 ICCES, vol.15, no.1, pp.9-18

A study of surface force on self-assembled monolayer of bio-microchannel

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Summary

In this paper, four kinds of biocompatible SAMs are used to improve adhesion property and fluorescence reaction property on specimen surfaces. The result of experiment shows that OTS film demonstrates contact angles are all larger than 100 degrees in different immersing time and it reveal the best hydrophobic property after 24 hours. The declination angle experiment demonstrates that the OTS film has best flowing property and same trend of friction coefficient; it indicates that the declination angle experiment can reveal the degree of microchannel adhesion property better than contact angle experiment. It can be found that the OTS film can reduce the number of protein adherence on the surface of microchannel in protein concentration examination to raise examination accuracy. Using fluorescence signal, therefore the fluorescence values will increases.

Keywords: microchannel, biomedical-chip, SAMs, adhesion force.

Introduction

Bio-MEMS are designed by applying theories such as molecular biology, genetic information, and analytic chemistry. Bio-MEMS are MEMS technique which uses chips, glass, or macromolecule as substrates, combines with semiconductor, automation, and other precise processing, etc. Nowadays, the Bio-chips which researched and designed by Bio-MEMS technique can be divided into two categories, sensing chip and processing chip [1]. The phenomena of tested liquid in microchannels would be different due to the influences of fluid category and speed, external force, surface roughness, geometric configuration and size. Bhushan [2] thought that the high adhesion between surface of microchannels and fluid would affect the bio-molecules on the surface of microchannels and limit its flow. The key points of the microchannels chip research are how to reduce the interaction between surface of microchannels and fluid, and how to reduce the adhesion between fluid and channels to make fluid flowing easily. Therefore, the research goals of this experiment are to promote the flowing speed of specimens; reduce the adhesion between specimens and surface of microchannels, and make more specimens flowing to tested area to raise the accuracy of examination.

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SAMs, in brief, are some monolayer films which contain active molecules on the surface, and it can adhere to substrate spontaneously to become well-regulated and compact monolayer films. This technique is famous because its fabrication process is very sample, and it can be used on any shape of substrate. In 1946, Zisman had used adsorbing surface-active agent (amine derivatives with long chain) to adhere on clean metal (platinum) to produce SAMs [3], but it had not been noticed at that time. In 1983, Nuzzo and Allara et al used disulfide to film SAMs on gold in the Bell Labs, and then they subsequently found organosilicon compounds adsorbed on SiO_2 and Al_2O_3 [4]. Since that SAMs were used widely in many areas. SAMs is formed by using the chemical reaction between special functionality and surface of substrate to adhere on substrate surface, and then the long chain molecule on the surface will push and press each other by Van der Waals Force to become well-regulated and compact films. The terminal functionality group will decide the final character of film surface. SAMs' forming is mainly affected by $-CH_2$, $-CH_3$ [5, 6], and substrate [6]. The forming of $–CH_3$ is also the main element to affect the surface adhesion and friction [7]. In 1995, Sukenik et al [8] formed SAMs on micromotor to reduce friction and adhesion during operation. J.N Ding et al [9] researched the friction and break phenomena of SAMs. In 2008, Yang and Clementz [10] indicated that plating a layer of tetraethoxysilane (TEOS) in the microchannels of PDMS material can let specimens flowing in channels well, and can also raise chemical resistance and durability of microchannels to enhance its strength. In 2009, Yazdi and Abdullah [11] suggested that microchannels could effectively reduce both friction and thermal irreversibilities through slip-flow conditions in convective heat exchange problems of liquid fluids.

In 2008, Yuan, He, and Lee [12] proposed that using ELISA to construct on the micro devices of polymer material to improve the traditional measure methods which is time-consuming and need considerable specimens. This technique is to change surface properties into polymethylmethacrylate (PMMA) by oxygen plasma to make the protein (Protein A) adhere on substrates much more easily, increases combination efficiency of antibody to raise fluorescence signal value, and improve signal-to-noise ratio during the test in microchannels. This new technique has great potentiality to improve ELISA, and also suitable to applications of other Immunobiosensors.

Experimental equipment and procedure

This paper mainly interprets four kinds of SAMs: Octadecyltrichlorosilane (OTS), Octadecyltrimethoxysilane (ODS), Octadecane thiol (ODT), and 1-Hexadecanethiol (HDT). Using these SAMs to film on BioMicrochannel Chips and take experiments on test pieces filmed with differential times. The equipments of this experiment are

Contact Angle Measurements, Atomic Force Microscope (AFM), Optical Microscope, Fourier-Transform Infrared Spectrometer (FTIR), Spectrophotometer, and X-ray fluorescence. In this experiment, it uses CD-ELISA as substrates. First, using 20mm$\times$20mm$\times$1mm test pieces to soak in alcohol solution and vibrate for 10 minutes by ultrasonic vibration washing machine. Then, soaking test pieces in DI water and vibrate for 10 minutes by ultrasonic vibration washing machine again, and then using nitrogen gas to blow the substrates to dry.

Using OTS, ODS, ODT, and HDT to mix with alcohol solution, stir these solution by electromagnetic stirrer to 10mM Moore concentration. Then, soaking these clean substrate in these solutions, the soaking time are 3, 12, 24, and 36 hours respectively, and the environment temperature is 20°.Taking out these test pieces after these soaking times, soaking them in DI water and vibrating for 10 minutes by ultrasonic vibration washing machine, finally, using nitrogen gas to blow these filmed substrates to dry.

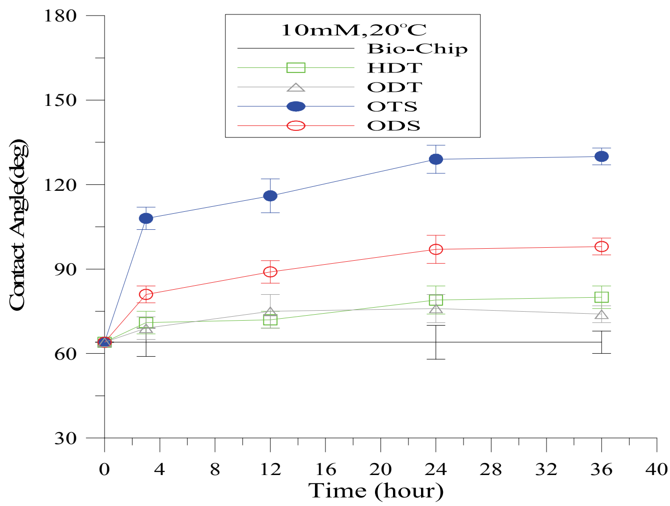
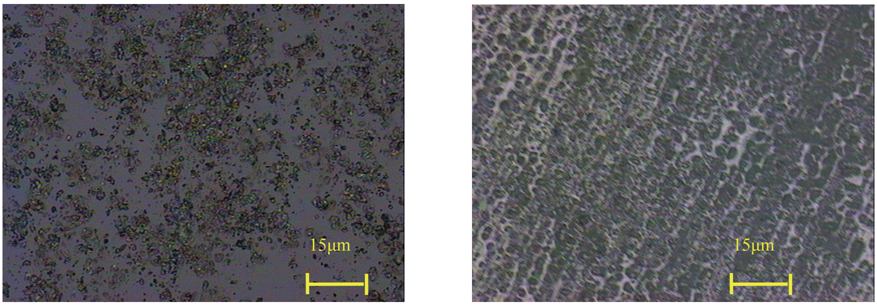


Figure 1: Contact angles comparison chart of different SAMs on bio-microchannel chips after different soaking times

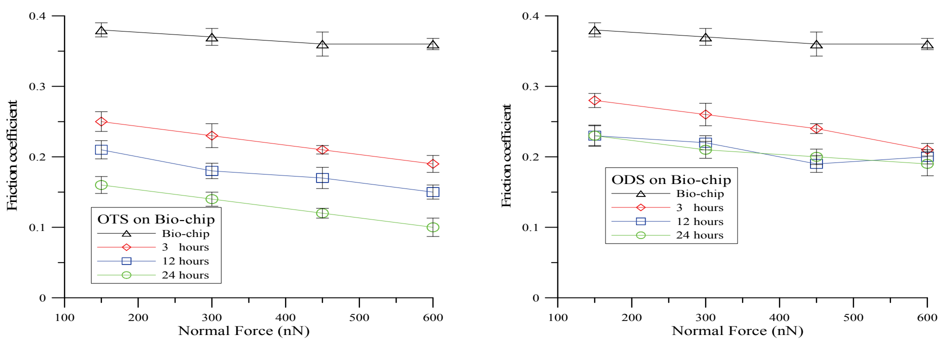
Results and discussion

Fig.1 is the comparison chart of SAMs contact angles which shows the films form on the bio-microchannel chips after different soaking times. In this experiment, taking 3 test pieces form each group, and measuring 5 points on each test pieces,



(a) 12 hours (b) 36 hours

Figure 2: Optic Microscope figure of OTS film on bio-microchannel after different soaking times



(a) OTS (b) ODS

Figure 3: Friction coefficient comparison chart of OTS, and ODS films on bio-microchannel chips after differential soaking times

then averaging 3 points from the median values. This figure shows that among the four solutions, OTS has the biggest contact angle in any soaking times; HDT and ODT have the smallest contact angle. At the time of the biggest contact angle, the contact angles of OTS and ODS increase as the time increases, and at the 24 hours time, the contact angles have the maximum values. The contact angles of HDT and ODT have stable condition after filming for 12 hours, and the contact angles will not have significant variation as time increases.Fig.2 (a) $\sim$ (b) are optical microscope figures of OTS SAMs on bio-microchannel chips after filming for 3 to 24 hours. Therefore, it is found that island matter increases as the soaking time increases, and because the major content of the island matter is hydrophobic CH_3, the covered area and density also increase as soaking time increase. This is also the reason for the increase of contact angle on test piece surface.

In order to explore flowing friction ability on SAMs, this experiment used AFM again to measure friction on surface films of PMMA, HDT, ODT, OTS, and ODS, and use the force and distance curve of AFM to analyze the relation between normal force and friction coefficient of SAMs. Fig.3 (a) ∼ (b) are friction coefficients comparison charts of OTS, and ODS films on bio-microchannel chips after different soaking times. Fig. 3 (a) shows that the friction coefficient of OTS film is 0.1 ∼ 0.25; it is the smallest friction coefficient among four kinds of SAMs and decreases as the forming time increases. It is found from Fig. 3 (b) that the friction coefficient of ODS film decline to 0.3∼0.2 after forming for 3 hours, and the decline range of friction coefficient is close after forming for 12 to 24 hours. It is assumed that this film is almost complete after forming for 12 hours, and forming for longer time just for more complete growth on the surface. In summary, when the smaller the friction coefficient of surface film is, the less loss of flow fluid is; and OTS and HDT films have much more this ability to let more tested liquids have more quantity during examination. From literatures [7, 8] it is learned that content of terminal functionality -CH_3 will affect the results, it can be explained that the mode between molecule bonds will affect stiff strength and friction ability.

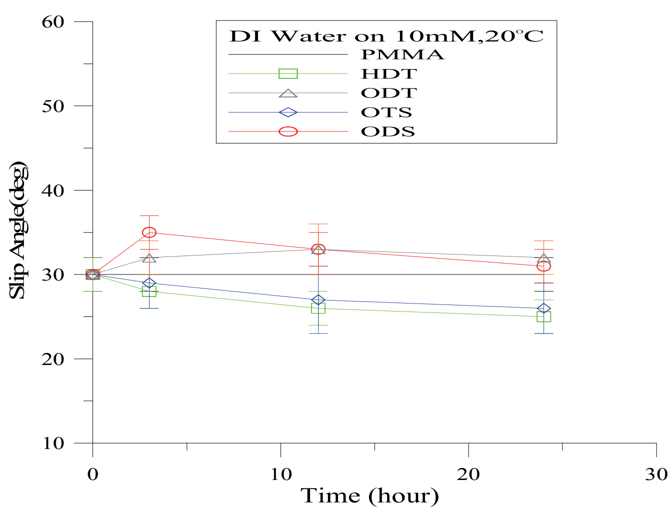


Figure 4: Declination angles comparison charts of DI water on different SAMs

In the case of test, the contact angle just is the static surface property. Some of fluids in channels flow by pump, some of fluids flow by centrifugal force (CD-ELISA), and this are the dynamic condition. In order to more realize the flowing

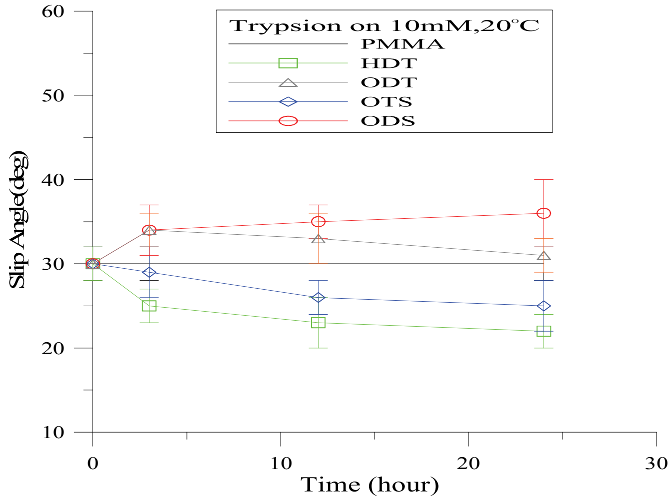


Figure 5: Declination angles comparison charts of and enzyme on different SAMs

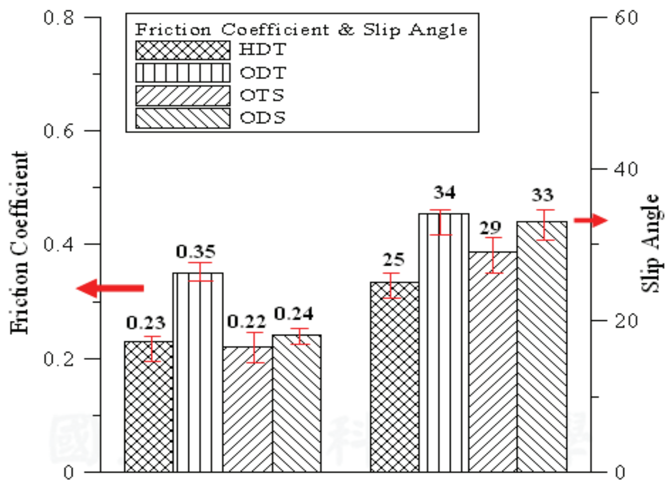


Figure 6: Friction coefficients and declination angles comparison chart of different SAMs(3 hours)

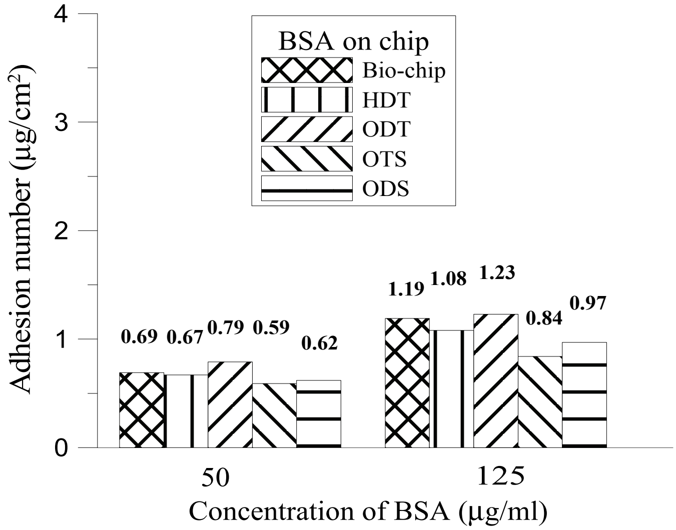


Figure 7: Result chart of protein residue concentration on surfaces of different SAMs after soaking for 24 hours

condition, this examination used enzyme solution which is normal used in biomedical examination to test the flowing condition. Fig.4 and fig.5 are comparison charts of declination angles of DI water and enzyme on each SAMs. Fig.4 shows that the declination angles of HDT films are 25° and 26° respectively after soaking in DI water for 12 and 24 hours; the declination angles of OTS films are 26° and 27° respectively after soaking in DI water for 12 and 24 hours are much better, both tow films' declination angles are smaller than 30° of the specimen without forming films. Fig.5 shows that the declination angles of HDT films are 22° and 23° respectively after soaking in enzyme water for 12 and 24 hours; and the declination angles of OTS films are 25° and 26° respectively after soaking in enzyme water for 12 and 24 hours, the declination angles are smaller than soaking in DI water. These results indicate again that these two kinds of SAMs are helpful to specimens' flowing on test pieces, and fig.4 and fig.5 have the same trend lines. In summary, this is found that the surface film of HDT has the better flowing ability, and the surface film of ODS has the worse flowing ability. The performance of flowing ability is HDT>OTS>ODT>ODS. Moreover, the results can be learned that the adhesion property of force which making liquid flow (declination angle experiment) is different to experiment results of contact angle (Fig.1).

In order to explore the relation between declination angle and friction coefficient of fluid further more, this experiment integrates the charts of friction coefficients and declination angles after forming for 3 hour. As fig.6 shows that the friction coefficients of SAMs fluids and the variation of declination angles are coincidence. This result indicates that the adhesion property of declination examination on bio-microchannels is more reference-worthy then regular contact angle. For bio-microchannel, both concentration and volume of specimen which flow to the tested area are very important. As this result, it not only explores how to reduce the quantity of adhesion, but also explores how to make the minimum quantity of adhesion on specimen in microchannels. Therefore, this experiment uses the protein concentration experiment to soak the tested pieces with different films in specific concentration of protein solution, and then to analyze the lowest quantity adhered of protein on various films surface. Fig.7 is result chart of protein concentration test on different SAMs. From the experiment statistics, it can be known that after forming the HDT, OTS, and ODS; the adhesions of them appear decline trend under the same test area. When the concentration is 50μg/ml, the adhesion quantities of unformed PMMA are decline from 0.69μg/ml to 0.67μg/ml, 0.59μg/ml, and 0.62μg/ml; and when the concentration is 125μg/ml, the adhesion quantity with OTS film is 0.84μg/ml. It indicates that in four kinds of films, the OTS film has the smallest protein adhesion property on surface; and in AFM adhesion experiment, it can also know that the adhesion of OTS film is the smallest. Therefore, it can be know that the protein adhesion quantity of OTS film after forming for 24 hours is the minimum, so it can let specimen lost the minimum specimen quantity. By these results, the OTS and ODS films have much better effect in this experiment, and it can reduce the adhesion property and survival rate between specimen and surface of micrechannels to let more quantities of cell flowing through microchannels and improve the tested speed and accuracy.

Conclusion

This study mainly explores the flowing and adhesion property of different SAMs on bio-microchannels. The following summarizes the experiment results and reasoning:

1. The contact angles of OTS film are over 100° when it soaking in different solutions for 24hours, so that it has the better hydrophobic and adhesion-resistant property than other films. With regard to adhesion, the decrease of surface energy is due to the increase of contact angle, and it also causes the reduction of adhesion force. The comparison of adhesion ability is OTS > ODS > HDT > ODT.

2. Declination angle is to simulate the thrust of actual fluid flowing by the effect of gravity, and it has more ability to indicate the pros and cons of flowing

property of fluids than contact angle. It is found that the flowing property is HDT>OTS>ODT>ODS, and the friction coefficients has the same trend in comparison with the friction experiment. Therefore, the declination angle experiment is an important indicator of microchannels.

3. In the examination of protein concentration, only forming ODT film, the adhesion quantity doesn't reduce; but the adhesion quantity of OTS, ODS, and HDT all reduce and OTS is the must significant. It can be know that OTS film can reduce the protein quantity on surface, and when it is used in test, it can reduce adhesion quantity of specimens on microchannel and improve test accuracy.

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