

Permanent Water Repellent Chemical Modification of Cotton Fabric with Reagents Containing Aromatic Rings

Xueyang Liu^{1,2}, Guang Yang², and Vitali Lipik^{3*}

¹*Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing 211816, China*

²*Institute for Sports Research, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore*

³*School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore*

(Received August 13, 2018; Revised September 20, 2018; Accepted October 7, 2018)

Abstract: In this work, reagents with different amounts of aromatic rings were reacted with hydroxyl groups of cotton, aiming for washing stability and water repellency of treated cotton fabric. Different conditions of chemical transformation were considered, including the influence of carbonyl and ester chemical bonds, the quantity of aromatic ring in the reagent, and the properties of obtained cotton fabric. High contact angles were reached with the maximum of 140° obtained at the usage of chlorotriphenylsilane. Six reagents used for cotton treatment have shown excellent washing stability, and their contact angles expressed the high water repellency of the fabric even after 10 washing cycles. Although mechanical properties of treated fabric were dropped for some samples due to the reduction of hydrogen bonds amount, stiffness of fabric decreased by up to 40 % which means softer fabric. The cotton fabric treated with reagent containing two aromatic rings exhibited the best properties of washing stability and water repellency.

Keywords: Cotton fabric, Water repellent treatment, Aromatic-ring reagents, Washing durability

Introduction

There is a demand for hydrophobic cotton fabrics for outerwear fabrication. Several large directions exist for making hydrophobic and superhydrophobic surfaces on cotton fabric – dipcoating, spray coating, polymerization techniques – in situ nanoparticle growth, chemical vapor decomposition (CVD) and plasma processing [1]. Mechanical stability of hydrophobic coating and its thickness are also very important parameters of fabric at the stage of fabrication and usage of apparel. Cotton fabrics targeted for outdoor tracking, camping, and casual wear should not increase in thickness and become stiffer and heavier after water repellent treatment. Namely, this drawback is intrinsic for the treatment of fabric by emulsions of fluoro- and silica-containing polymers as well as different types of polymerization. Based on this, treatments of cotton fabrics by small molecules oriented mainly for blocking of hydroxyl groups represent an interest from fabric properties and practical application.

The majority of chemical modification of cotton surface now are realized by fluorinated compounds, which are known to have remarkable hydrophobic-lipophobic properties [2] due to the acceptable cost of treatment and availability and regardless of their ecologically unfriendly background. But a huge increase of non-fluorinated treatment and rise of ecological awareness will create more and more problems for the application of fluorinated compounds in industry. Alternative direction to fluorinated compounds is the application of molecule with long alkyl chains [3]. Long alkyl chains can be attached to the cotton surface by

alkylation with preliminary acetylation, mercerization and allylation with bromination [4]. An interesting approach is to make oxidation of primary OH groups of cotton by laccase/2,2,6,6-Tetramethylpiperidinoxy (TEMPO) treatment, obtaining aldehyde instead of -OH group, which were then used for the reaction with octadecylamine [5]. But from the industrial point of view, usage of multistep reactions, expensive chemicals and methods with weak control will significantly increase the price of treatment. One step methods could be very attractive for industrial application. An example is the usage of diblock copolymer in which one part provides water-repellent property whereas another part bearing alkoxy-silane or epoxy groups can be chemically attached to the OH group on the cotton surface [6]. But the application of epoxy-, azo-, and aldehyde-containing compounds for the reaction with the OH group in apparel is risky because of hygiene requirement for apparel. Another significant problem with the usage of the OH group for the reaction with different reagents aiming at hydrophobicity is low stability during washing in an alkaline environment. Low stability of many chemical bonds attached to the oxygen of the OH group during washing cuts off a lot of interesting chemical approaches in the fabrication of water hydrophobic cotton. The ideal would be direct fluorination of cotton by fluorine gas with the removal of the OH group and the formation of a stable C-F chemical bond [7] but with the aggressiveness of reagent and complicity of creation continuous technology, e.g. open reactor built some hurdles for industrial application.

An interesting direction opening now is the application of aromatic and polyaromatic structures for hydrophobic coating regardless the fact that the treatment of cotton by

*Corresponding author: vitali@ntu.edu.sg

benzoyl chloride was known for quite a long time and has been improved significantly since 1929 [8]. Chemical stability, hydrophobicity, high breathability, and fluorine-free composition of aromatic structures look very attractive to develop water-repellent surface on cotton fabrics. Contact angle 146 degrees is more than enough for industrial application. Such result authors have shown for cotton covered by diamond-like carbon [9]. Authors Ye *et al.* [10] saw a brilliant possibility of applying a simple aromatic ring which increases contact angle from about 125 degrees in the case of application of only fluorinated compounds [11] till 141 degrees if fluorinated compound includes just one aromatic ring. A very interesting approach of creating hydrophobic properties consisted in the usage of aromatic dyes based on anthraquinone [12]. Besides the above-mentioned attractive properties, we can also presume that chemical modification of the OH group by aromatic compounds will be more stable at washing in an alkaline environment due to of steric factor and size of attached groups. Considering current tendencies and the stated constraints, we decided to develop a method of chemical modification of cotton fabric with the application of aromatic compounds, targeting simplification and reduction of steps of chemical treatment which should make it more attractive for industrial application. We studied the influence of a number of aromatic rings in the reagent used for treatment on water repellent and mechanical properties of fabric as well as on stability during washing in alkaline milieu. To fulfill our tasks, aromatic compounds containing one, two and three aromatic rings, with different functional reactive groups were selected for study.

Experimental

Materials

Benzyl chloride, benzoyl chloride, 1-naphthoyl chloride, chlorodiphenylmethane, triphenylmethyl chloride and chlorotriphenylsilane, pyridine, triethanolamine and dichloromethane were obtained from Sigma-Aldrich and used as received. Commercial non-colored 100 % cotton fabric (plain weave with specific density 120 g/m²) was purchased from Spotlight, Singapore. The fabric was rinsed with distilled water and dried at 120 °C before use.

Modification of Cotton Fabric

We applied different conditions of a chemical reaction between aromatic ring containing reagent and hydroxyl groups of cotton aiming to find the most effective method of treatment. In all experiments 0.4 g cotton samples (5 cm by 5 cm) were used. A separate set of six final samples with size 10 by 10 cm was prepared separately for stiffness measurement. The cotton was treated with benzoyl chloride with 10 to 15 times their weight in a solution of 10 wt% of

benzoyl chloride in pyridine for half-an-hour at 80 °C [13]. Reaction with 1-naphthoyl chloride was realized similarly but with the addition of triethylamine and at room temperature within 4 hours. The molar ratio of -OH groups in cotton to -Cl in 1-naphthoyl chloride and triethylamine was 1:10:10. Treatment of cotton by benzyl chloride and chlorodiphenylmethane was realized in pyridine at reflux within 8 hours. The solution contained 1 wt% of imidazol. Treatment of cotton by triphenylmethyl chloride and chlorotriphenylsilane was realized within 4 hours in pyridine at room temperature [14] or 5 minutes at reflux. All experiments were carried out under nitrogen. The treated fabrics were rinsed in dichloromethane then in distilled water and dried in an oven at 80 °C until they attained a constant weight.

Characterization

Contact Angle

Contact angle measurement was carried out using Contact Angle Dataphysics OCA 20 (Dataphysics, Germany). The fabric was placed on a glass slide using a double-sided adhesive tape to ensure that sample is uniform. For every sample, 10 µl of deionized water was dropped at room temperature. SEA 20 software is used here for analyzing. Static contact angle was measured after 15 seconds when water droplet comes into contact with the fabric. Five contact angle measurements were conducted on different positions of the fabrics and the average values were calculated. The fabric was tested repeatedly after being washed once, 5 times and 10 times.

Field Emission Scanning Electron Microscopy

The morphology of cotton samples before and after chemical treatment was observed via Field Emission Scanning Electron Microscopy (FE-SEM, JSM-6340F).

Washing Stability

The washing durability was evaluated by a washing procedure described in ISO 6330-2012 Standard: Domestic washing and drying procedures for textile testing. The test was performed using a standard front-loading laundering machine. The fabric sample with size of 50 mm×50 mm was laundered in aqueous solution containing 0.15 % (w/w) detergent (AATCC 1993 reference detergent WOB).

Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) Perkin Elmer Frontier with an Attenuated Total Reflection (ATR) cell was used to determine the changes in cotton composition before and after chemical treatment. The resolution of 4 cm⁻¹ accumulating 32 scans was applied.

Mechanical Testing System

The tensile test had been performed at room temperature with Mechanical Tester MTS C43 in a film tension mode. Each sample was prepared with a size of 10 mm by 40 mm. A load cell of 100 N was used. Five measurements for each

type of fabric were performed.

Stiffness Testing

Stiffness of samples was measured according to ASTM D4032-94 (2001) using a tester with a pneumatic actuator from Gester. Sample was flattened to remove the crease and cutted into 102 mm×102 mm and then placed on the orifice platform below the plunger. The plunger was active for the full stroke length which is 6.3 mm and the peak force value was automatically generated and taken. Pressure was maintained at 324 kPa during testing.

Results and Discussion

Chemical Modification of Cotton Fabric

We studied the influence of different conditions of chemical modification of cotton such as time, temperature, type of gas atmosphere, nature of formed chemical bond between cotton and reagent, the number of aromatic rings in reagent molecule on hydrophobic and mechanical properties of fabric and stability during washing. Pyridine and triethylamine were used for the scavenging of hydrochloric acid, which is eliminated during reaction. These solvents were used for synthesis in laboratory conditions for clean experiment to avoid byproducts. At industrial level such reactions can be tuned for aqueous environment with high

pH [15]. Besides common cotton, we also used mercerized cotton preliminarily treated in 18 % solution of NaOH for 4 hours at room temperature for better reactivity and accessibility of OH groups for the transformation [16]. Only six representative samples with a permanent water repellent property are discussed in our work. The contact angle of the best cotton samples after chemical treatment is presented in Figure 1. Possessing data about water repellency of samples would be useful to know how many hydroxyl groups in cellulose units participated in the reactions; what happened with the fabric at micro level; how chemical treatment changed properties of fabric; and, from a practical point of view, it would be useful to study how stable the result of chemical transformation during washing.

The solid state of fabric and the presence of primary and secondary hydroxyl groups in the structure of cellulose complicate the analysis of a product after reaction. Estimation of the reaction can be done using gravimetry because the majority of used reagents have a molecular weight comparable to or higher than the cellulose unit. Even in a case where only one of the hydroxyl groups (primary, for example) in cellulose unit reacts with a reagent, which has one aromatic ring, the final weight of treated cotton fabric should increase by almost 50 %, and the result should be seen easily by weighing the sample before and after treatment. Then weight gain can be used for the analysis of reaction yield. Data about the change of samples weight is given in Table 1. There are two visible trends from data presented in Table 1. A higher amount of aromatic rings in reagent gives smaller yield. Possible reason for this phenomena is a steric factor when a large molecule is subjected to space constraint during the reaction with a hydroxyl group. The second visible and logical phenomenon is that carbonyl chloride containing chemicals are more reactive compared with simple chlorides. Based on the data presented in Table 1, we can speculate that probably only layers of cellulose close to the surface of cotton fibers are subjected to chemical

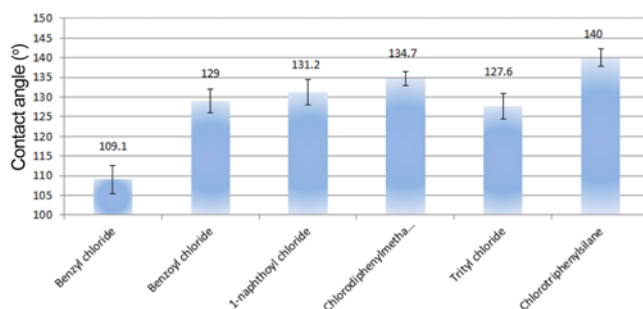


Figure 1. Contact angle of cotton fabrics after chemical treatment.

Table 1. Weight change of cotton samples after chemical treatment

	Chemicals used for treatment	Specific density (g/cm ²)	Increase in weight as compared to raw cotton (%)	Yield of reaction from all OH groups (%)*
	Raw untreated cotton	0.126±0.006	-	-
1	Benzyl chloride**	0.209±0.012	65.9±3.3	39.5±2.0
2	Benzoyl chloride	0.216±0.011	71.4±3.6	37.1±2.2
3	1-naphthoyl chloride	0.175±0.008	38.9±2.3	13.6±0.7
4	Chlorodiphenylmethane	0.134±0.008	6.4±0.4	2.1±0.1
5	Triphenylmethyl chloride	0.169±0.008	34.1±1.8	7.6±0.4
6	Chlorotriphenylsilane	0.142±0.009	12.7±0.7	2.7±0.1

*Yield of reaction was calculated by the following way. Theoretical weight increase was calculated assuming that all -OH groups of cotton participated in reaction. This value was used as 100 % theoretical yield of reaction. The ratio between practical and theoretical weight increase expressed in percent was used as the yield of reaction [23] and **reaction with benzyl chloride was successful only when cotton was preliminarily treated in 18 % of NaOH at room temperature within 4 hours.

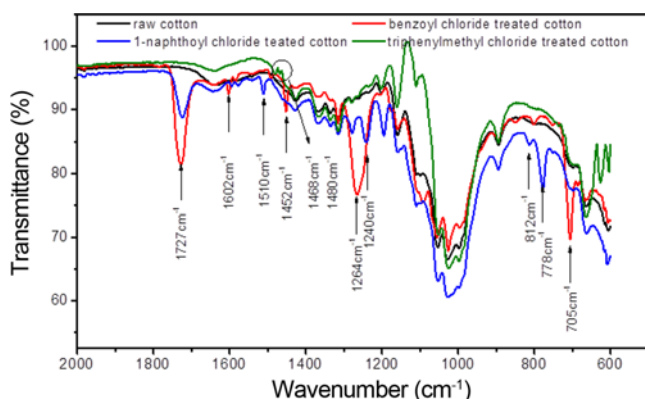


Figure 2. FTIR spectra of original and treated cotton fabrics.

transformation, and only primary hydroxyl groups participate in reactions.

FTIR Spectra

The FTIR shows the change in the spectra of cotton samples before and after chemical treatment. Expanded wave number area from 2000 till 500 cm^{-1} where differences among spectra of initial cotton and cotton treated with reagents with one benzene ring (benzoyl chloride), one naphthalene ring (1-naphthoyl chloride) and three benzene rings (triphenylmethyl chloride) are presented in Figure 2. The changes in the fabric after treatment by benzoyl and naphthoyl are clearly seen in FTIR spectra. The peaks observed in 1727 cm^{-1} and 1240 cm^{-1} (stretching) are corresponding to ester groups $-\text{CO}-\text{O}-\text{R}$ and $=\text{CH}-\text{CO}-\text{O}-$, reflecting the result of the reaction of OH groups of cellulose with benzoyl chloride and 1-naphthoyl chloride, while the peaks 1264 cm^{-1} (assimetric stretching) may come from aryl-alkyl ether [17], interring stretch or C-H in plane bending [18] that may point on some byproducts formation. The peaks around 778 cm^{-1} , 812 cm^{-1} and 1510 cm^{-1} are the

results of the α -naphthalene ring [19]. The peaks of 1468 cm^{-1} and 1480 cm^{-1} are the phenyl groups due to triphenylmethyl chloride [20]. The peaks in 705 cm^{-1} and 1602 cm^{-1} could be monosubstituted benzene [21,22]. FTIR spectra of samples after the reaction with chlorodiphenylmethane and chlorotriphenylsilane does not show significant differences compared with untreated cotton possibly because of the low yield of reaction (Table 1).

SEM Analysis

It can be observed on SEM pictures that the surface of a raw cotton fabric is smooth with no roughness. The SEM images of the treated cotton fabrics show the deposition of varied irregularly shaped materials on the fiber surface. These may have resulted from the rearrangement of surface cellulose due to the formation of a thin coating layer on the initial cellulose. The surface roughness of these six finished fabrics is also different from each other. Based on SEM pictures, we may say about small modification of fabric surface structure and formation of side products generated during the coating process. These side products deposited on the surface of fibers even after rinsing are clearly seen in Figure 3(c). The cotton fabric after treatment with chlorotriphenylsilane showed highest contact angle at the interface with distilled water and may partly have been contributed by the physical roughness due to the rearrangements of fiber surface after treatment (Figure 3(g)). In addition to SEM pictures, it should be noted that the color of the fabric turned yellowish during the chemical treatment with benzoyl chloride, all other five samples maintained original white color like untreated fabric.

Mechanical Properties of Cotton Fabric before and after Chemical Treatments

It was logical and expectable that the blocking of hydroxyl groups leads to the reduction of the amount of hydrogen

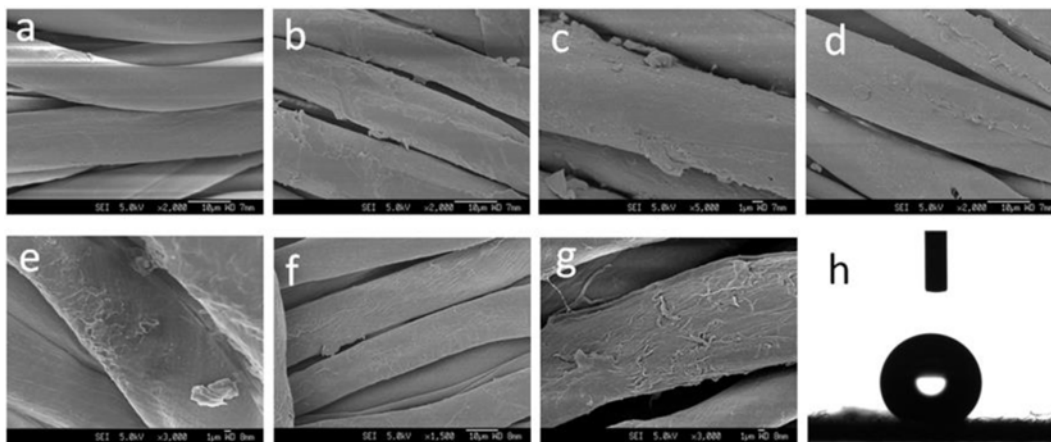


Figure 3. SEM images of (a) initial cotton and (b) benzoyl chloride, (c) benzoyl chloride, (d) 1-naphthoyl chloride, (e) chlorodiphenylmethane, (f) triphenylmethyl chloride and (g) chlorotriphenylsilane treated cotton fibers, and (h) water drop on 1-naphthoyl chloride treated sample.

Table 2. Mechanical properties of cotton fabric before and after chemical treatment

	Reagent used for treatment	Peak load (N)	Elongation at break (%)	Stiffness (N)
	Raw cotton	34.96±1.05	13.0±0.6	23.0±1.6
1	Benzyl chloride	26.87±1.03	12.7±0.6	16.2±1.3
2	Benzoyl chloride	23.98±1.10	4.6±0.2	24.0±1.6
3	1-Naphthoyl chloride	15.93±0.79	6.1±0.4	14.3±1.2
4	Chlorodiphenylmethane	16.08±0.75	2.7±0.2	20.5±1.5
5	Trityl chloride	23.97±1.12	12.7±0.6	13.0±1.1
6	Chlorotriphenylsilane	17.98±0.73	4.4±0.2	17.5±1.5

bonds which definitely decreases mechanical properties of treated cotton fabrics. The results of mechanical testing of initial and treated cotton are provided in Table 2. It is obviously seen that the mechanical properties of treated cotton dropped compared with raw material. Fabric became distinguishably stiffer after the treatment by benzoyl chloride, which is confirmed by measurement. The biggest reduction of the mechanical strength of cotton fabric is typical for samples treated by reagents containing two aromatic rings. We may presume that in the case of application of reagents with two aromatic rings it could be an alignment between cellulose cyclic units and attached aromatic groups. It could significantly shield the interaction among fibers and lead to the reduction of mechanical properties. Analyzing the correlation between the yield of reactions and mechanical properties of obtained samples, we can conclude that the highest correlation exists between peak load and yield of reaction – 0.75.

Contact Angle and Washing Stability

Stability of fabric treatment is important and should be checked constantly during development because a lot of coatings where chemical bond appears between hydroxyl groups and reagent are not stable in an aqueous alkaline environment. Contact angles of cotton after treatment and after 1, 5 and 10 washings are presented in Table 3.

After chemical treatment, all six samples exhibited good water repellent properties. The chlorotriphenylsilane-treated sample even showed a contact angle of 140° which is the

highest here and is much higher than the traditional water repellent fabrics treated by industrially used chemical methods. The surface morphology of fabric after chlorotriphenylsilane treatment was observed under SEM and showed in Figure 3(g). The conger-like strips distributed on the surface of fibers, which are around a few-hundred-nanometer wide and 2-3 micrometer long, greatly increased the surface roughness. All the samples held out within five washing cycles except the benzyl chloride treated fabric which turned out to be hydrophilic after one washing. Four samples kept their water repellent properties after ten washings. Interestingly, some samples showed a higher contact angle after one washing, like benzoyl chloride, 1-naphthoyl chloride and chlorodiphenylmethane, while all samples gradually lose the water repellency with higher washing cycles, except benzoyl chloride and 1-naphthoylchloride which both could retain its hydrophobicity and achieved an average contact angle of 119.3° and 127.6°, respectively, after ten washes. These two samples could be considered as having good washing durability, even though a drop in the contact angle from the initial reading of 129.0° and 131.0°, respectively, was observed. It is still a good indication, as the stability of the coating suggests that there might be changes to the surface morphology of the fabric and with further research can do done towards this direction. Between these two water repellent treatments with high stability during washing, treatment with 1-naphthoylchloride represents higer interest for the industrial application because it does not change the color of fabric.

Table 3. Contact angle of cotton fabric after chemical modification and different amounts of washing cycles

Chemical used	Contact angle (°)			
	Unwashed	1 wash cycle	5 wash cycles	10 wash cycles
Benzyl chloride	109.1±3.2	Hydrophilic	-	-
Benzoyl chloride	129.0±4.6	133.7±2.6	124.8±4.2	119.3±3.1
1-naphthoyl chloride	131.2±3.7	135.4±3.5	126.5±3.9	127.0±3.7
Chlorodiphenylmethane	134.7±2.8	140.5±3.1	118.7±3.3	118.4±3.0
Triphenylmethyl chloride	127.6±2.5	126.5±3.1	115.1±3.4	Hydrophilic
Chlorotriphenylsilane	140.0±2.6	135.9±3.2	129.4±3.8	119.3±3.1

Conclusion

In this work, cotton samples treated with six different reagents, containing one to three aromatic-rings in the structure, revealed high water repellent property with water contact angle over 120 degrees. The cotton sample treated with chlorotriphenylsilane achieved contact angle of 140°, which is comparable with nanomaterial treating method. High contact angle allows suggesting that high amount of aromatic rings in the reagent chosen for the reaction and in the case of high yield of reaction could modify the structure on the surface of cotton fibers. Cotton samples after reaction with benzoyl chloride and 1-naphthonal chloride have not only shown high water repellency but retained high washing durability even after 10 washing cycles. The sample treated with benzoyl chloride scarified the hand feeling stiffness and lost the purity of white color. Thus, the 1-naphthoyl chloride one-bath chemical treatment has a useful combination of features necessary for industrial implementation: one-step reaction, stability during washing, high contact angle, reduced stiffness and untouched color. This reagent and method of cotton treatment request detailed study in terms of optimization for future application in industry.

Acknowledgments

This work has been carried out in the Joint Innovation center of Institute for Sport Research and Sportmaster Group of Companies Pte Ltd., and financed by Sport and Fashion Management Pte Ltd.

References

1. H. Teisala, M. Tuominen, and J. Kuusipalo, *Adv. Mater. Interfaces*, **1**, 1 (2014).
2. M. Pagliaro and R. Ciriminna, *J. Mater. Chem.*, **15**, 4981 (2005).
3. E. I. Muresan, G. Balan, and V. Popescu, *Ind. Eng. Chem. Res.*, **52**, 6270 (2013).
4. C. Sawatari, Y. Sekiguchi, and T. Yagi, *Text. Res. J.*, **68**, 508 (1998).
5. Y. Yu, Q. Wang, J. Yuan, X. Fan, P. Wang, and L. Cui, *Carbohydr. Polym.*, **137**, 549 (2016).
6. Z. Shi, I. Wyman, G. Liu, H. Hu, H. Zou, and J. Hu, *Polymer*, **54**, 6406 (2013).
7. J. Maity, P. Kothary, E. A. O'Rear, and C. Jacob, *Ind. Eng. Chem. Res.*, **49**, 6075 (2010).
8. C. S. Webber and C. J. Staud, *U.S. Patent*, US1831274A (1931).
9. D. Caschera, B. Cortese, A. Mezzi, M. Brucale, G. M. Ingo, G. Gigli, and G. Padeletti, *Langmuir*, **29**, 2775 (2013).
10. H. Ye, Z. Li, and G. Chen, *J. Appl. Polym. Sci.*, **130**, 4410 (2013).
11. X. Liu, G. Yang, and V. Lipik, *Mod. Chem. Appl.*, **5**, 204 (2017).
12. J. Salabert, R. M. Sebastián, and A. Vallribera, *Chem. Commun.*, **51**, 14251 (2015).
13. R. Andreas, *U.S. Patent*, US2103018A (1937).
14. J. Röhrling, A. Potthast, T. Lange, T. Rosenau, I. Adorjan, A. Hofinger, and P. Kosma, *Carbohydr. Res.*, **337**, 691 (2002).
15. A. M. Felix, D. P. Winter, S.-S. Wang, I. D. Kulesha, W. R. Pool, D. L. Hane, and H. Sheppard, *J. Med. Chem.*, **17**, 422 (1974).
16. F. I. Sadov, M. V. Korchagin, and A. I. Matetskii, "Chemical Technology of Fibrous Materials", Mir Publishers, Moscow, 1978.
17. L. H. Briggs, L. D. Colebrook, H. Fales, and W. Wildman, *Anal. Chem.*, **29**, 904 (1957).
18. Z. Hinedi, C. Johnston, and C. Erickson, *Clays Clay Miner.*, **41**, 87 (1993).
19. D. R. Lide, "Handbook of Organic Solvents", CRC Press, Boca Raton, 1994.
20. W. C. Wu, L. F. Liao, C. F. Lien, and J. L. Lin, *Phys. Chem. Chem. Phys.*, **3**, 4456 (2001).
21. L. Marin, B. Simionescu, and M. Barboiu, *Chem. Commun.*, **48**, 8778 (2012).
22. R. J. Clark, C. D. Flint, and A. J. Hempleman, *Spectrochim. Acta Part A*, **43**, 805 (1987).
23. Z. A. Rogovin, "Chemistry of Cellulose", Khimiya, Moscow, 1972.