average contact angle readings of chitosan were slightly lower than the average contact angle of the distilled water droplet on the native PDMS, which is 110°. Therefore, this shows that chitosan droplet solution was more hydrophilic by nature, compared to distilled water.

Based on the average contact angles obtained by treating the surface-modified PDMS for 1 minute, pH 4.0 and pH 6.0 of chitosan solution faced a significant drop in the contact angle, from the hydrophobic region of contact angle on native PDMS sample, and reached an average contact angle of within the region of hydrophilic (less than 90°). While pH 4.5 and pH 5.0 of the chitosan droplet

contact angle remained within the same hydrophilic region of the average contact angle. However, pH 5.5 of chitosan droplet contact angle showed an unusual reading, that was slightly lower than the average contact angle obtained from the control set but remained in the hydrophobic region (more than 90°). This condition could be due to the characteristics of its hydrophilic-hydrophobic within the chitosan solution itself.

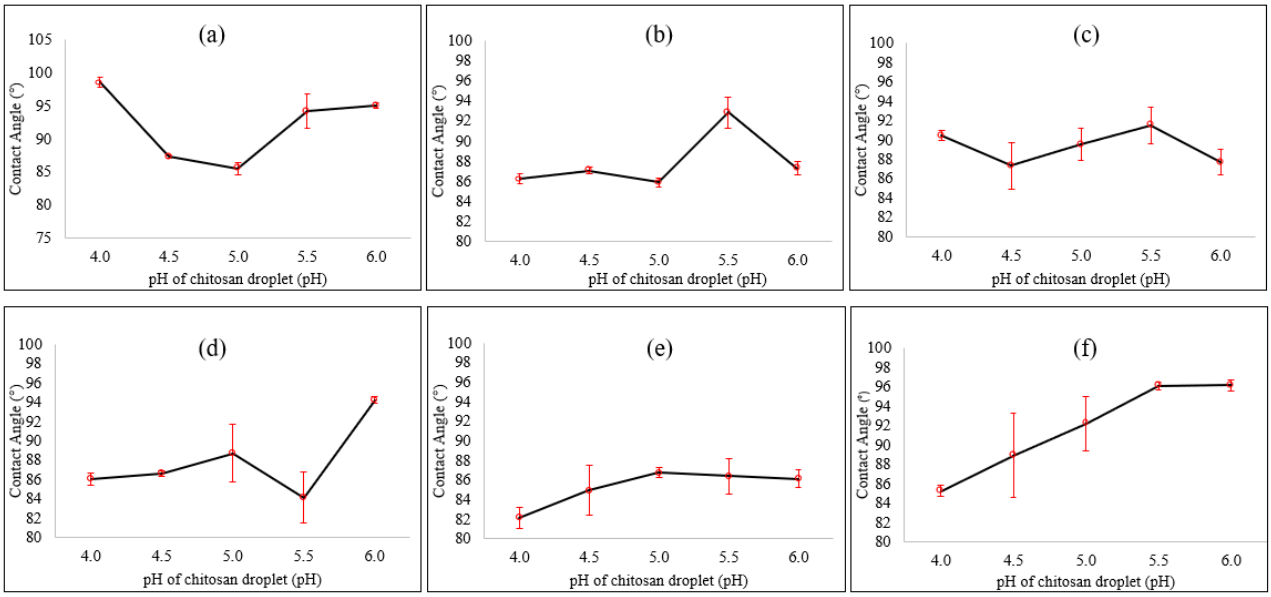

Fig. 1. Graph of contact angle versus pH of chitosan droplet on (a) native PDMS, at (b) 1 minute, (c) 5 minutes, (d) 10 minutes, (e) 15 minutes and (f) 20 minutes of treatment time of surface-modified PDMS

Table 1 Contact angle obtained from the wettability study of chitosan droplet on the native (control) and surface-modified PDMS

pH of chitosan droplet	Treatment time					
	Control	1 minute	5 minutes	10 minutes	15 minutes	20 minutes
4.0	98.524	86.249	90.418	86.037	82.130	85.242
4.5	87.301	87.045	87.351	86.601	84.931	88.913
5.0	85.502	85.896	89.532	88.695	86.735	92.206
5.5	94.113	92.866	91.511	84.124	86.406	96.095
6.0	94.975	87.293	87.689	94.222	86.131	96.170

The definite trend of the contact angle from the 1-minute treatment of surface-modified PDMS can be seen in the 5 minutes treatment of surface-modified PDMS. However, there was an increase in the contact angle of pH 4.0 chitosan droplet compared to the 1-minute treatment contact angle, due to the presence of dust particles, which then affected the hydrophilic interaction between the pH 4.0 chitosan contact angle with the surface-modified PDMS. The uneven surface of the PDMS sample was also a factor which affects the SEO 300 Touch Manual Contact Angle Analyzer from analyzing the proper angle of the chitosan droplet.

When surface-modified PDMS was treated for 10 minutes, the same trend was observed for pH 4.0, pH 4.5, and pH 5.0 of the average contact angle of chitosan droplet compared to the 1 minute and 5 minutes treatment of surface-modified PDMS. Meanwhile, pH 5.5 took an unexpected turn, showing a hydrophilic average contact angle of less than 90°. The explanation for this could be the fault while treating the PDMS sample as it could have been immersed in the piranha solution for more than 10

minutes. Since both the piranha solution and the PDMS samples were colourless, it took a long time to search for each piece of PDMS soaked in it with a pair of glass rods. Hence, resulting in a hydrophilic region of the pH 5.5 chitosan droplet. As for pH 6.0, a hydrophobic average contact angle was obtained for the same reason in pH 4.0 of chitosan droplet in the 5 minutes treatment surface-modified PDMS. The limitation that caused a sudden change from hydrophilic to hydrophobic was the presence of dust particles on the surface-modified PDMS.

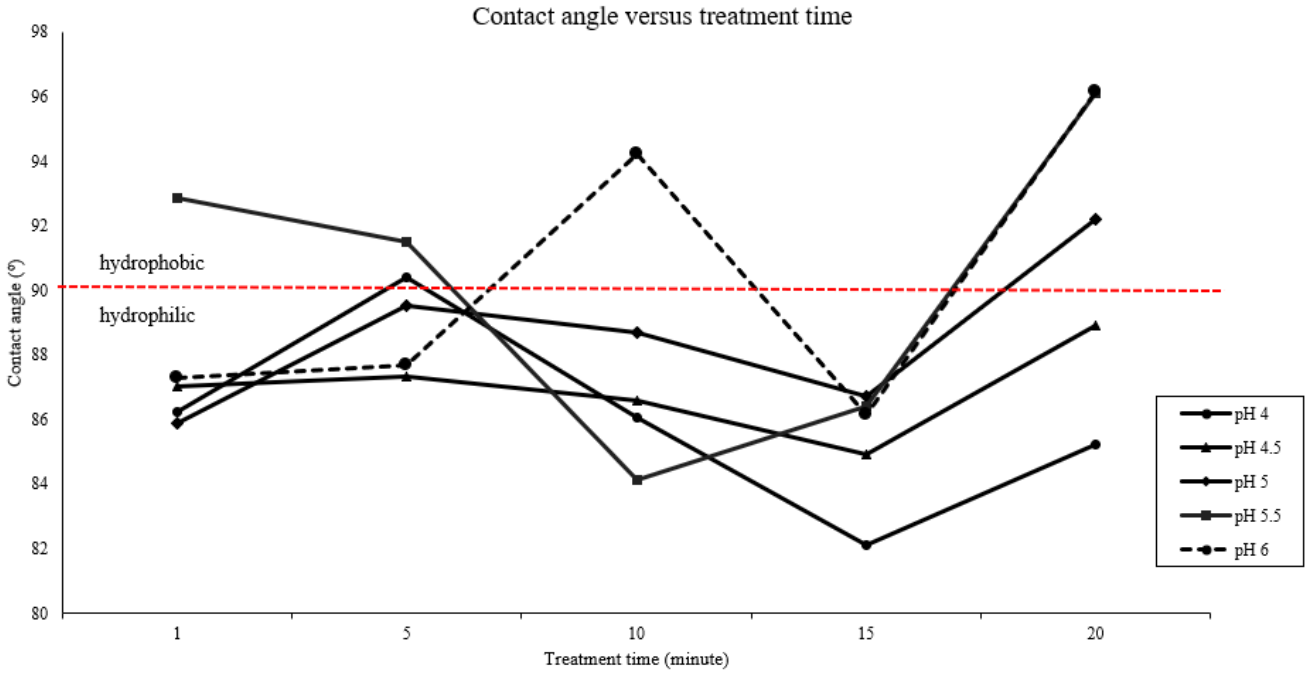

Fig. 2. Graph of contact angle versus treatment time according to chitosan pH

Fifteen minutes of treatment showed an overall hydrophilic contact angle of less than 90°. This finding proves that within 15 minutes, the hydroxyl ions reacted completely to the PDMS. Within 15 minutes, the potassium hydroxide solution was able to spread all hydroxyl ions evenly onto the PDMS sample. Hence, with 15 minutes of treatment, a high wettability can be observed, which is desirable when high wettability microbeads or coating of chitosan on the microchannel is desirable for microfluidics application.

As for 20 minutes, the trend of the average contact angle graph was akin to the 15 minutes treatment of surface-modified PDMS. An increase of average contact angle was observed from pH 4.0, pH 4.5, and pH 5.0 of the chitosan droplet. This finding shows that the wettability of the chitosan droplet decreases with increasing pH of the chitosan droplet solution. Meanwhile, pH 5.5 of chitosan droplet may be due to its hydrophilic-hydrophobic property, and pH 6.0 was due to the presences of dust particle.

Therefore, if the high wettability of microbeads is desirable, the oil in water dispersion, within the microchannel or coating of chitosan catalyst on the surface of the microchannel must be obtained, the treatment of the surface-modified PDMS for 15 minutes gives the best wettability results. However, if low wettability of microbeads, for example, water in oil dispersion, is desired within the microchannel, the use of chitosan of pH 4.0, pH 5.5, and pH 6.0 in native PDMS gives the best result in the average contact angle.

4. Conclusion

The PDMS samples were modified by using piranha solution to react with the methyl group the PDMS, which gives free hydroxyl ions to attach onto the Si molecule on the PDMS. The hydroxyl ions were then spread evenly onto the surface of PDMS using a potassium hydroxide solution. The wettability of varying chitosan droplet onto the surface-modified PDMS was analyzed and compared with the wettability results obtained on the native PDMS. It was found that surface-modified PDMS treated for 15 minutes, achieved an overall hydrophilic surface. Therefore, this gives a high wettability of the chitosan solution to be coated onto the inner wall of the microchannel. However, if lower wettability is desired to obtain chitosan microbeads within the microchannel, pH 4.0, pH 5.5, and pH 6.0 of chitosan solution can be used.

Acknowledgement
The authors would like to express the gratitude towards the financial support from Centre of Excellence for Research, Value Innovation and Entrepreneurship (CERVIE), UCSI University under Pioneer Scientist Incentive Fund (PSIF) with project code, In-Proj-In-FETBE-056.

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