

GREEN MATERIAL FROM NATURAL RUBBER-COATED FABRIC AS A SUSTAINABLE SOLUTION IN REMOVING OIL FROM WATER

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Abstract

Oil removal from water has become more important for environment sustainability since there are many cases of oil leakage accidents. Oil spills, whether caused by accidents or other factors, can have devastating effects on aquatic ecosystems and wildlife. To clean up by utilizing green materials, it can mitigate the environmental impact of oil spills and align with the principles of conservation science. Therefore, in this work, an attempt was made to clean oil contamination using rubber foam attached with cotton fabric. The enhancement of hydrophobicity would increase the efficiency of oil removal. The cotton fabric was coated by natural rubber (NR) foam and subsequently treated with hexadecyltrimethoxysilane (HDTMS) as hydrophobic agent. The results show the treated NR-coated fabric exhibited excellent oil absorption, oil selectivity and completely removed the oily layer from water. It is because hydrophobic enhancement of cotton fabric and rubber foam surfaces were achieved at 157° and 140°, respectively. The formation of hydrophobic agent with rough surface was revealed by SEM micrographs. From the results, the prepared NR-coated fabric presented an attractive hydrophobic property with simple preparation and high efficiency of oil removal. It could be said that NR-coated fabric is a green material potentially used as a perfect oil-separator to relieve the pollution from oil contamination. Conservationists and researchers can work together to raise awareness about the benefits of using green materials for oil spill cleanup, fostering a sense of environmental stewardship.

Keywords: oil removal; superhydrophobic; hydrophobicity; rubber-coated fabric; oil and water separation

Introduction

It is undeniable that water is very important in life. Oil contamination in water causes serious water pollution and endanger to marine species, human being, food chain, industries of fishing and tourism. In the past decades, there are many oil-spill cases occurred and most of them have not recovered fully. It is not easy to remove the oily layer from the top surface of water, completely. In addition, the growing industries such as mining, textiles, food and petrochemicals generate oil contamination from discharging oily wastewater [1]. Therefore, it needs proper and urgent management after leakage or spill. There are several techniques to clean up oil from water such as using chemical, skimming, burning, absorption [1, 2]. Conventional oil spill cleanup methods, such as chemical dispersants, can further disrupt ecosystems and harm the environment.

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Absorptive materials is quite interesting due to less consequent effects, low cost and uncomplicated usage. The use of green materials for oil removal aligns with the concept of sustainability, a key principle in conservation science. Natural rubber-coated fabric, being derived from renewable resources, offers a sustainable alternative to synthetic materials or single-use products for cleaning up oil spills. This approach reduces the demand for non-renewable resources and minimizes waste generation, both of which are fundamental aspects of conservation efforts. NR possesses hydrophobic property absorbing non-polar liquid and oil. Its oil absorption efficiency can be improved by producing as a foam thus oil can go through the cellular structure rapidly [2, 3]. However, little water could probably be obtained. Cotton fabric was used to support the weak NR foam in the case of over absorption of non-polar liquid or oil. Moreover, cotton fabric can be converted from hydrophilicity to hydrophobicity by chemical treatment [4, 5]. As mentioned previously, it is difficult to separate oil and water completely and foam structure may allow little water goes through. This is a challenging issue for developing materials with high efficiency of oil selection to deal with this problem. Therefore, an attempt was made to enhance hydrophobicity of both NR foam and cotton fabric surfaces.

Previously, hydrophobicity of cotton fabric was enhanced using silane. Hydroxyl groups in cotton could form bonds with silanol groups in silane [4, 5]. *Pran K Saha et al.* [6] improved the hydrophobicity of nonwoven cotton fabric using HDTMS. The results showed that the water contact angle (WCA) increased with increase of HDTMS amount. Hua Zhou et al. successfully prepared superhydrophobic cotton fabric by coating with fluorinated alkyl silane (FAS) and silicone rubber. It revealed that the contact angle of water, acid solution and alkaline solution were greater than 150° [7]. One of the main applications of superhydrophobic materials aims for oil and water separation [8, 9]. A few researches improved the WCA of NR by other methods for example coating with polyethylene solution [10] and using silicone rubber. Since hydroxyl groups are no present in NR but as double bonds which could react with thiol group in tris(3-mercaptopropionate) (TMP) [11]. Therefore, TMP was used as a linkage between NR and HDTMS in pretreatment step.

The development of green materials for oil removal involves scientific research and innovation. Conservation science encourages the use of cutting-edge technologies and approaches to address environmental challenges. By researching and developing effective, eco-friendly materials for oil spill cleanup, scientists contribute to both conservation efforts and the advancement of sustainable practices. The aim of this study is to prepare green and high efficiency oil separator from natural rubber and cotton fabric. Its efficiency was improved by enhancement of hydrophobicity of both NR foam surface and cotton fabric surface. Functional groups, WCA and surface morphologies of samples were observed. Oil absorption selectivity and oil removal were performed. The untreated NR foam coated on cotton fabric was prepared for comparison.

Experimental part

Materials

Natural rubber latex (NRL) and all chemicals (potassium oleate, sulphur, zinc diethyldithiocarbamate (ZDEC) and zinc-2-mercaptobenzothiazole (ZMBT), diphenylguanidine (DPG), zinc oxide (ZnO) and sodium silicofluoride (SSF)) were provided by Research Rubber Institute of Thailand. Benzene that was used as oil in this work was supplied by Bangchak Corporation Public Company Limited. Tris(3-mercaptopropionate) (TMP) and hexadecyltrimethoxysilane (HDTMS) were purchased from S.M Chemical Supplies Company Limited. Ammonium hydroxide (NH₄OH) was obtained from QReC Company Limited.

Natural rubber coated on fabric

Firstly, the NRL was mixed with 1.5phr potassium oleate and 1phr sulphur (S) in mixer batch and stirred at 300rpm. After that, ZDEC and ZMBT at 1phr of each chemical were also added into the mixture. The mixture was stirred at speed of 800rpm. Then DPG was added and

stirred for another 3 minutes and followed by ZnO for another 1 minute. Finally, SSF was put into wet foam and stirred for another 1 min. Subsequently, the viscous foam was casted onto the cotton fabric with thickness of 3 mm. It was placed in room temperature for 60 minutes for stabilization. The reaction was next done through steaming process for 20 minutes. The samples were dried in oven for 24 hours.

Hydrophobic enhancement

The obtained fabric coated by NRL foam was immersed in the solution of 0.5mL of TMP, 100mL DI water mixed with 28% NH_4OH for 6mL for 30 minutes before shaking in hot water for another 30 minutes. TMP was purposely used as a linkage between silane and rubber. After that, the surface of substrate was treated by 10% HDTMS. Then it was cured at 110°C for 1 hour and left at room temperature for 24 hours before characterization.

Methods

FTIR

Fourier transform infrared spectroscopy (FTIR) was used to compare the functional groups of untreated and treated samples. FTIR spectra measurements were carried out with Nicolet iS50 FTIR Spectrometer in ATR mode. The spectra were recorded in the range of $400\text{-}4000\text{cm}^{-1}$. The samples were washed by ethanol for several time before characterization.

SEM

The surfaces morphologies of both rubber and fabric sides were observed using scanning electron microscope (SEM) (JEOL 6480LV). Before SEM observation, all samples were fixed on aluminum studs and coated with thin gold layer.

Contact Angle

The water contact angle was measured using wetting angle measurement (KYOWA, DM-CE1) with droplets of $\sim 5\mu\text{L}$. Three different parts of surface were measured and averaged.

Oil selectivity

The oil selectivity was investigated by dipping the sample into the mixture of oil and water. It was placed in water through the oil on top layer for 5 seconds. After that the sample was then observed for the staining of water. The water was dyed in purple while oil is yellowish transparent.

Absorption

The selectivity of absorption was also observed by wiping. The small volume of oil and water mixture was prepared by dropping 0.3mL of oil and 0.3mL of water onto petri dish. The sample was placed onto the liquid mixture for absorption. The rubber side was place first for 3 seconds and followed by fabric side for another 3 seconds, performed for 3 rounds. After that the absorbed samples were taped to remove the excess liquid. The residue was measured by syringe. The absorption was evaluated.

The removal of oily layer from the top of water surface was performed by placing the rubber-coated fabric onto oil/water mixture. Firstly, the oily liquid was stirred using magnetic bar at speed of 500rpm for 15 minutes. After that the sample with size of $2 \times 2\text{cm}^2$ was placed on the liquid mixture and oscillated on the top of liquid surface for 15 seconds. Finally, the surface of mixture liquid was observed for the performance of oil removal.

Results and discussion

FTIR characterization

ATR-FTIR spectra for both sides of untreated and treated samples are as shown in figure 1. On fabric side, the absorption bands at $3200\text{-}3550\text{cm}^{-1}$ appeared in both untreated and treated cotton fabric. These peaks are assigned to -OH in cotton fabric and -OH from silane. The peaks at $2850\text{-}2915$ and $1360\text{-}1425\text{cm}^{-1}$ are attributed to C-H (stretching) and CH_3 (bending) groups respectively [12, 13]. The treated surface presented those peaks with higher intensity from the

hydrocarbon chain from HDTMS compared to untreated surface. It also shows the peak at 1199cm^{-1} which is the characteristic of Si-O-CH₃ group [5, 14].

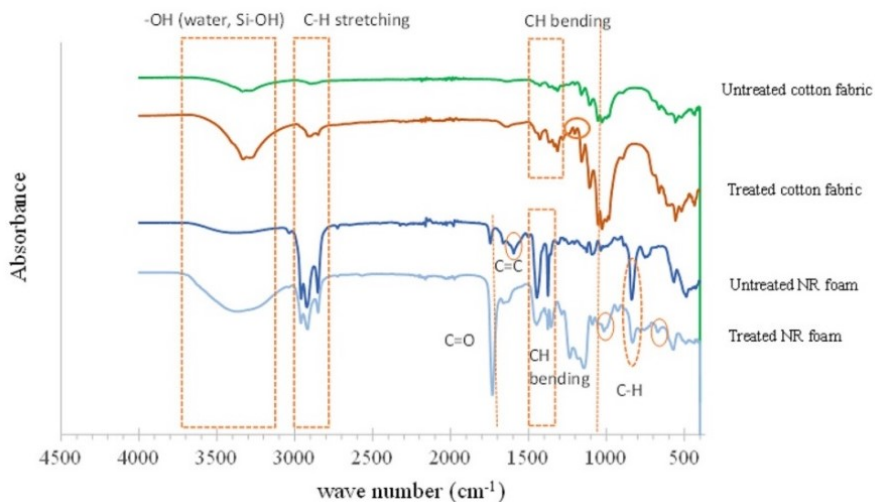


Fig. 1. FTIR spectra of cotton fabric surface and NR foam surface with and without treatment

The spectrum of pristine natural rubber (NR) presented bands around $2840\text{--}2975\text{cm}^{-1}$ attributing to C-H bond (stretching) from CH₃. The characteristic bands at $1375\text{--}1445\text{cm}^{-1}$ are assigned to C-H deformation. Besides, the small absorption band at 1595cm^{-1} corresponds to C=C bond of the cis-1,4-polyisoprene [15, 16]. The absorption intensity was absent after treatment, which could be due to the formation with TMP. The peak of C-H (out of plane deformation) at 897cm^{-1} presented more obviously probably due to C-H from silane [16]. Several new peaks were observed in the treated NR spectrum that were not present in the untreated NR spectrum. The presence of C=O group at 1680cm^{-1} revealing the presence of TMP. The bands characteristics of silane are indicated at 670cm^{-1} (-CH₃ rocking and Si-C stretching), 1010cm^{-1} (Si-O-Si stretching) and $3100\text{--}3700\text{cm}^{-1}$ (condensed Si-OH) [17].

Wettability

Surface wettability was measured by water contact angle. The water contact angle on treated surfaces of cotton fabric and NR foam were studied and the results obtained are as shown in figure 2. Hydrophobicity is an essential phenomenon to imply the oil absorption behaviour at $>90^\circ$ water contact angle. It was investigated that on untreated cotton fabric, there is no presence of water droplet. It was not surprising due to a good water absorption behaviour or hydrophilicity of general cotton. Interestingly, after treatment with HDTMS, the water contact angle value of cotton fabric increased greatly and obtained superhydrophobic characteristic at 157° . For NR foam side, the treated surface obtained much improvement of water contact angle from 118° to 140° .

Figure 2c shows the enhancement of hydrophobicity of cotton fabric after treatment. The water droplet in the round shape presented on treated surface of cotton fabric while on untreated surface, water was absorbed immediately after dropping. Moreover, the droplet of hydrophobic vegetable oil was also investigated. The flat shape of oil was found on untreated cotton fabric even though oil is hydrophobic, but cotton is hydrophilic. It is probably due to the liquid oil could go through the gap in weaving structure of fabric. However, it revealed the better oil absorption

after treatment compared to on untreated fabric. Similarly, it could be noticed the hydrophobicity enhancement on treated NR foam surface. It revealed the better round shape of water droplet compared to untreated one. Figure 2e and f shows the rolling of water droplet on the inclined planes of treated surfaces. The water droplet rolled on treated cotton fabric surface perfectly implying the low adhesion on surface. However, on NR foam surface, rolling of water droplet need the larger angle of inclined plane. From the results, it could be said that HDTMS improve hydrophobicity of both cotton fabric and NR foam surfaces.

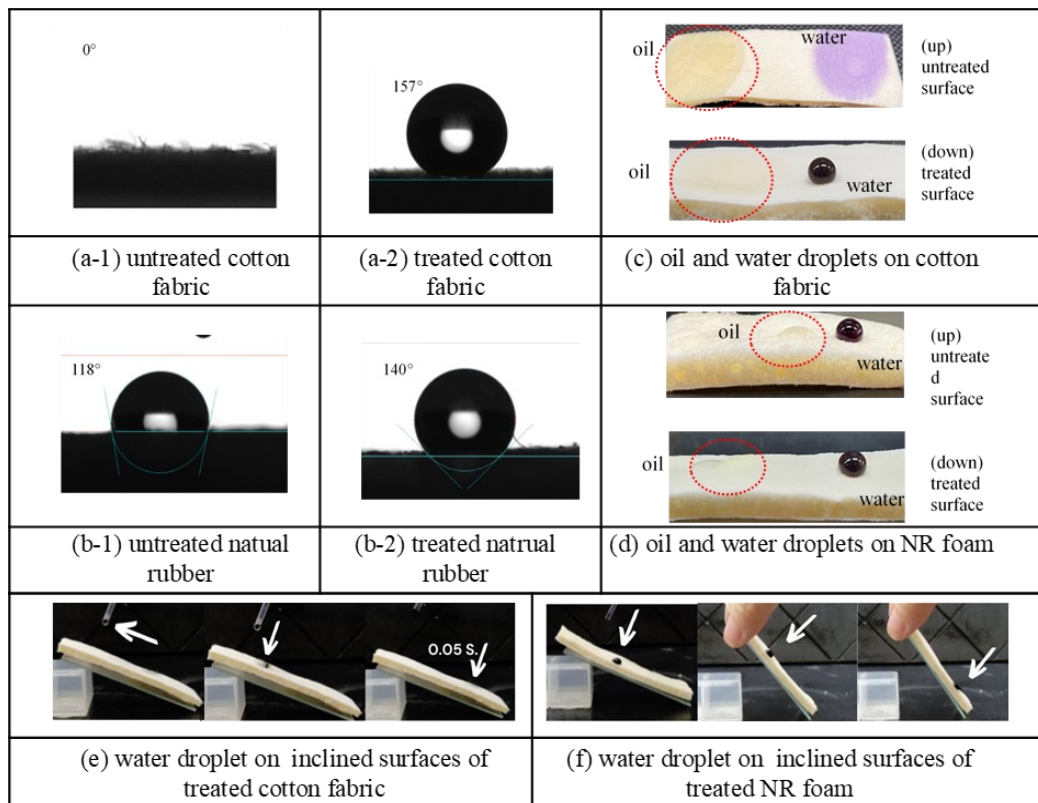


Fig. 2. Water contact angle of cotton fabric surface and NR foam surface with and without treatment

Surface morphology

The SEM micrographs of cotton fabric and NR surface before and after treatment are shown in figure 3. The micrographs presented smoother surface of untreated cotton fabric compared to treated one. The HDTMS also formed the aggregated layer on fiber surface which is obviously seen in figure 3b-3. HDTMS contains long chain hydrocarbon providing hydrophobicity behaviour. The tiny hydrophobic roughness would reduce the surface contact between water droplet and substrate surface, therefore the significant improvement of hydrophobicity was obtained as superhydrophobicity. In the case of rubber, fuzzy surface was found on treated rubber foam which is also probably from the long hydrocarbon chain of HDTMS. On the other hand, the untreated rubber foam revealed the coarse surface with micro pores. Originally, abundant fibrils are typically found in cotton fabric that possess roughness in

micro scales. This is the reason why hydrophobicity of cotton fabric was much better enhanced than that of NR foam surface as shown in figure 2.

Oil selectivity and removal

The absorption selectivity was evaluated as shown in figure 4a. It was found that the treated NR-coated fabric absorbed much less water than the untreated one while both untreated and treated samples could absorb oil very well. It is because rubber foam is hydrophobic material which prefers to absorb non-polar liquid. At the same time, the cotton fabric is well-known as a high-water absorption material. In addition, rubber foam contains a lot of pores which water is able to go into the cellular structure. However, after treatment by HDTMS, hydrophobicity of cotton fabric and rubber foam were increased significantly (as seen from WCA values) resulting the increment of water repellence. This is why the amount of absorbed water is very low.

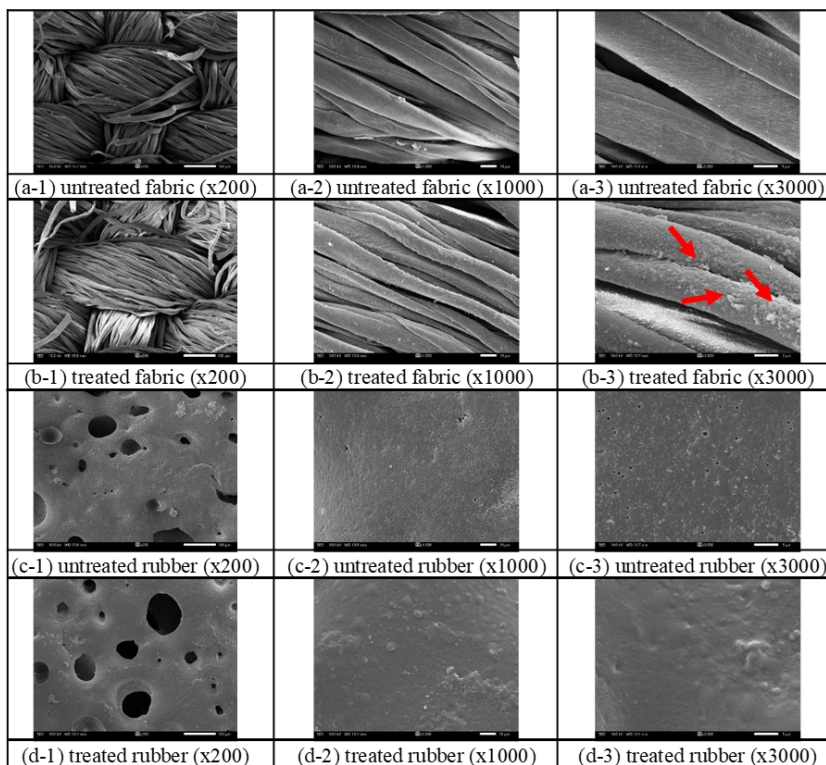
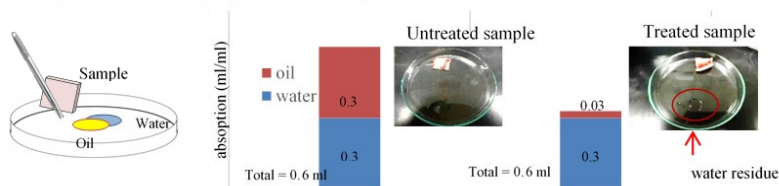


Fig. 3. SEM micrographs of cotton fabric surface and NR foam surface with and without treatment

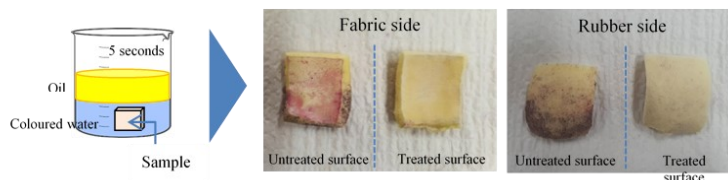
Oil selectivity was also studied by immersing through oil and water layer (Fig. 4b). The density of oil is less than that of water, thus the oil is in the upper layer while water layer is in the bottom layer. The water was dyed with purple to differentiate easily from oil. The result showed that the treated NR-coated fabric did not absorb the water for both sides, unlike the untreated sample that could obtain some of the water inside of sample. As mentioned above, water may also go into cellular structure of the foam.

The removal of oily layer was performed by placing the sample into the oil and water mixture. As shown in figure 4c, it was observed that the NR-coated fabric could remove oily layer from mixture liquid completely (observed by naked eyes) while it was still seen on the top layer of the mixture liquid after using the untreated sample.

(a) Absorption selectivity by wiping



(b) Absorption selectivity by immersion



(c) Oily layer removal

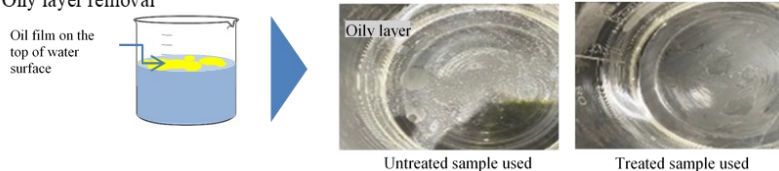


Fig. 4. Oil absorption selectivity and oil removal of NR-coated fabric with and without treatment

From the results, it could be concluded that the NR-coated fabric that was treated by HDTMS provided great performance of oil removal and oil selectivity due to the obvious enhancement of surface hydrophobicity.

Conclusions

NR-coated fabric was prepared by casting NR foam on cotton fabric. The enhancement of hydrophobicity was conducted as post treatment. It successfully enhanced the hydrophobicity of both cotton fabric surface and NR surface using HDTMS. Hydrophobicity of cotton fabric could be enhanced dramatically, showing the superhydrophobic characteristic with WCA at 157° . In addition, NR surface was also obviously enhanced, showing the hydrophobicity with WCA from 118° to 140° . SEM micrographs revealed the formation of micro roughness on cotton fiber and fuzzy surface on NR. This results the superb oil absorption selectivity and oil removal of treated NR-coated fabric. From the results, enhancement of surface hydrophobicity increases efficiency of oil removal and selectivity. By employing sustainable, eco-friendly solutions to mitigate the impact of oil spills, the research contributes to the preservation of ecosystems and the protection of natural resources, which are at the core of conservation efforts.

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