HYDROPHOBICITY ENHANCEMENT OF $SiCl_4$-TREATED COTTON CLOTH MODIFIED BY POTS AND DMDCS

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Abstract:Comparison of hydrophobicity enhancement of cotton cloths modified by 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (POTS) and dimethyldichlorosilane (DMDCS) was studied. The cotton cloths were firstly pretreated with $SiCl_4$ in order to fabricate the silanol groups on the cotton cloth surface prior bonding to POTS and DMDCS. Surface morphology and weight percent of Si modified cotton cloths were investigated by SEM and EDS techniques, respectively. With 20 mins contact time and 6 successive cycles in atmosphere of $SiCl_4$ vapour resulted in optimum amount of Si covered on the pretreated cotton cloths. After that the $SiCl_4$-treated cotton cloths were then separately modified with POTS and DMDCS by chemical vapour deposition method. Hydrophobicity of the modified cotton cloths were determined by contact angle measurement. The contact angle of water of POTS-$SiCl_4$-treated cotton cloth and DMDCS-$SiCl_4^{'}$ treated cotton cloth were 158° and 138°, respectively. It can be explained that the hydrophobicity of POTS-$SiCl_4$-treated cotton cloth surface better than the others.

1. Introduction

Surface modification of cellulosic fiber can be done by different methods to obtain a wide range of characteristics of the surface such as roughness [1],surface charge, surface energy [2] and hydrophobicity [3].Superhydrophobic surfaces treatment, with water contact angle greater than 150 degree various has attracted attention due to their applications in water-repellency [4], lubricity [5], self-cleaning [6], anti-fouling [7] etc. Techniques for preparation of super-hydrophobic surface treatment have been investigated for example coatings [8], immersion [9], diffusion [10], thermal spray and welding using advanced heat sources like plasma [11], physical vapor deposition (PVD) [12] and chemical vapour deposition (CVD) [13].Over the past several decades, CVD has become an increasingly important process for the manufacture of thin film materials [14]. The advantages of CVD are the capability of producing highly dense material and ability to control crystal structure [15], surface morphology and orientation of the CVD products [16]. CVD technique has more attractive advantages for growth of a thin film on the desired materials surface because of good coverage on patterned or rough surface and low chemical reagent consumption [17].There are many worksapplied a CVD techniqueinthe surface modification onvarious materials. Quarmyne and Chenprepared a nanoscale inorganic layers on polymer film substrates and activated by the spontaneous adsorption of poly(vinyl alcohol)(PVA); silica and titania were subsequently condensed on these surfaces by sequential vapour phase reaction with either silicon tetrachloride ($SiCl_4$) or titanium tetrachloride ($TiCl_4$) and water [18]. Wang *et al.* fabricated the superhydrophobic wood surface via a sol-gel process followed by a fluorination treatment of 1H, 1H, 2H, 2H- perfluoroalkyltri-ethoxysilanes (POTS) reagent [19]. Chaimngoen *et al.* prepared the hydrophobization of the PVA fiber mats by dimethyldichlorosilane and methyltrichloro-silane in the vapour phase at room temperature [20].

This research focused on the hydrophobicity enhancement on cotton cloth by pretreating with nanoscale inorganic surface layers of $SiCl_4$ followed by POTS and DMDCS. Reaction time and number of cycles for fabrication of $SiCl_4$ thin film on the cotton cloth were also optimized prior modification by POTS and DMDCS. The amount of $SiCl_4$ deposited on cotton cloth was investigated by energy dispersion X-ray spectroscopy (EDS). The surface morphology changing after treatment was observed by scanning electron microscopy (SEM). Finally, the contact angle of water for all modified cotton cloths were also measured.

2. Materials and Methods

2.1 Materials

Cotton cloths used in this work were in the size of 3x3cm^2 and bleached. Silicontetrachloride ($SiCl_4$), 1.0 M solution in dichloromethane, 1H, 1H, 2H, 2H-perfluorooctyl-triethoxysilane (POTS) (98%) and dimethyldichloro-silane (DMDCS) (99.5%) were purchased from Sigma-Aldrich. All of the chemicals were used as received without further purification.

2.2 Preparation of $SiCl_4$-treated cotton cloth

All cotton cloth samples were dried in a Schlenk flask andpurged with N_2 for 30 mins. After that the samples were separately exposed to $SiCl_4$ vapour at various time via a cannula connecting flask in a steady stream of N_2 at room temperature to optimize the deposition time. Finally, sample containing in the flask was purged with N_2 for 5 mins, and were then left in the air. Furthermore, in order to study the cycle number of reaction affecting on the Si content on cotton cloth, the fabrication of $SiCl_4$ on the cotton cloth at various cycle number of reaction was also carried out.

2.3 Modification of $SiCl_4$-treated cotton cloth by POTS and DMDCS

$SiCl_4$-treated cotton cloths were modified by POTS and DMDCS via the CVD method. $SiCl_4$- treated cotton cloth sample was placed into a sealed vessel containing 1 μl of POTS. The sealed vessel was put in an oven at 125 °C for 2 hto enable the silane group of POTS vapor to react with the hydroxide group of $SiCl_4$ completely.After that, the vessel was opened and heated at 150 °C to remove the free POTS molecules.

In case of $SiCl_4$-treated cotton cloth modified by DMDCS, the sealed vessel was put in an oven at 60-70 °C for 1 hr. Finally, the superhydrophobic cotton cloth surface was obtained.

2.4 Characterization

The morphological structure and chemical composition of the cotton cloth and $SiCl_4$-treated cotton cloth surface were investigated by scanning electron microscopy (SEM) (JEOL JSM-5910LV) and energy dispersive spectrometer (EDS) (OXFORD INSTRUMENTS), respectively. The wettability was characterized by the measurement of the water contact angle on the superhydrophobic surface using a Sessile drop method. The selfmade contact angle meter captured image of 1μl of deionized water and analysed by using an image analysis software.

3. Results and Discussion

3.1 Morphology and the chemical composition of the cotton cloth and $SiCl_4$-treatedcotton cloth surface

The morphology of the untreated and treated cotton cloth surface using SEM shown in Fig.1. The smooth surface of the untreated cotton cloth can be observed. Fig. 1 (B) shows that the silica particles deposit on the cotton cloth and coat on the cotton cloth surface. The silica particles are adhered onto cotton cloth surface through the chemical bond between hydroxyl groups of cotton cloth surface and silica particles [21]. The arrangement of silica clusters between each silica particles, thus roughening the cotton cloth surface dramatically.

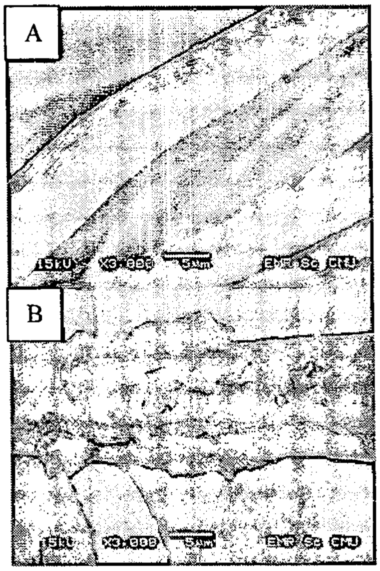

Figure 1. SEM images of (A) untreated cotton cloth and (B) $SiCl_4$-treated cotton cloth

Electron dispersive X-ray spectrometer (EDS) was employed to investigate the chemical composition of $SiCl_4$-treated cotton cloth surface, compared to the unmodified one. Fig. 2(A) and (B) represent the EDS spectra of the untreated cotton cloth and the $SiCl_4$-treated cotton cloth surface, respectively. The EDS spectrum of untreated cotton cloth shows two peaks of C and O elements, whilst three prominent peaks of C, O and Si elements of $SiCl_4$-treated cotton cloth are observed. It indicated that $SiCl_4$ was successfully coated on the surface of cotton.

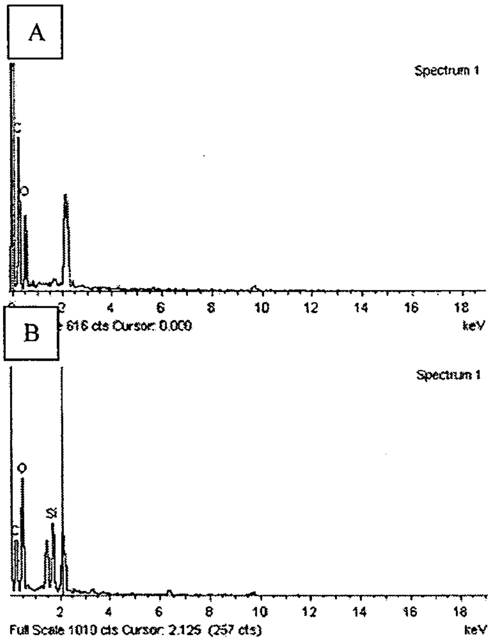

Figure 2. EDS results of (A) untreated cotton clothand (B) $SiCl_4$-treated cotton cloth

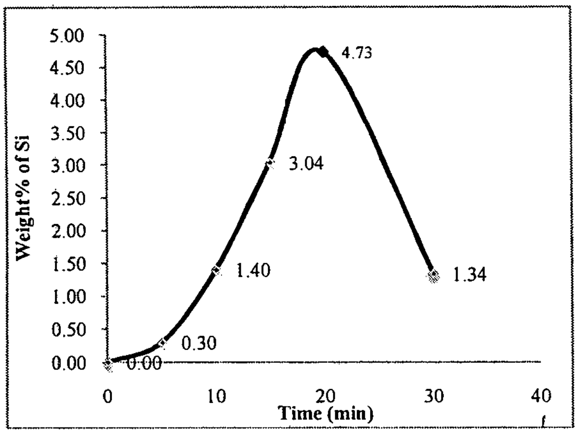

Figure 3.The amount of silicon deposition on the $SiCl_4$-treated cotton clothat various reaction time.

Si content deposited on the $SiCl_4$-treated cotton clothsurface at various deposition times was investigated, as shown in Fig. 3. The result showed that the amount of deposited Si on cotton cloth surface was increased corresponding to the deposition time.The maximum amount of Si was 4.73% (wt) at 20 mins and after 20 min, the amount of Si decreased. This reduction of $SiCl_4$ content may be caused by the agglomeration formation of deposited Si that lead to incompletely coating [22]. Therefore, cotton cloths were treated with $SiCl_4$ for 20 mins.

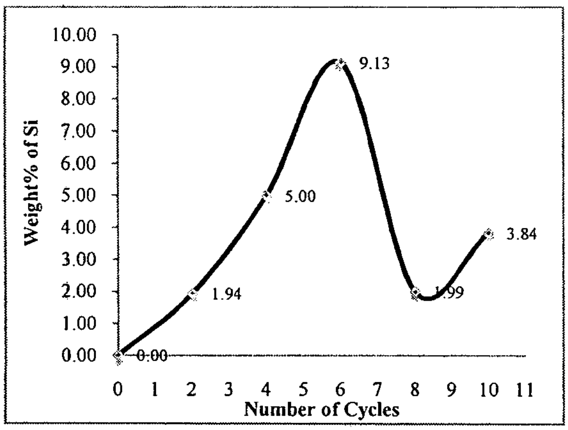

Figure 4.The amountof silicon deposition on the $SiCl_4$-treated cotton clothat various number of cycles reaction.

In Fig. 4, number of reaction cycle (number of repeating deposition of $SiCl_4$ via CVD on the cotton cloth surface) affected on the Si content on the cotton cloth surface was investigated. It can be clearly observed that the amount of deposited Si increased with the number of reaction cycles, the result agrees with the reaction between cross-linked PET-PVOH and $SiCl_4$ [18]. At 6 cycles, the amount of $SiCl_4$ was observed at 9.13% (wt). The decreasing of Si content at the higher 6 cycles of $SiCl_4$ pretreatment may have the same reason with the case of effect of reaction time.

3.2 Wettability of POTS-$SiCl_4$-treated cotton cloth and DMDCS-$SiCl_4$-treated cotton cloth

The wettability was measured by using contact angle of liquid on the solid surface. If the contact angle of water droplet on the surface is less than 90°, the surface were usually classified as hydrophilic. Otherwise, it is usually classified as hydrophobic if the contact angle were greater than 90°. If on a surface whose water contact angle is greater than 150°, it can be regarded as superhydrophobic [23].

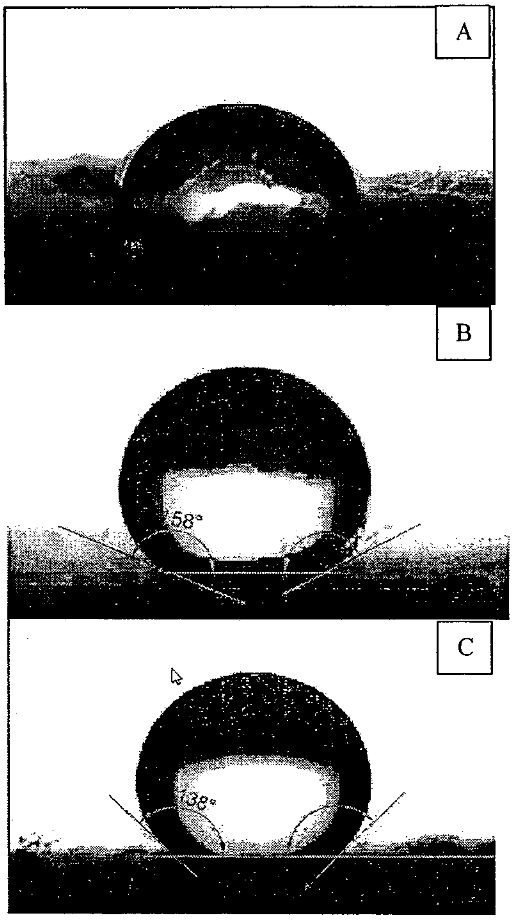

Figure 5.Photograph images of a water droplet on different surfaces: *i.e.* (A) untreated cotton cloth, (B) POTS-$SiCl_4$-treated cotton cloth, and (C) DMDCS-$SiCl_4$-treated cotton cloth.

Fig. 5 shows the photographs of water droplets on the surface of the untreated cotton cloth, the POTS-$SiCl_4$-treatedcotton cloth and the DMDCS-$SiCl_4$-treatedcotton cloth, as indicated by A, B, and C, respectively.The untreated cotton cloth and $SiCl_4$-treated cotton cloth exhibited a contact angle at 69° and nearly 0° for a water droplet due to hydrophilic property the water droplet was spread over on its surface that indicated hydrophilic property. The surface of POTS-$SiCl_4$-treated cotton cloth achieved the water contact angle about 155°. Additionally, DMDCS-$SiCl_4$- treated cotton cloth surface exhibited the water contact angle about 137°.It indicated that the formation of POTS and DMDCS on cotton surface exhibits superhydrophobic and hydrophobic property, respectively, because the structure of POTS is longer chain of hydrocarbon than DMDCS. Thus it exhibits superhydrophobic.

4. Conclusions

Si clusters formation on cotton cloth surface was obtained after pretreatment with $SiCl_4$. The optimum reaction time for pretreatment was observed at 20 min. Moreover, it was revealed that the number of reaction cycle affected Si content on cotton cloth. Contact angles of water of POTS-$SiCl_4$-treated cotton cloth and DMDCS-$SiCl_4$-treatedcotton cloth were compared. It can be seen that the higher efficiency for hydrophobicity enhancement on cotton cloth of POTS-$SiCl_4$ modification with respect to DMDCS-$SiCl_4$-treated cotton cloth. However, cotton cloth surface modification by DMDCS should be selected to enhance the hydrophobicity of cotton cloth in large scale due to low cost and good hydrophobic property.

Acknowledgements

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