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摘要

本次參加研討會發表二篇論文，分別為 “Improving rubcete by enhancing the hydrophilic property of the rubber crumb through the partial oxidation method” 與 “On morphologies of sodium dodecyl sulfate thin films on the glass substrate” . 兩篇論文皆刊登於大會論文集，且二篇論文皆獲得大會頒發”研討會最佳論文獎” “Best conference paper award” . 其中morphology of sodium dodecyl sulfate thin films的論文，更經大會推薦刊登在Materials (SCI, impact factor 2.728) 之著名期刊 (Materials **2017**, 10, 555).

目錄

目的	1
過程	1
心得與建議事項	1
會議流程與會照片	2
發表論文全文	8

目的

IEEE 是國際上極重要的學會，參加由 IEEE 所舉辦的會議可與學術界交流且獲致最新的研究趨勢。材料領域的研究，在 IEEE 也逐漸被重視，未得到最新的研究方向訊息，所以決定參加此研討會，以其與世界各地的研究人員做最直接的交流討論。

過程

據研討會資料顯示，此次研討會共有 1863 論文投稿，經審稿後接受 730 篇刊登於研討會論文集。我們投稿的兩篇論皆被接受發表於會議論文集，且兩篇論文都獲大會頒發最佳論文獎。其中討論 SDS morphology 的論文更獲大會推薦發表在知名期刊“materials”，可謂成果豐碩。研討會參與過程如所附照片。

除參加研討會外，筆者更到附近北海道大學觀察他們溫室構建的情況，與使用的塑膠披覆材料，因為溫室建構之主要披覆材料也是筆者正在進行的研究工作，北海道大學的相關資料，值得參考。蒐集的相關照片亦呈現在此報告中。

心得與建議

IEEE 是國際極重要的學學會，此次在日本北海道舉行，參與者來自各國的大學教授與研究學生，盛況空前，筆者帶博士班學生與會，透過研討會的交流，可以很直接且詳細地了解到其他國家的相關研究進展。因為主題領域極廣，現場與各領域的研究人員可以進行對話交流，獲益良多。在會場內時，本系博班學生陳紀堯同學與來自各國的研究生，密切交談，。陳紀堯同學第一次參加此盛大的國際研討會，用英文與外籍朋友溝通。經由此種國際研討會的經驗，提升其程度與視野，對本校的學生是極重要的培養工作。研討會過後，學生也了解到自己不足之處，需要再加強改進，對一個博士班學生而言，參加 IEEE 是個非常難得且寶貴的經驗，使其受益良多。建議學校建立一定的機制，鼓勵研究生盡量參與國際研討會。

會議流程與照片

Conference Agenda

Venue: Hotel emisia, Sapporo, Japan

Language: English

Pre-Conference Schedule		
Saturday, May 13, 2017		
2:00pm	6:00pm	Sponsor Showcase (Grand Ballroom)
4:00pm	8:00pm	Early Conference Registration and Conference Information Collection (Reception Hall)

Main-Conference Schedule		
Sunday, May 14, 2017		
8:00am	9:00am	Conference Registration and Conference Information Collection (International Conference Room, Building A)
9:00am	9:20am	Opening Ceremony (International Conference Room, Building A)
09:20am	10:00am	Keynote Speech 1 (International Conference Room, Building A)
10:00am	10:20am	Coffee Break
10:20am	11:10am	Keynote Speech 2 (International Conference Room, Building A)
11:10am	12:00am	Keynote Speech 3 (International Conference Room, Building A)
12:10pm	1:30pm	Lunch (Ballroom)
1:30pm	5:30pm	Poster session (Ballroom)
1:30pm	5:30pm	Breakout Sessions of ICASI 2017, Oral (International Conference Room, Building A1, A2, A3 and A4)
6:00pm	8:30pm	Conference Dinner (Ballroom)

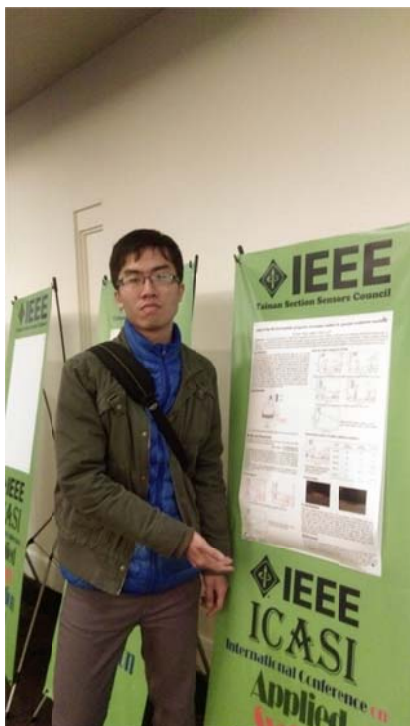
Main-Conference Schedule		
Monday, May15, 2017		
8:00am	9:00am	Conference Registration and Conference Information Collection (International Conference Room, Building A)
9:00am	12:00am	Breakout Sessions of ICASI 2017, Oral (International Conference Room, Building A1, A2, A3 and A4)
9:00am	11:50am	Poster session (Ballroom)
10:40am	11:00am	Coffee Break
1:00pm	05:30pm	Breakout Sessions of ICASI 2017, Oral (International Conference Room, Building A1, A2, A3 and A4)
1:30pm	4:30pm	Poster session (Ballroom)

Main-Conference Schedule		
Tuesday, May 16, 2017		
8:00am	9:00am	Conference Registration and Conference Information Collection (International Conference Room, Building A)
9:00am	12:00am	Breakout Sessions of ICASI 2017, Oral (International Conference Room, Building A1, A2, A3 and A4)
9:00am	11:50am	Poster session (Ballroom)
10:40am	11:00am	Coffee Break
1:30am	5:30am	Breakout Sessions of ICASI 2017, Oral (International Conference Room, Building A1, A2, A3 and A4)
1:30pm	2:50pm	Poster session (Ballroom)

Main-Conference Schedule		
Wednesday, May 17, 2017		
8:00am	9:00am	Conference Registration and Conference Information Collection (International Conference Room, Building A)
9:00am	9:20am	Closing Ceremony
9:20am	12:00am	Sponsor Showcase (Ballroom)



筆者與大會學術委員合影



學生現場解釋論文內容





發表之論文獲選最佳論文(1)



發表之論文獲選最佳論文(2)



北海道大學溫室

Improving the hydrophilic property of crumb rubber by partial oxidation method

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Abstract

The purpose of this study is to find out an acceptable condition to get the suitable crumb rubber for producing rubberized cement paste. A batch reactor was used and the reaction temperature, the oxygen content, and the oxidant used were studied in the experiments. Fourier transfer infrared spectroscopy (FTIR) was used to explore the function groups on the surface of the crumb rubber and in the cracking oil. The area ratio of S=O to C-H (sp^3) in the IR spectrum was chosen as an index for evaluating the performance of the reaction. In the experiment, a colloid probe of C-S-H was prepared to measure intermolecular interaction forces between rubber films by using an atomic force microscope, which results showed the interaction force would increase. The possible reaction condition was discussed in detail in this study.

Keywords : partial oxidation, crumb rubber , Fourier transfer infrared spectroscopy, rubcrete

Introduction

A large amount of waste tyres are generated all over the world every year. As waste tyres are not easily biodegradable after a long period of landfill, this is not only an environmental problem but also a waste of natural resources. It is well known that the crumb rubber can be used as an additive to form a cement matrix composite, the rubcrete. Because the rubcrete has the ability to absorb a large amount of energy under compressive and tensile loads [7-9], it was recommended to be used in circumstances where vibration damping was required, such as in highway construction as a shock absorber or sound barriers and in buildings as an earthquake

shock-wave absorber [7, 8, 11]. As the rubcrete is a useful material, many studies focused on modifying the crumb rubber to improve it to be a better additive of the concrete. However, the hydrophobic crumb rubber can't be well distributed in the cement hydrate, and it can't bond firmly with the cement hydrate, the rubcrete has less mechanical strengths than that of the concrete [1-6, 10]. In order to promote the use of the rubcrete, it is believed that the reduction of mechanical strengths of rubcrete is an important problem to be solved.

Lee et al [2] suggested that the loss in mechanical strengths may be improved by proper surface treatment of the crumb rubber. Segre and Joekes [13] suggested the rubber particles have a rough surface will improve the bonding with the cement matrix. Chou et al [14] showed that the NaOH treatment can enhance the adhesion of tire rubber particles to the cement paste. Thus, the mechanical properties of the rubcrete with the.

NaOH-treated rubber crumb were improved in comparison with that of the rubcrete with the as-received crumb rubber. Siddique and Naik [15, 18] gave a detailed review on this topics.

In this study, the crumb rubber was partially oxidized to enhance its hydrophilic property. Reactions were conducted under various condition. Iron (III) oxide was used as the oxidant in the experiments. The functional groups on the surfaces of treated crumb rubber and the cracking oil were observed with FT-IR. Cement pastes with the treated crumb rubber and the as-received crumb rubber were prepared for observing the distribution of the crumb rubber within the cement hydrate.

Experimental

Fig. 1[17] shows the apparatus used in this study. It is a batch reactor. The waste tyres were produced by Cheng-Hsing Rubber Co., Taiwan. Waste tires were mechanically ground and screened to 300–600 μm . The temperature within the reactor was controlled by an electrical heating system. The flow rates of air and nitrogen were controlled and recorded to get the air/nitrogen ratio. There were three air /nitrogen ratios (1/0, 1/4, and 0/1). The temperature were kept at 200°C or 250°C. Iron(III) oxide was used as the oxidant. The gas flow rate is 100 $\pm$ 10ml/min.

The oxidant (0 ~ 0.1 wt%) and the crumb rubber were mixed and put in the reactor. In every experiment, air and nitrogen with desired air/nitrogen ratio flew through the reactor at least 30 min before the reaction occurring. The reaction conducted for an hour. The treated crumb rubber and the cracking oil were analyzed with FTIR. The cement paste with the crumb rubber (6 wt % of cement) was prepared and observed with an optical microscope(OM) in this study. The first type of Portland cement by Taiwan Cement Co. was used. All specimens were prepared with the water/cement

ratio of 0.5 to assure sufficient water in cement pastes.

Results and discussion

The area of the stretching absorption of hydrocarbon of sp^3 bond (C-H) and the area of the stretching of absorption of SO_2 and SO (area of S) were integrated. The area ratio of S=O to C-H (sp^3) in the IR spectrum was chosen as an index for evaluating the performance of the reaction.

$$\text{Area ratio} = \frac{S = O \text{ stretching area}}{C - H \text{ stretching area}}$$

The absorption in the region of $1100-1000 \text{ cm}^{-1}$ is the stretching absorption of the two S=O of R- SO_2 -R, the region of $980-960 \text{ cm}^{-1}$ is the S=O bond stretching absorption of R-SO-R. The region of $2800-3100 \text{ cm}^{-1}$ is the C-H(sp^3) stretching adsorption, and the region of $1400-1500 \text{ cm}^{-1}$ is the C-H (sp^2) bending adsorption. The region of $1500-1700 \text{ cm}^{-1}$ is the aromatic C-H stretching adsorption.

The cracking oil

Fig 2(a) is 200°C and Fig 2 (b) is 250°C are showing IR spectra of the cracking oil treated with various oxygen/nitrogen ratios and use oxidant or not. The area of the stretching absorption of hydrocarbon of sp^3 bond (area of H) and the area of the stretching of absorption of SO_2 and SO (area of S) were integrated. The area ratios (area of S/area of H) of these two area values were calculated for various oxygen / nitrogen ratios and depicted in Fig. 3. From Fig 2(a) and Fig 2 (b) the IR spectra are nearly the same, it can be shown that the composition of the cracked oil is similar. From the Fig 3 and Table1, at the 200°C that at the high oxygen without oxidants content and at low oxygen with oxidant content, the ratios are closely. It can be shown that the oxidant can effectively break the rubber crumbs bonding at the similar place. From the IR spectrum can be speculated that the bond broken is nearly the aromatic, carbon chain and some sulfur oxide compounds. In the Fig3 and Table1 of the 200°C and the oxygen / nitrogen=0.04 has different results that is the reaction with oxidant has more hydrophilic property than without oxidant part. The results can prove the ferric oxide at the reaction processors can provide the oxygen atoms to make sulfur oxidant. At the 250°C , at the high oxygen content have drastic reaction, so produce amounts of bond breaking. And it could find that the condensed oil at 250°C without oxidant of the S=O/C-H ratio is nearly 200°C with oxidant, which can show that the lower temperature can reach the same purpose.

Reacted rubber analyzed by FT-IR

The Fig 4(a) and Fig 4(b) are IR spectra of the treated crumb rubber at 200°C and

250°C without oxidant analyzed by FT-IR. And the pure rubber S=O/C-H ratio is 1.12. The crumbs would start bond breaking, but at the same time the sulfur would be oxidized, too. From the Fig 4(a) and Fig 4(b) can be clearly found near 1500 cm⁻¹ near the obvious differences. The region is aromatic C-H stretching peaks, and at the 200 °C can be clearly found that can be interpreted as rubber crumbs to leave more aromatic C-H bond vibration. And at the all nitrogen content at the 1500 cm⁻¹ was spilt into 2 peaks that can be presumed that at the absence oxygen content, the number of broken bonds near the aromatic is less than others content. And the molecular weight is relatively larger and analyzing by FT-IR that resulting the vibration is slow and occurring the red shift. At the 250°C and 1500 cm⁻¹ the peaks were not clearly to see, and there may be more bond break near the aromatic, so the peaks become small.

From the Table2 and Fig6 are the S=O/C-H ratios of treated rubber crumbs at 200 °C and 250°C. From the Table2 compare the 200°C and 250°C the ratios of no use oxidant. From the Fig 4(a) at the high oxygen content of the ratio at 200°C is very closely to the untreated rubber crumbs, but at the low oxygen content and non-oxygen of the ratios are very low. Therefore, it can be shown that in the case of high oxygen content, the rubber may produce an oxidation reaction more than the bond breaking, but in the case of low oxygen and anaerobic content, there may be a large number of bonds broking was happened. Compare the Fig 4(b) and Table2 about the 250°C. The ratios of the crumbs are smaller than untreated that can prove at 200°C the crumbs would not produce oxidant, and the other word is that at 250°C bond breaking faster than produce. But at the gas ratio equal 1/4 the S=O/C-H and used oxidant is larger. It can prove again that at the 200°C and low oxygen content with oxidant can get a better result.

The Fig 5(a) and Fig 5(b) to comparing the Fig 6 and Table 2 are all the contents of the rubber crumbs. At the 200 °C, the low oxygen content, the gas ratio is air/nitrogen=1/4 and with oxidant has the highest ratio. It can say that the rubber crumbs under such condition would have much hydrophilic property, even larger than the ratio of untreated rubber. At 250°C was opposite, at the same low oxygen content has higher ratio at without the oxidant, too. However at the 250°C with oxidant, the low oxygen content still has the higher ratio than the others. It can say that the rubber crumbs at the low oxygen content can have a more complete oxidation. If the oxygen or temperature is too much or too high, it will produce bond broken faster than the produce. And comparing Fig5 to Fig4, it can find out the peaks near the 1500cm⁻¹. The peaks are nearly the same, it can say that no matter use oxidant or not. At the same temperature, the bond broken places are at the same place. The results show that the temperature decides the bond broken place and the oxygen and oxidant decide the number.

The Fig4(b) and Fig 5(b) can find some obvious main peaks at 1100 cm^{-1} and 3000 cm^{-1} . At the 250°C the rubber crumbs can break many S-S bonds and C-S bonds that the rubber crumbs to present so sulfone or another sulfur compounds. At the 250°C with enough oxygen content the crumbs can easy to oxidize. But if the high temperature and enough oxygen simultaneously exist, the ratio will be decrease that can evidence from Fig6. At the 200°C and with oxidant content the ratio has obviously increased that prove the oxidant proving the oxygen atoms to the sulfur as oxygen. The evidence is that the low oxygen content 250°C without oxidant and 200°C with oxidant which has nearly ratio, so it prove again at low temperature with oxidant can get the nearly 250°C without oxidant. From the Fig6 show clearly, the rubber crumbs are over oxidize. The ratio is smaller than low oxygen content.

Detected the surface of rubber oxidation condition

Fig7 is comparing the untreated rubber crumbs to other four kinds conditions. The crumbs were washed by acetone that named decrease air ratio and add “ac”. The results of Fig 7 and Table 3 are showing that much oxygen and high temperature determine the hydrophilic property. This part is using organic solvent to wash out the materials on the surface of the rubber crumbs. It can determine the oxidant materials leaving on the surface or the surface really become sulfur oxides. The results show the results of the crumbs that wash by organic solvent. Reacted by 200°C and pass-through the organic solvent to wash, the ratios are increase. But at the 250°C ratios are opposite. The results show that at 200°C the bond breaking was not strongly, so only a little material adsorption on the surface was washed off. But at the 250°C was opposite, the ratios decrease after washed off.

Rubber separation, strength and contact angles

From the Table4 can find that the reacted crumbs compressive strength compare to untreated crumbs. The three columns respectively that the column1 present pure cement, column2 present adds 6% untreated rubber and column3 present adds 6% treated rubber crumbs. The strength has obvious strength 3.5 times than untreated. The 6% of rubber crumbs added, the strength would not change too much, and still have 0.85 times than pure cement. The surface of treated crumbs mixes with cement evenly. If the combine and separation are not equally, the compressive strength will present weak.

The Fig 8 is the result of the rubber separation in the cement. And it can show that from the circle place the treated rubber in Fig 8(a) and untreated in Fig 8(b) The Fig 8(a) can see clearly the treated rubber is evenly separation in the cement, but in the Fig 8(b) of unevenly separation. The two places are showing clearly. The rubber in

Fig 8(b) has float up to the surface, but the Fig 8(a) is opposite. The results show that the treated rubber crumbs has obviously hydrophilic, so can separate in the cement. The Fig 9(a) show the contact angle that can see a drop of water stay on the surface and the contact angle is about 64° and 57° degree. And the Fig 9(b) show the water penetration in the rubber cement that representative the interface and surface have a lot of pores.

Viscous force

It can be seen from Fig. 10 that the C-S-H is attached to the probe and forms a white film at the tip of the AFM probe [18]. Fig 11 shows the viscous force generated by the AFM scanning rubber sheet on the probe of Fig 10. From Figure 11 can be seen without modification, modified at 200°C, and 250 °C rubber sheet 3 kinds of conditions. The viscous force of the untreated rubber sheet is concentrated more than 100nN and less than 300nN. To 200 °C modified rubber sheet is concentrated in more than 200 nN and less than 400 nN. To 250°C modified rubber sheet is concentrated in more than 300 nN and less than 500 nN. The results can show that. The results show that at the higher the temperature and the same gas ratio, it will be greater the viscosity force. It can prove that. It can be proved that the properties of the modified rubber surface can be achieved by a simple method.

Conclusions

From the cracking oil, they are C-H or C-H₂ on aromatic, C-H bending and some sulfur oxide compounds. At 200°C in the case of high oxygen content the cracking oil have higher S=O/C-H ratio. At 250°C, the ratio of most conditions is low because of the rapid cracking of the rubber crumbs. Treated rubber crumbs. Rubber crumbs at 200°C, the high level oxygen content in the reactor was favorable for the condensate. However at 250°C, the lower oxygen content was preferred. The oxidant, ferric oxide, could provide oxygen in the absence of oxygen in the reactor. In addition to 200°C with the addition of oxidant, the others ratio are decrease. Treated crumbs can be uniformly dispersed in the cement, and the contact angle is also large. The viscous force will increase when the treated temperature increase.

Table 1 the S=O/C-H ratio of the condensation oil

Rubber	S=O Stretching	C-H Stretching	S=O/C-H
AO10	80	460	0.17
AO20	30	500	0.06
AO30	20	300	0.07

AO11	40	180	0.22
AO21	80	430	0.19
AO31	40	520	0.07
BO10	30	330	0.09
BO20	50	590	0.08
BO30	4	100	0.04
BO11	50	230	0.23
BO21	40	600	0.07
BO31	10	150	0.07

Table 2 the S=O/C-H ratio of the reacted rubber crumbs

Rubber	S=O Stretching	C-H Stretching	S=O/C-H
AR10	89	76	1.17
AR20	17	50	0.34
AR30	45	118	0.38
AR11	50	76	0.65
AR21	44	30	1.46
AR31	37	54	0.68
BR10	92	128	0.72
BR20	89	87	1.02
BR30	83	244	0.34
BR11	57	366	0.15
BR21	162	190	0.85
BR31	177	343	0.51

Table3 compare to S=O/C-H of the rubber crumbs through the acetone to wash out the organic compounds

Rubber	S=O Stretching	C-H Stretching	S=O/C-H
untreated	72	65	1.12
AR20ac	28	23	1.2
BR20ac	35	57	0.61
AR21ac	42	26	1.61
BR21ac	25	45	0.55

Table4 the compressive of the rubber cement

replace	w/	React	Compressive strength (MPa)
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d	c	ed rubber	mean
0%	0.		49.86
6%	5	UR	12.22
		C100p	42.75

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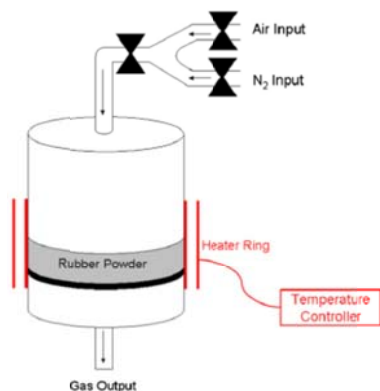


Fig. 1. Experimental apparatus for partial oxidation of trye crumb rubber.[17]

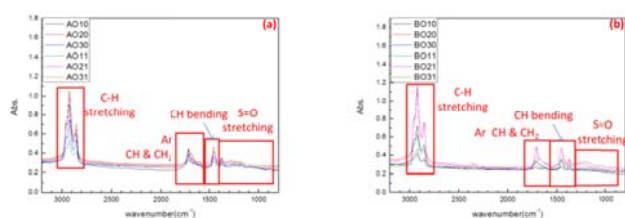


Fig 2 The IR spectra of the cracking oil at (a)200 °C (b) 250°C (notation WXYZ; W is temperature: A=200°C, B=250°C; X is condition: O=oil, R=rubber; Y is air/nitrogen ratio: 1=all air, 2=1/4, 3=all nitrogen; Z is oxidant: 0= no use, 1= use)

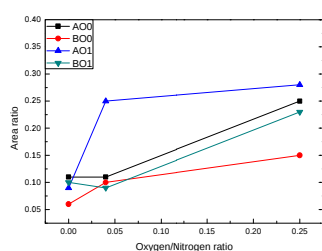


Fig 3 Effects of the oxygen content on the area ratio in the cracking oil (notation WXY; W is temperature: A=200°C, B=250°C; X is condition: O=oil, R=rubber; Y is oxidant: 0= no use, 1= use)

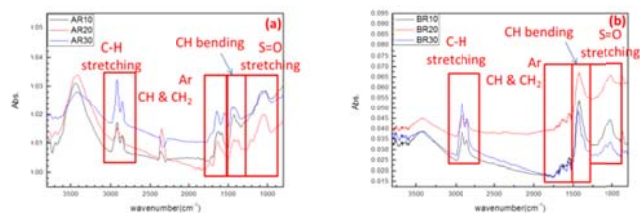


Fig 4 The IR spectra of the treated crumb rubber without oxidant (a) 200°C (b) 250°C (notation WXYZ; W is temperature: A=200°C, B=250°C; X is condition: O=oil, R=rubber; Y is air/nitrogen ratio: 1=all air, 2=1/4, 3=all nitrogen; Z is oxidant: 0= no use, 1= use)

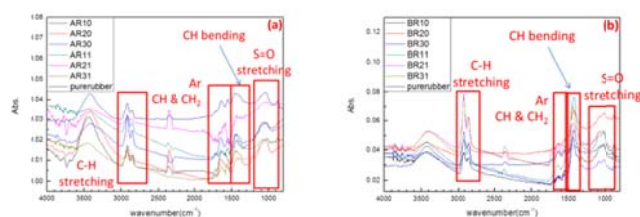


Fig 5 The IR spectra of comparing the condition (a) 200°C (b) 250°C (notation WXYZ; W is temperature: A=200°C, B=250°C; X is condition: O=oil, R=rubber; Y is air/nitrogen ratio: 1=all air, 2=1/4, 3=all nitrogen; Z is oxidant: 0= no use, 1= use)

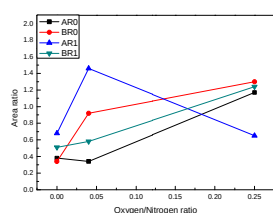


Fig 6 Effects of the oxygen content on area ratio on the surface of the crumb rubber (notation WXY; W is temperature: A=200°C, B=250°C; X is condition: O=oil, R=rubber; Y is oxidant: 0= no use, 1= use)

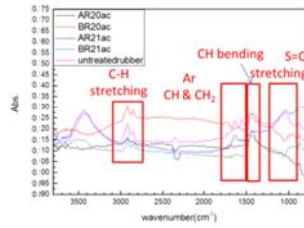


Fig 7 reacted rubber crumbs wash out organic materials by acetone (notation WXYZac; W is temperature: A=200°C, B=250°C; X is condition: O=oil, R=rubber; Y is air/nitrogen ratio: 1=all air, 2=1/4, 3=all nitrogen; Z is oxidant: 0= no use, 1= use; ac=wash by acetone)

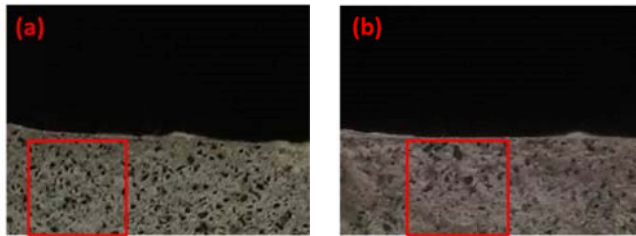


Fig 8 the optical microscope figure of the rubber separation in cement (a)treated rubber crumbs; (b) untreated rubber crumbs

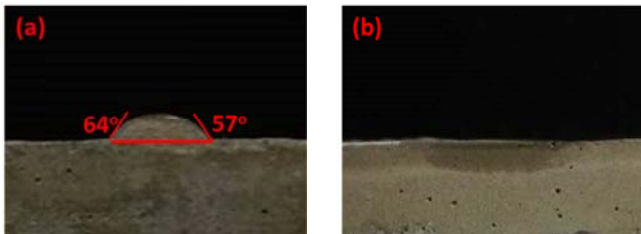


Fig 9 up is the contact angle; the water penetration (a) treated rubber crumbs; (b) untreated rubber crumbs

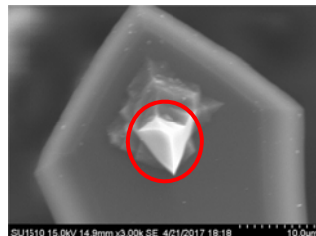


Fig 10 the red circle is C-S-H gel on the AFM probe

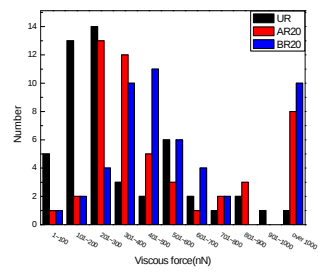


Fig 11 The viscous force about untreated rubber (black), 200°C (red), and 250°C (blue) at air/nitrogen = 1/4

On morphologies of sodium dodecyl sulfate thin films on the glass substrate

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Abstract

The surfactant film on the solid surface has attracted much attention because of its scientific interest and applications such as micro or nanoscale templates for microfluidic devices. The anionic surfactant SDS with various charged inorganic salts aqueous solution dried on the glass substrate under ambient condition. The Atomic Force Microscopy (AFM) was employed to observe the micro-structure of SDS thin films. The effects of inorganic salts on the morphology of the SDS films were observed and discussed. The results of experiments demonstrated that pure SDS film formed patterns of long parallel, highly ordered stripes. The existence of inorganic salt disturbed the structure of SDS film due to the interaction between cationic ion and the anionic head groups of SDS. The divalent ion has greater electrostatic interaction with anionic head groups than that of the mono-valent ion and cause a gross change in the morphology of SDS films.

Keywords: Surfactant adsorption film, Atomic Force Microscopy, sodium dodecyl sulfate

Introduction

Surfactant is widely used as chemical ingredients in cleaning agents, emulsifiers, pigments, inks, and anti-foaming agents etc. When surfactant solution is dribbled on the solid substrate and solvent evaporation, the remaining particles will form various patterns on the surface. The morphology of surfactant on solid substrate depends on many factors, such as (i) ionic functional groups of surfactant; (ii) surfactant concentration; (iii) surface charge and hydrophilic/hydrophobic property of surface; (iv) counter ion etc. (Advances in Colloid and Interface Science 110 (2004) 75– 95) The design of assembly structure has attracted much attention because of its scientific interest and promising applications such as colloid stabilization, printing industry or micro or nanoscale templates for microfluidic devices. The Atomic Force Microscopy (AFM) is a powerful technique to observe the assembly structure of surfactant on the surface under dry condition directly. Over the few past decades, many works have been studied the morphology and structure of different ionic surfactants on various

substrate, including graphite, silica, mica, metal etc.

From the result of previous studies, ionic surfactant form flat sheet or semi-cylindrical structure on hydrophobic substrate or surface with opposite charge with tail groups, whereas ionic surfactant aggregate into a shape of bilayer, cylinders or spheres structure on hydrophilic substrate or surface with same charge through electrostatic interaction.

In the ionic surfactant/opposite charge surface system, electrostatic force play an important role in surfactant structure. Many literatures discussed the effect of ionic strength or counter ion on organization of ionic surfactant molecules by addition of salts. William A. Ducker et al studied the influence of mono-valent electrolytes HBr, KBr, and N(CH₂CH₃)₄Br on the CTAB aggregation on mica. The CTAB forms flat sheet structure on the surface but the structure is transformed to cylinders with increasing addition of HBr and KBr. (*Langmuir* **1999**, *15*, 160-168) William A. Ducker et al also investigated the effect of metal halide (CsBr, CsCl, KCl, LiCl, LiBr) salts on surface aggregation of CTAC. They found that a structures transformed from a bilayer to cylindrical micelles to globular micelles by addition of alkali cations in the order Li⁺ < K⁺ < Cs⁺ at same concentration. In addition, the structure anion would bind to CTA⁺ headgroup and result in the structures transformation. (*J. Am. Chem. Soc.* **1998**, *120*, 7602-7607)

On the other hand, the experiments about the influence of salts on anionic surfactant aggregation at surface were also conducted. William A. Ducker et al studied that effect of the concentration of NaCl on SDS surface structure on graphite. The addition of NaCl reduces the repulsive interactions between the negatively charged head groups and result in the close spacing between hemicylinders. (*J. Phys. Chem.*, Vol. 100, No. 8, 1996) The same result was evidenced by the study of molecular dynamics simulation. (*Langmuir* 2009, 25(16), 9006–9011) The influence of the divalent ions on the morphology of SDS at graphite was also explored by William A. Ducker et al as well. They found the divalent ions would enhance the adsorption density and don't change the shape of aggregation conspicuously. (*Langmuir* **1997**, *13*, 1463-1474)

In this study, thin films of an anionic surfactant SDS with various charged inorganic salts were prepared on the surface of glass slide. An AFM was employed to observe the structure of these films. The effects of salts on the morphology of the SDS film were discussed.

Experimentals

All water in the experiment was pre-treated by a Milli-Q system and had a conductivity of 18 MO cm^{-1} . Sodium dodecyl sulfate was purchased from Sigma (purity, 92.5-100.5%). NaCl (J.T.Baker, 99.7%), KCl (Choneye pure chemicals, 98%), Cesium Chloride, CsCl (Merk, 99.5%), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Hayashi Japan, 99.7%), MgCl_2 (Riedel de haen chemicals, 99%), NaI (Choneye pure chemicals, 99%), NaNO_3 (Showa chemical, 98.5%) were used as the electrolyte addition. Sodium dodecyl sulfate (SDS) was prepared at 2mM and 8.1 mM concentrations. SDS/Inorganic salts aqueous solutions were prepared at 8.1 mM concentrations.

The boron silicate glass slide was cleaned with 75% ethanol to remove organic impurities and then rinsed with ultrapure water from Milli-Q system before use.

A drop of solution with the volume of $15 \mu\text{L}$ was transferred to the glass surface with a pipette. The glass with the solution drop was kept at 25°C and a humidity of 60% for 24 hour. Water evaporated and the surfactant film formed.

All films were imaged by Atomic force microscopy (JPK , Axiovert 200) with intermittent contact mode. The AFM probes were Tap 150Al-G Silicon probes, which were purchased from Budget Sensors

Results and discussion

The morphologies of the thin films were presented in three types of AFM image which is the error trace, the height image, and 3D reconstruction. The error trace is the first derivation graph, which gives the real surface of the sample. The height image displays the height of the surface with various color. The 3D height map is useful for determining three-dimensional patterns of molecules accumulation.

Structure of the SDS aggregation

Figure 1a and 1b shows the AFM surface height images and cross-section profiles of the morphology of SDS aggregates at glass slide. Whether the concentrations of SDS is 2mM or 8.1mM, the structure of the SDS molecular appear as linear and parallel stripes. The cross-section height profiles is along the black line in AFM height image. It provides the height variation over SDS aggregate structure. For 2mM SDS concentration, each adsorbed structure of 0.15- 0.35 μm height and 3-8 μm width were observed. At the concentration of 8.1 mM which is the critical micelle concentration (CMC) of SDS solution, the adsorbed structure feature similar result. The height and width of the structure is about 0.4-0.8 μm and 5 to 8 μm . From the two images, each stripe is a formation of flat layer and the distance between them is about 2 μm .

The drawing of partial enlargement from figure 1a are shown in figure 2. The edge of the parallel is very level and smooth. The maximum height in this two samples is

circa 0.2 μm and 0.88 μm respectively. Figure 2c is an AFM image of the error trace from figure 1d which is the raw data and gives the real image of the structure. It is evidenced clearly that SDS molecules were self-assembled to form ordered structure on glass slide by layer by layer deposition. We also observe that the formation of the layer has an orientation outwards (indicated by the arrow in figure 1e). This phenomenon was assigned to the outward capillary flow during evaporation. On the basis of the results, the thickness of the adsorbed structures were affected with the surfactant concentration but the morphologies and aggregates structures did not change.

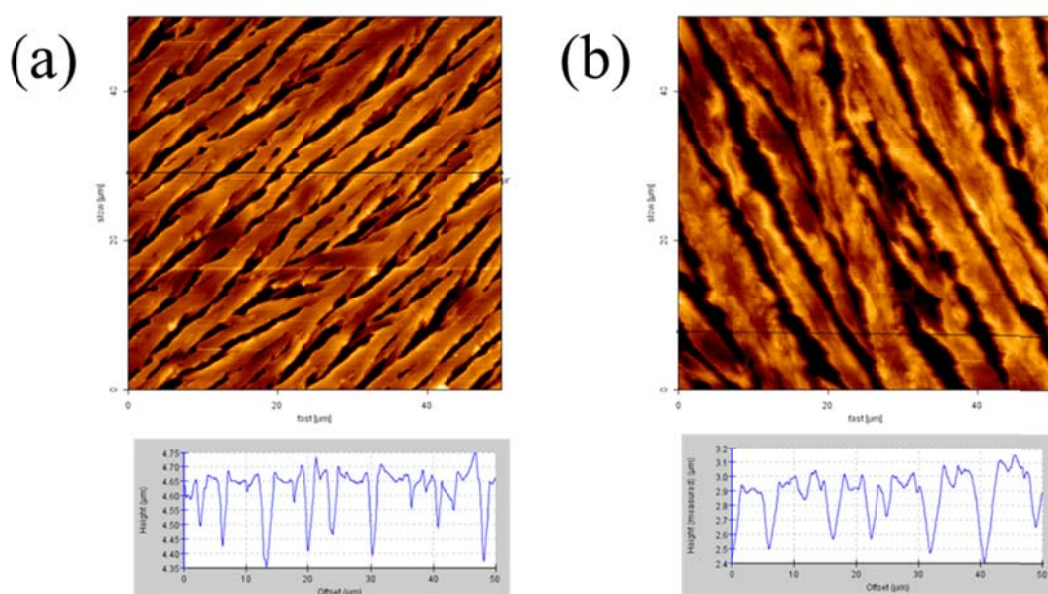


Fig 1 50 $\mu\text{m} \times 50\mu\text{m}$ AFM images and cross-section height profiles (a) at 2 mM and (b) at 8.1mM.

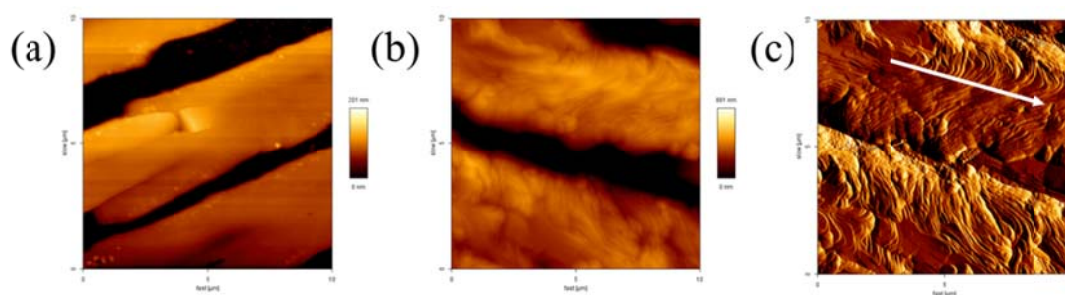


Fig 2 10 $\mu\text{m} \times 10\mu\text{m}$ AFM images (a) at 2 mM and (b) at 8.1mM, (c). AFM error trace images from (a)

Effect of cation on structure of the SDS aggregation

To better understand the influence of cation on morphology of SDS films, we prepared a solution of 8.1mM SDS and 8.1mM alkali chloride (Na^+ , K^+) or alkaline earth chloride (Mg^{2+} , Ca^{2+}) to form a thin film .

Figure 3a and 3b show the results of the SDS/mono-valence ions films. When SDS was coexistent with mono-valence ions, the transformation from linear stripe to rice plant was obtained. The SDS molecules in flat layer structures stretched out and the spacing between stripes is decreased. The maximum height of structure in SDS/NaCl and SDS/KCl is 344 nm and 235 nm which were lower than the height of SDS film (ca. 900nm). However, SDS/di-valence ions films were shown in figure 3c and 3d. When SDS was mixed with di-valence cation, SDS molecules assembled disorderly and no regular structure was observed. The results demonstrated that the existence of inorganic salt interfered with the structure of SDS. Due to the electrostatic interaction between cationic ion and the anionic head groups of SDS, the counter ions is more sensitive than co ions. With enough electrolyte in the system, the counter ions dominate in the stern and diffuse layer and hence reduce the repulsive interaction (increase the attractive interaction) between DS^- molecules. The effect of valence and concentration of counter ion was considered. In our case, all concentrations of SDS and electrolytes are constant at 8.1mM. So the principle reason is the valence of the counter ion. The SDS molecule aggregation multiplies with adding the multi-valence ions. The phenomenon was formalized in the Shultz-Hardy rule (Ref):

$$\text{Critical Coagulation of Concentration } C. C. C \propto \frac{1}{z^6}$$

Where z is the valence of counter ion. The critical coagulation concentration (CCC) is defined as the minimum concentration of colloidal particles for coagulation. For $z=1$ and 2, the ratio of the CCCs value are thus 1 and $1/2^6$ (0.016). At same concentration of electrolytes, higher valence counter ion could give a greater coagulation behavior. Thus, the divalent ion has much more electrostatic interaction with anionic head groups than that of the mono-valent ion so it causes a significant impact on changing the morphology of SDS film.

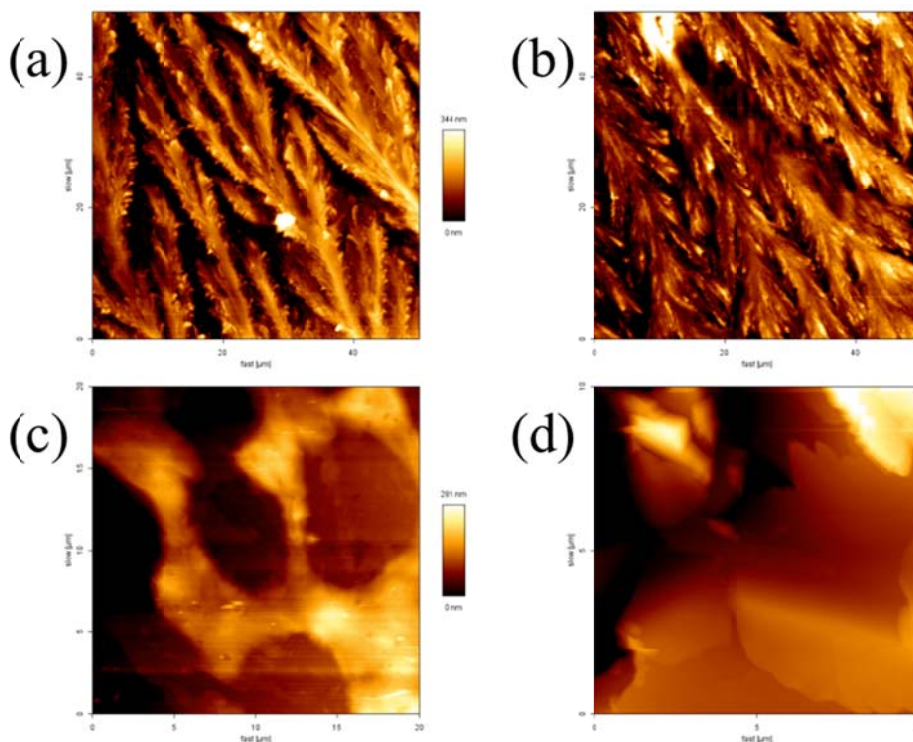


Fig 3 AFM images of SDS/inorganic salts aggregates at glass slide. (a) SDS/NaCl (b) SDS/KCl (c) SDS/CaCl₂ (d) SDS/ MgCl₂

Effect of anion on structure of the SDS aggregation

From above experiments, The regular stripes structure of SDS was affected slightly by the addition of Na⁺ or K⁺ at fixed anion. To further understand whether the SDS structure transformation was influenced by the anion or not. So we conducted the experiment that 8.1mM SDS and 8.1mM sodium inorganic salt (NaCl, NaI, or NaNO₂) solutions to be the thin films and the results are shown in figure 4.

It is more observed clearly that SDS molecules near the periphery of flat layer structures stretched out and branched pattern was obtained. It is found that the maximum height of structure in SDS/NaCl, SDS/NaI and SDS/ NaNO₂ is 338 nm, 243 nm and 187 nm respectively which were much lower than the height of SDS film. These patterns are similar to the images in the figure 3a and 3b.

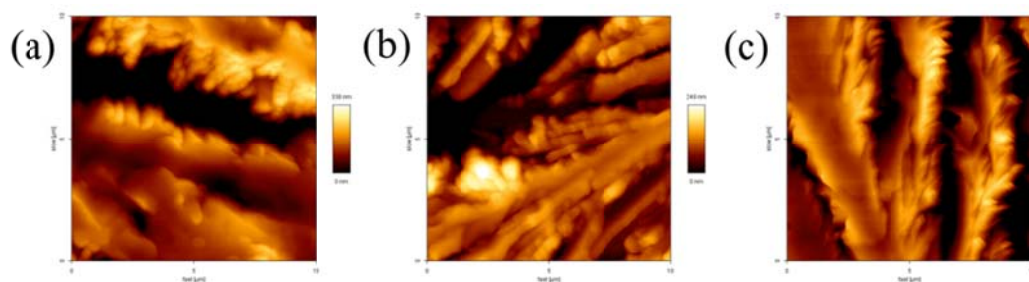


Fig 4 AFM images of SDS/inorganic salts aggregates at glass slide. (a) SDS/NaCl (b) SDS/NaI (c) SDS/NaNO₂

Formation of SDS multilayers

It is known that the addition of larger size mono valence ion would cause the lower adsorbed structures without changing SDS concentration. In the case of the thin film from 8.1mM SDS in the presence of 8.1mM CsCl solution, the branched pattern are shown in Figure 5a. The maximum height is decreased to 33.9 nm which is far lower than the results of the other SDS/ mono valence ion systems. Observation from the 3D reconstruction image in figure 5c, the SDS structure is a formation of lamella which are stacked by the layers. Figure 5b is a cross section of an indentation site in the figure 5a and shows the thickness of the SDS layers is approximately 5 nm. According to the study from Bernardes and co-workers (Ref), the hydrophobic part of one SDS bilayer is about 4 nm and each sulfate group has 0.6 nm length. Hence, the result is corresponding to the height of one surfactant bilayer.

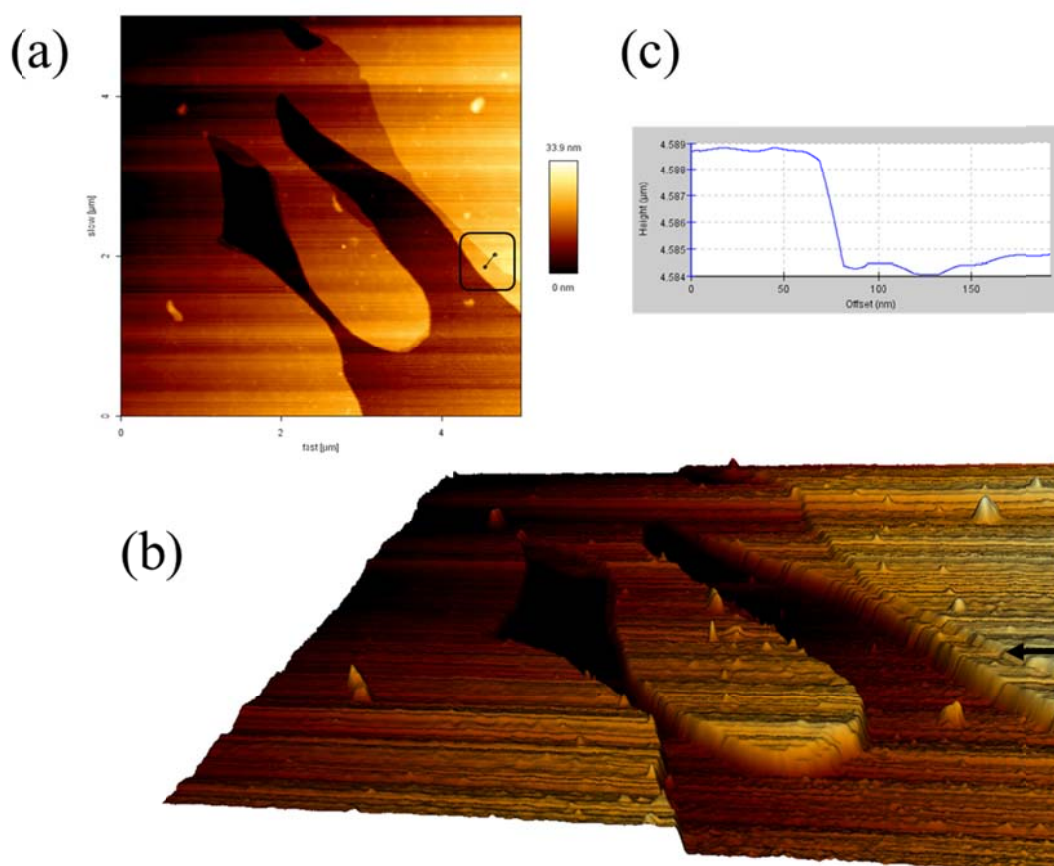


Fig 5 AFM result of SDS/CsCl aggregates at glass slide. (a) Height image (b) 3D image (c) cross-section height profiles along the line in (a)

Discussion on adsorption mechanism

The mechanism to explain the formation of aggregated structure from both of SDS and SDS/mono valence ions system are shown in figure 6. It is well known that the boron silicate substrate is a negatively charged surface with hydrophilic property and the DS^- has a negative charge head group.

The mechanism for the SDS system is shown in figure 6a. When SDS solution was dropped on the glass surface, sodium ions first adsorbed onto the substrate through attractive electrostatic interaction, and the negative DS^- head group adsorb on the Na^+ ion layer and the hydrophobic carbon chain of SDS upward. And then, the hydrophobic carbon chain of SDS links together by the van der Waals force to form a deposited bilayer. After that, according to the charge regulation mechanism from Bernardes and co-workers (Ref), Na^+ ions penetrate into the negative interface between the DS^- head groups to compensate charge density in the drying process. A lamella structure of stacking bilayers forms.

With the addition of inorganic salts, excess cations exist in the spacing between stripes. SDS molecules were attracted by excess mono valence cation ions and extended laterally instead of stacking, as shown in figure 6b. It therefore caused strip shape SDS changed to the oryza or leafy shapes and the reduction of the stack thickness.

Because the large size of cesium ions results in a lower charge density, the interaction force between these ions and the substrate is poor. The SDS molecules are susceptible to move with solvent flow, resulting in a wider range of diffusion, the mutual attraction force between SDS molecules is low in this case. Hence, without decreasing the SDS concentration, we still get the SDS bilayer by adding the large ions.

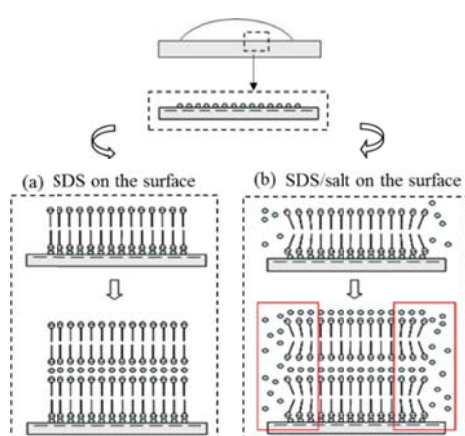


Fig 6 possible mechanisms for surfactant adsorption on glass slide. (a) SDS (b) SDS/mono salts

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