International Journal of Theoretical and Applied Research (IJTAR)
ISSN: 2812-5878

Homepage: https://ijtar.journals.ekb.eg

Original article

Vision for a better future with synthesized polyurethane amide as an enhancer for cotton fabric properties

*E.A.Zayed[1] *, N.A.Alian[1], Elshimaa H.Goma1[1] , N.O Shaker[1]*

[1] *Chemistry Department, Faculty of Science, Al-Azhar University (Girls Branch), Nasr city, 11754, Cairo, Egypt.*

ARTICLE INFO

Received 21/08/2024
Revised 31/10/2024
Accepted 10/12/2025

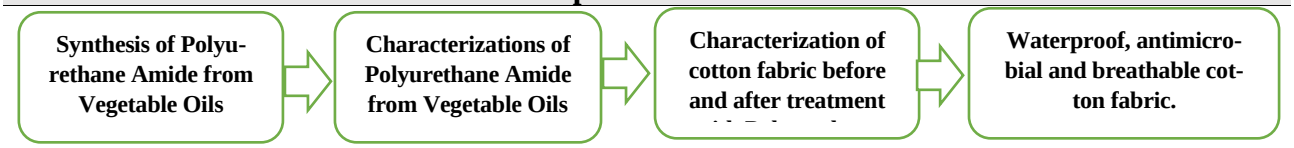
Keywords

Polyurethane Amide resin
Cotton fabrics
Hydrophobic textiles
Linseed Oil
Rice Bran Oil

ABSTRACT

This research focuses on obtaining a waterproof, antimicrobial and breathable cotton fabric while maintaining its essential hygienic properties. To achieve this goal, different formulations of polyurethane amide resin [PUA] synthesized from vegetable oils as sustainable sources, specifically Linseed Oil and Rice Bran Oil, were used. Their chemical composition was confirmed using different techniques such as HPLC, FTIR and ^{1}H-NMR. Physicochemical characterization, such as hydroxyl value, iodine value, and saponification value of PUA, was performed by standard methods. Cotton fabrics were treated by immersion in modified polyurethane amide resin with amino silicone fluid used as a fabric softener, and were characterized before and after treatment using various techniques such as FTIR, SEM and EDX. The performance of the resin coatings was evaluated in terms of Drying time, Film Resistance, Flexibility, Film Thickness, Scratch hardness [pencil Test], Pinhole Test, Stripping Test and Adhesion properties. The results showed good performance of polyurethane amide resins, promising their use as effective surface coating materials. In addition, treated cotton fabrics have water contact angles exceeding 134 degrees, with water absorption of treated cotton fabrics decreasing from 45.00 % to 6.21%. The treated cotton fabrics were shown to be breathable with vapor permeability levels of 7.6 x 10^{-4} g [m day Pa]$^{-1}$ which was similar to untreated cotton fabric. This sustainable approach can therefore be easily scaled up and may be a valuable therapeutic alternative to preserved historical textiles in museums or outdoor environments, as well as highly hydrophobic textiles for clothing or sportswear.

Graphical abstract



1. Introduction

Polyurethane [PU] is one of the most versatile polymers and is widely used in many applications such as foams, coatings, insulators, adhesives, paints and upholstery [1]. As with many polymers, polyurethane relies on petrochemicals as raw materials for its main components. In fact, many researchers nowadays have focused on replacing petroleum resources with renewable sources to improve the sustainability of polyurethane [2]. Polyurethane is manufactured by polymerization reactions between Ester Amide of [Linseed and Rice Bran Oils] With Toluene Diisocyanate [TDI] at varying ratios of [−NCO/OH] [0.5:1−2:1]. Renewable materials such as vegetable oils are promising raw materials for the manufacture of polyurethane components. Incorporating a portion of vegetable oil can enhance the thermal stability and mechanical strength of polyurethane [3, 4]. Recent advances in polyurethane applications have increased its potential, with modifications and addition of additives and nanomaterials to enhance its properties [5].

Improving the physical properties of cotton fabrics using polyurethane oil and silicone oil as fabric softeners provides an innovative way to improve textile performance [6]. Through the introduction of polyurethane treatments, cotton fabrics gain a large number of beneficial properties. These include increased durability,

* *Corresponding author*
E-mail address: emanzayd222@gmail.com

DOI: 10.21608/IJTAR.2024.314068.1083

water resistance, and flexibility, making them suitable for a wide range of applications [7]. Polyurethane also enhances the dimensional stability of the fabric, reducing shrinkage and wrinkling tendencies. Furthermore, this process can impart a soft, luxurious feel to cotton, increasing its comfort and tactile appeal. The treated fabric forms a hydrophobic surface, which prevents water from penetrating and wetting it and protects the textile fibers from abrasion, maintaining their hygienic and breathable properties [8]. Hydrophobic and fluid-repellent textiles have been extensively studied in recent decades to make them effective in applications such as oil-water separation [9, 10]. Self-cleaning fabrics [11, 12] and breathable and water-repellent clothing [13, 14]. Overall, the synergy between cotton and polyurethane opens up ways to create textiles that combine natural comfort with modern functionality, meeting the needs of diverse consumers in various industries.

A group of studies have explored the use of polyurethane to enhance the properties of cotton fabrics [15]. Lei [16] synthesized silicone-modified polyurethane which significantly improved the flexural, surface, compressive properties, mechanical behavior, water repellency, and air permeability of cotton fabrics. Likewise, Fan [17] found that a thin layer of polyurethane applied via spray polymerization doubled the abrasion resistance of cotton fabrics without compromising their natural properties. Tabasom [18] focused on the modification of cellulosic fabrics, including cotton, using polyurethane acrylate copolymers, with particular emphasis on emulsion stability. Furthermore, the development of sustainable polyurethane dispersions from vegetable oils has shown promising results in enhancing the tensile strength and antibacterial properties of polyester/cotton fabrics [19]. Collectively, these studies highlight the potential of polyurethane in enhancing the properties of cotton fabrics.

The goal of this research is to easily implement the environmentally friendly polyurethane manufacturing steps at a much lower temperature [lower energy consumption] and without any liquid or gaseous waste. In addition to creating a waterproof, antibacterial and breathable cotton fabric without sacrificing any of its vital health properties. In this work, we prepared polyurethane amide resin from vegetable oils and confirmed the chemical composition using different techniques such as HPLC, FTIR and 1H-NMR and then modified them with silicone oil. To produce a durable, waterproof, breathable and antibacterial cotton fabric composition. Hydrophobic finishing is therefore performed on highly hydrophobic textiles for clothing or sportswear as well as on historical textiles preserved in museums or outdoor settings.

2. Materials and Methods

2.1 Materials

2.1.1 Linseed Oil and Rice Bran Oil are obtained as a commercial sample. Diethanolamine [DEA], Polyethylene glycol [PEG 2000], Toluene diisocyanate [TDI], Di Butyl Tin Dilaurate [DBTDL] and Amino Silicone fluid were supplied by Merck [Germany].

2.1.2 Cotton fabric

The cotton fabric was supplied by Misr Helwan Company, plain woven and bleached 100% cotton, with 180 ± 5 g/m^2 bulk density and 24 thread count/cm in each direction.

2.2 Methods

2.2.1 Synthesis of methyl esters of linseed oil and rice bran oil

The process involved preparing methyl esters of linseed oil and rice bran oil through acid-catalyzed esterification. In a 500 ml round bottom flask, 100g of oil, 300 ml of methanol, and 1 ml of concentrated sulfuric acid were combined. The mixture was refluxed for 4 hours in a water bath. After the reaction, excess methanol and distilled water were added. The contents were then transferred to a separating funnel and the lower aqueous layer was removed. The upper organic layer was washed 2-3 times with sodium carbonate solution to eliminate un-esterified fatty acids. The esters were then purified by distillation under 4-5 mm Hg pressure [20].

2.2.2 Synthesis of fatty diethanolamides from methyl ester of linseed oil [DEALO] and rice bran oil [DEARO]

Fatty diethanolamides of linseed and rice bran oils were prepared using the method of Mahapatra S.S. et al. [21]. 3.45g of diethanolamine with 0.5% sodium methoxide [with respect to the ester] was heated to 110-115°C. Then, the methyl ester of the oil was added over 1 hour, and heating was continued for another 3 hours. N, N-Bis [2-hydroxyethyl] fatty diethanolamides of linseed and rice bran oil were then purified, yield % were 75 and 79.

2.2.3 Synthesis of linseed and rice bran oils polyurethane amides [PUALO] and [PUARO]

6.87 mmol of fatty diethanol amides were added to the calculated amount of polyethylene glycol [PEG] as a chain extender, and 0.05 wt% of DBTDL was used as the catalyst [with respect to the diol]. The mixture was placed in a three-necked round-bottom flask fitted with a mechanical stirrer, a nitrogen inlet, and a dropping funnel. Xylene was added to the mixture, and stirring was continued for 10 minutes at room temperature. The calculated amount of toluene diisocyanate [TDI] [0.5:1, 1.0:1, 1.5:1, and 2.0:1] was added dropwise over a period of 15-30 minutes. The reaction mixture was then heated to 40-50°C with stirring until the solution became viscous.

2.2.4 Characterization of fatty diethanolamides and polyurethane Amides resins from linseed and Rice bran oil

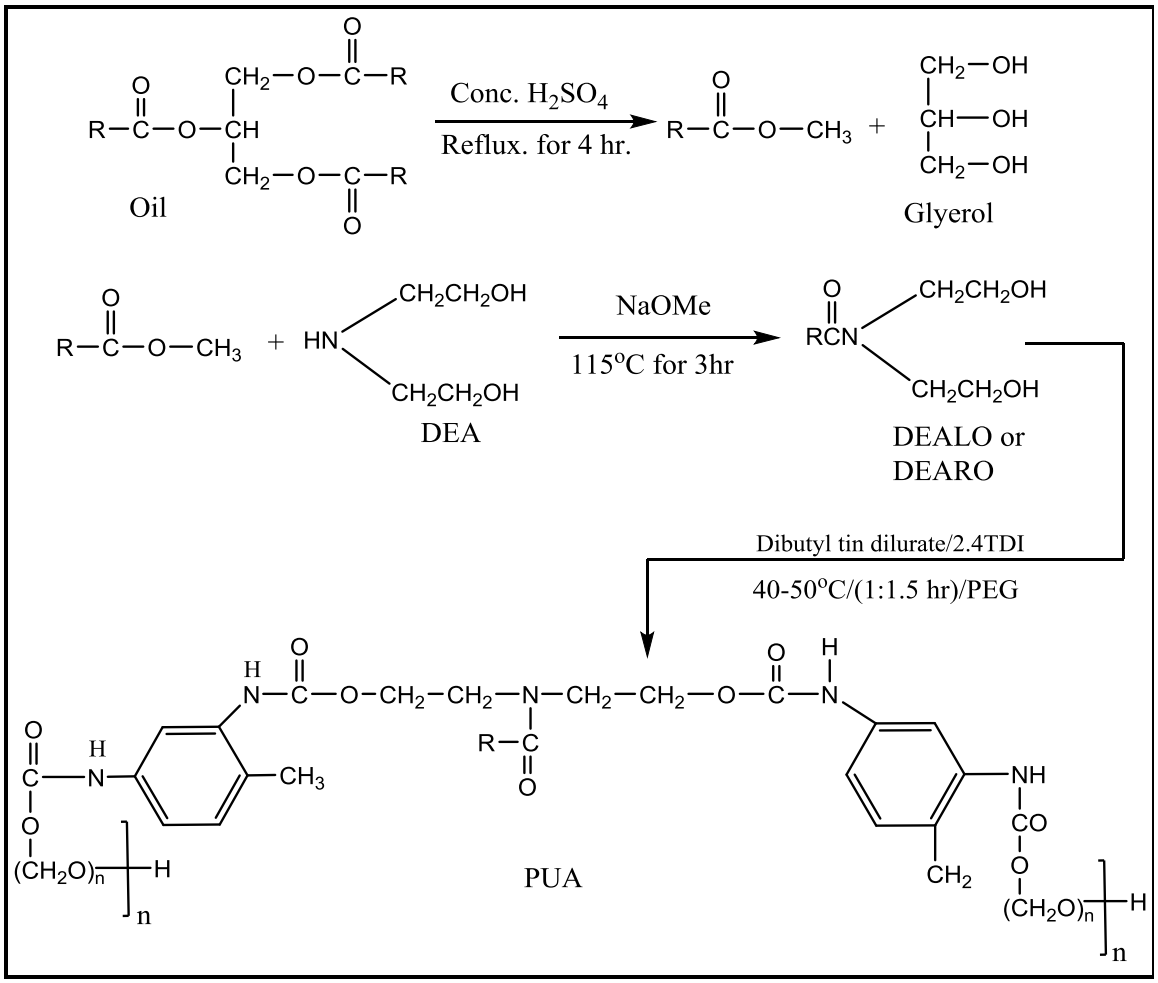
2.2.4.1 Physicochemical Characterization

Physicochemical properties of oils, DEAL, DEARO, and PUAS such as:

Acid Value [22]: The Number of milligrams of KOH required to neutralize the acidity of one gram of sample. **Hydroxyl Value** [23]: milligrams of Potassium hydroxide [KOH] equivalent to the hydroxyl content of 1 gm of

the oil. **Iodine Value** [24]: The weight of Iodine absorbed by 100 grams of the material and **Saponification Value [S.V]** [25]. The number of milligrams of potassium hydroxide [KOH] or sodium hydroxide [NaOH] required to saponify one gram of fat under the conditions specified were reported in Table [4] .

The Scheme [1] .Clearly illustrate the preparation of polyurethane Amide resins based on linseed and Rice bran oils.



DEA: diethanol amine **2, 4 TDI: 2, 4 Toluene diisocyanate**

PEG: Polyethelene glycol 2000

DEALO, DEARO: N,NBis(2-hydroxyethyl)fatty diethanol amides of Linseed oil and Rice bran Oil

2.2.4.2 Chemical characterization

The chemical structure of synthesized compounds was confirmed by:

- High performance liquid chromatography [HPLC]. analysis was made on a Buchi 688chromatograph with UV detector.
- The FTIR spectra. Transform IR [FTIR] Nicolet Magna –IR 750 spectrometer [Madison .WI] using KBr pellet and on a FX-100.
- ^{1}HNMR spectrometer [polo Alto CA]. using tetramethyl Silane as internal standard and $CDCI_3$ as the solvent.

2.2.4.3 Mechanical Characterization of Polyurethane Amide Resin

Touch dry:[26] the sample under investigation was poured on a glass plate panel and allowed to dry for a suitable or prescribed period for the paint to dry. **Surface dry:** [27] the same film used for touch dry was used to test the surface dry. **Water Resistance:** [28] this test method covers the basic principle for testing water resistance of coatings by the complete immersion of coated specimens in distilled water at ambient temperature. Immersion in water can cause the degradation of coatings. **Alkali resistance**: [29] the test panels were coated with the material to be tested and allowed to dry for 24 hours. The edges were coated by dipping in molten paraffin wax. **Acid resistance:** [30] the panels were prepared in the same manner as in the previous items and immersed to half the length in solution containing 20 gram of sulphuric acid [sp. gr.1.84], per 100 ml of water and allowed to stand for 24 hours at room temperature. **Solvent resistance:** [30] the coated panels were immersed in benzene/mineral turpentine solvent mixture [1:3 by volume] for 15 minutes at room temperature. The panels were removed from the test solvent followed by drying in vertical position for one hour. **Scratch Hardness by Pencil Test**: [31] the

purpose of this test is to assess the ability of the surface coating to withstand scratching. **Flexibility [Bend] Test**: [32]: the test was performed to determine the adhesion power of the varnish to the substrate by the bending apparatus. 5 x 15 cm tin panels was coated by the varnish, and dried. **Measurement of film Thickness**: [33]: the instrument used for measuring the dry film thickness [DFT] was the "Rossman Dial Thickness Gauge Model 233", manufactured by Ericksen. **Pinhole Test:** [34] test which verifies the continuity of the coating shall be carried out on coated surface before and after the coat has been completely cured. **Stripping Test**: [34]: the panel shall be placed on a flat surface with the coated side up. A sharp blade, held at approximately 60° to the surface should be pushed so that the blade has attendance to lift the coating. **Adhesion [Cross Hatch Test]:** [35] adhesion is a very important property of a paint system, and some empirical information can be obtained by the cross hatch test. **Specular Gloss:** [36] the degree of gloss of a coated film possesses may be directly measured using a glossmeter.

2.2.5 Purification of cotton fabrics

Cotton fabrics were scoured in aqueous solution containing 5% of sodium dodecyl sulfate at 50^0C for an hour to remove waxes and impurities, then rinsed thoroughly in distilled water and dried at room temperature then the fabric was cut into pieces of [5 × 20] cm^2 size before applying the treatments.

2.2.6 Hydrophobic treatment of cotton fabrics with Polyurethane Amide resin and Amino Silicone [MPUALO-Cotton fabric]

The cotton fabrics were impregnated in an aqueous solution of polyurethane amide PUALO and Amino Silicone liquid, which is usually used as a fabric softener, in the presence of an aqueous polyurethane dispersion using isopropyl alcohol as an auxiliary solvent for an hour. The impregnated fabrics are squeezed to extract as much of the solution as possible. After that, the lined cotton fabrics are dried in an oven at a temperature of 80 ^{0}C for 30 min. After fabric processing, all processed fabrics are analyzed, inspected and tested in order to check the finishing effect and associated properties.

2.2.7 Surface characterization of cotton fabrics before and after treatment by modified Polyurethane Amide Resin [MPUALO [1.5]].

2.2.7.1 Chemical and morphological characterization

Cotton fabrics before and after treated with Polyurethane Amide result is obtained by ratio 1:1.5 [TDI: polyol] were characterized with Fourier Transform Infra Red Spectroscopy [FTIR] and scanning electron microscopy [SEM] [a Quanta FEG 250 Czcch Republic electron microscope]. Elemental analysis was performed using Energy-dispersive spectroscopy X-ray [EDX].

2.2.7.2 Physical Characterization

To determine the effect of the treatment on the cotton fabric, the five different samples were analyzed and tested for their hydrophobic properties such as **Wettability test** [37] by wicking [water absorption][The water absorbance properties of treated and untreated cotton fabrics with MPU were evaluated by using static absorption test according to the American Association of Textile Chemists and Colorists [AATCC] test method 21-1972.] , **Spray test**[38][A specified amount of distilled water is sprayed centrally onto a slanted test sample, and its spray rate is determined by comparing the appearance of the sample to descriptive standards, or the AATCC Spray Test Evaluation Chart.] , **Contact angle measurement** [39] [Contact angle ranges from 0^o for complete wetting of a surface to 180^o for complete non-wetting. In the case of water on a surface, a contact angle of less than 90^o characterizes the surface as hydrophilic and hydrophobic if the contact angle exceeds 90^o] **Water vapor permeability** [40] [Water vapor permeability [WVP] of the untreated and treated fabrics was determined at 25°C and under 100% relative humidity gradient ΔRH [%] according to the ASTM E96 standard method] , **Elongation %**[41] [Elongation: The change in length or width of fabric at breaking force expressed as a percentage is called elongation]

3. Results and Discussion

3.1 Fatty acid compositions of linseed and rice bran oils

The HPLC analysis of fatty acids composition found in the linseed and rice bran oils used in this work as summarized in Table [2].

3.2 Chemical structure confirmation of synthesized compounds [DEALO, DEARO, PUALO and PUARO]

FTIR and ^{1}H NMR analysis were illustrated in figures [1-4] and Table 3.

Table 1: Classifications of the untreated and treated cotton fabrics

Types of Samples	Sample Code	Sample Composition [PUALO – Si] % [V / V]
Cotton fabric	C_0	Untreated cotton fabric
	C_1	50-50
	C_2	60-40
	C_3	70-30
	C_4	80-20
	C_5	90-10

Table 2. Fatty Acid Composition of Linseed oil and Rice Bran oil determined by HPLC analysis.

Fatty Acids Compositions		Weight %	
		Linseed Oil	Rice Bran Oil
Saturated	Palmitic C:16 $CH_3[CH_2]_{14}COOH$	5.9	21.5
	Stearic C:18 $CH_3[CH_2]_{16}COOH$	3.49	3.5
Unsaturated	Oleic C:18 :1 $CH_3{-}[CH_2]_7{-}CH{=}CH{-}[CH_2]_7{-}COOH$	30.3	38.4
	Linoleic C:18:2 $CH_3[CH_2]_4CH{=}CHCH_2CH{=}CH[CH_2]_7COOH$	11.5	34.4
	Palmitoleic C:16:1 $CH_3[CH_2]_5CH{=}CH[CH_2]_7COOH$	0.41	–
	Linolenic C:18:3 $CH_3[CH_2]_4CH{=}CHCH_2CH{=}CH[CH_2]_7COOH$	48.4	2.2

3.3 Physicochemical Characterization of synthesized compounds [DEALO, DEARO, PUALO and PUARO]

The physicochemical properties of synthesized compounds [DEALO, DEARO, PUALO, and PUARO] are shown in Table 4. Methyl ester value is indicated by very low acid value [3.2mg/KOH]. The formation of the fatty diethanol amides is evident from their high hydroxyl value as shown in Table [4]. It has been found that with the progressive increase of TDI in the fatty diethanolamides of linseed and Rice bran oils, the hydroxyl value of LOPUA and ROPUA decrease.

3.4 Mechanical characterization of Polyurethane amides [PUALO and PUARO]

3.4.1 Drying characteristics:

Both air –drying and Stoving drying times were carried out for PUALO and PUARO. The coated films on strips were cured at ambient temperature [30± 2]^{0}C under atmospheric conditions without driers or curing agents. The results of evaluation of films properties of PUALO and PUARO resins are shown in Table [5]. From the results, the drying time reduces on increasing the amount of the NCO/ OH ratio in the resins. The good drying time can be attributed to the presence of increasing amount of reactive free NCO groups in the resins that react with moisture and subsequently from cross linked products. The dried films were post-cured at 80 ^{0}C, and the coating performance was examined. The best curing performance of PUALO resin was observed after 1 hour, whereas the best curing performance of an alkyd resin based on PUARO was observed after 2 hours. This phenomenon can be attributed to a high degree of crosslinking that results from the reaction between the free isocyanate groups and the free hydroxyl group in the amide.

The isocyanate help to link polymer molecules together and higher degree of crosslinking occurred because of the presence of free isocyanate groups in polyurethane resin which react with moisture to form the corresponding amine which further react with active hydrogen of the polymer and form crosslinking structure.

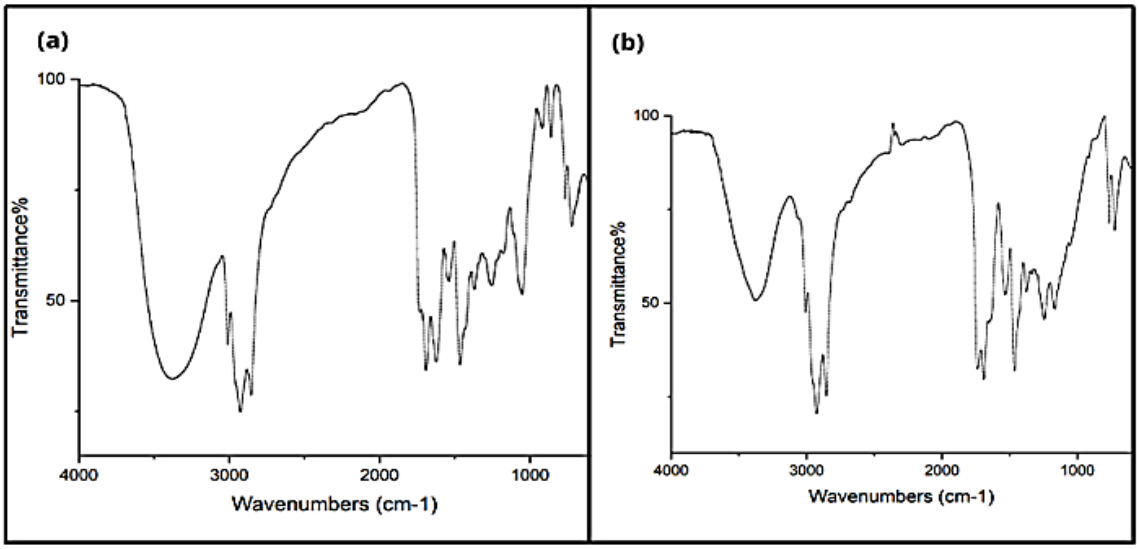


Fig. 1. FTIR Spectra of the DEALO [a] and DEARO [b]

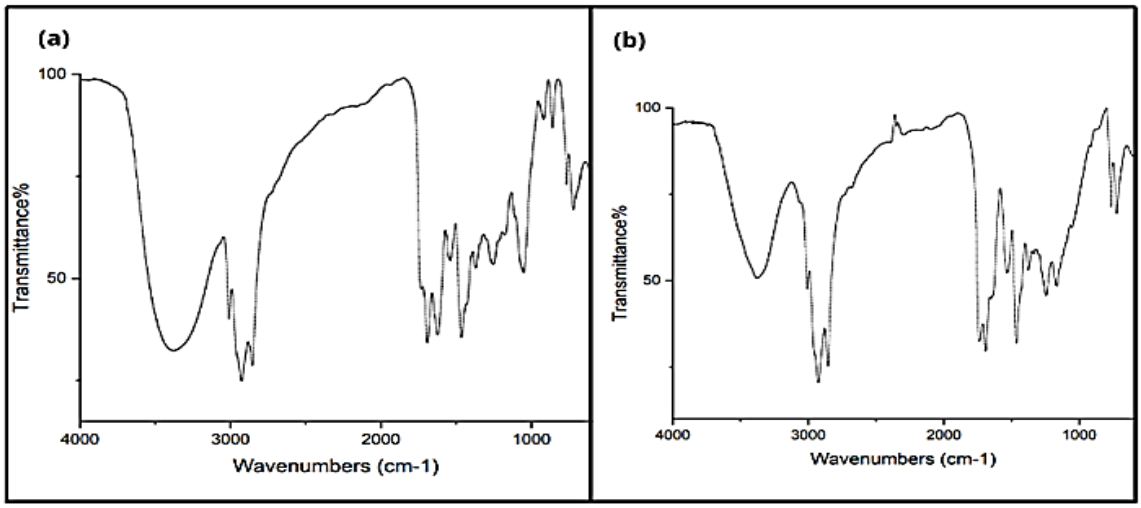


Fig. 2. FTIR Spectra of the PUA LO [a] and PUARO [b].

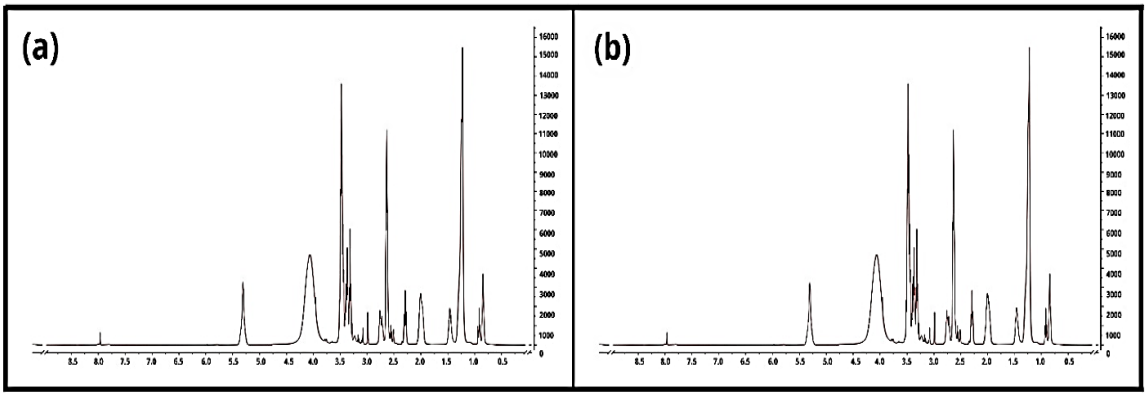


Fig. 3. ^{1}H NMR spectra of the DEALO (a) and DEARO (b).

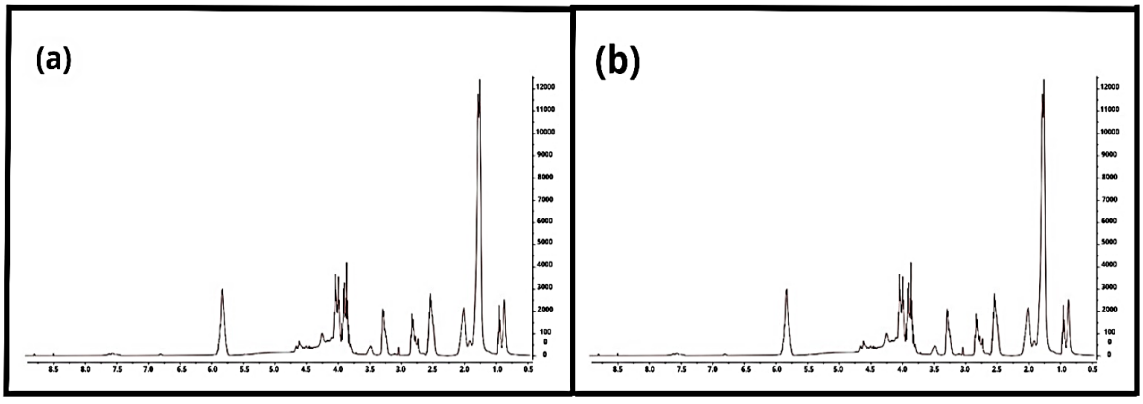


Fig. 4. ^{1}H NMR spectra of the PUALO [a] and PUARO [b].

3.4.2 Chemical resistance

The evaluation of Chemical resistance for PUALO and PUARO was carried out in distilled water, acid [20% sulphuric acid], alkali [10%sodium hydroxide], and solvent [benzene/turpentine] were used. The chemical resistance data [Table 6-10] revealed that, the PUALO and PUARO resins have excellent chemical resistance in all test media except the alkali resistance improved by increasing the NCO/ OH ratio in the resins. This may be because these resins do not have any hydroxyable functionality as polyester or polyester amide resins. The water resistance studies show no sign of film failure for stoved films of linseed and rice bran oils up to the end of the test period. On the other hand, air–dried films show film failure at early stages compared with stoved films. Similarly, PUALO resist film failure more than PUARO Table 6. The alkali resistance of almost all films of modified alkyds, as expected, indicated lower resistance values compared with data of water and acid resistances for alkyd resin based on

PUALO and PUARO. The solvent resistance of the films of the modified alkyds Shows satisfactory results as shown in Table [9].

The mechanical properties of both air–dried and stoved films of poly [urethane amide] resins based on linseed oil and rice bran oil [PUALO and PUARO] are shown in Table [10]. Based on the results, the gloss at 60^0 and the stripping test both passed. Because of the polyurethane linkage and aromatic content in PUALO and PUARO, the polyurethane amide resins have good adhesion. Additionally, the scratch test yielded remarkable results. The difunctional isocyanate cross-linker's rigid structure is responsible for this outstanding performance. The results of the bending test show that all of the resins are extremely flexible because of the hydrocarbon chains of the fatty acids in oils and the flexible ether linkages present in PEG. Due to their aromatic bond, PUALO and PUARO resins have exceptional mechanical qualities because they have the ideal combination of hardness and flexibility. This could be explained by the PUALO and PUARO resins' sufficient linear structural contribution. The PUALO-based modified alkyd resin performs better in mechanical tests than the PUARO-based modified alkyd resin.

Table 3. FTIR and ^{1}H NMR spectra data of synthesized compounds [DEALO, DEARO, PUALO and PUARO]

Functional groups	FTIR [cm^{-1}]		^{1}HNMR δ [ppm]		FTIR [cm^{-1}]		^{1}H NMR δ [ppm]	
	DEALO	DEARO	DEALO	DEARO	PUALO	PUARO	PUALO	PUARO
—OH [alcoholic]	3392	3416	5.4	5.32	3379	3377	5.6	5.33
—NH deform	–	–	–	–	1692	1692	–	–
−C═O Amide Carbonyl	1643	1640	2.0-2.1[CH_2 adjacent to amide carbonyl]	2.0[CH_2 adjacent to amide carbonyl]	1637	1633	2.3[CH_2 adjacent to amide carbonyl]	2.3[CH_2 adjacent to amide carbonyl]
—C=C—	1622	1632	2.1[CH_2 attached to [C=C]	2.0[CH_2 attached to [C=C]	1623	1649	2.0[CH_2 attached to [C=C]	2.0[CH_2 attached to[C=C]
C−N	–	–	–	–	1051	1053	–	–
Aromatic	–	–	–	–	765	765	7.2	7.2
CH_3[TDI]	–	–	–	–	–	–	2.7	2.8
CH_3[terminal aliphatic]	1454	1464	0.88	0.85	1465	1464	0.87	0.87
CH_2 chain	2853-2925	2852-2923	1.3-1.5	1.18-1.30	2854-2925	2853-2924	1.24-1.26	1.2-1.3

Table 4. Physico-chemical characteristics of synthesized compounds [DEALO , DEARO , PUALO and PUARO]

Characteristics	Color		DEA		PUA 0.5		PUA 1.0		PUA 1.5		PUA 2.0	
	linseed oil	Rice Bran	DEALO	DEARO	PUALO	PUARO	PUALO	PUARO	PUALO	PUARO	PUALO	PUARO
Color	Yellow Brown	Yellow	Brown	Bale Yellow	Yellow	Bale Yellow	Yellow	Bale Yellow	Yellow	Bale Yellow	yellow	Bale Yellow
Hydroxyl Value [mg KOH/g]	100.1	90.1	440.2	200.4	112.13	80.31	108.5	75.4	77.2	60.2	63.1	48.15
Iodine value [g iodine/100g]	195	180	150	155.9	90.3	75.3	86.1	70.3	65.2	56.1	45.1	40.4
Saponification value [mg KOH/g]	230	187.3	270	200.3	193.5	235.6	89.4	215.2	82.1	163.4	75.61	141.5
Acid value	37	40	10.4	8.34	7.2	6.1	5.1	5.5	4.3	4.9	3.2	4.1

Table 5. Drying time characteristic of Polyurethane amides resins [PUALO and PUARO]

Resin	Air drying [min]		Stoving at 80˚C							
	L.O	R.O	10min[L.O]	10min[R.O]	30min[L.O]	30min[R.O]	1hr[L.O]	1hr[R.O]	2hr[L.O]	2hr[R.O]
PUA 0.5	150	180	ST	T	VST	ST	HD	VST	-	HD
PUA 1.0	70	90	ST	T	VST	ST	HD	VST	-	HD
PUA 1.5	30	40	ST	ST	VST	VST	HD	VST	-	HD
PUA 2.0	10	15	ST	T	VST	VST	HD	VST	-	HD

T: Tacky HD: Hard Dry S T: Slightly Tacky VST: Very Slightly Tacky

Table 6. Distilled water resistance of Polyurethane amides resins [PUALO and PUARO]

Resin	Air –Dried films Immersion period days												Stoved –Dried films Immersion period days											
Name	1		6		12		18		24		30		1		6		12		18		24		30	
	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O
PUA 0.5	E X	EX	E X	EX	EX	EX	EX	EX	EX	EX	G	G	E X	EX	EX	EX	EX	EX	EX	EX	EX	EX	EX	G
PUA 1.0	E X	EX	E X	EX	EX	EX	EX	EX	EX	EX	G	G	E X	EX	E X	EX	EX	EX	EX	EX	EX	EX	EX	G
PUA 1.5	E X	EX	E X	EX	EX	EX	EX	EX	EX	EX	G	G	E X	EX	EX	EX	EX	EX	EX	EX	EX	EX	EX	G
PUA 2.0	E X	EX	E X	EX	EX	EX	EX	EX	EX	EX	G	G	E X	EX	EX	EX	EX	EX	EX	EX	EX	EX	EX	G

EX : Excellent , almost no change . G : good . P : Poor [complete film failure]. F : fair [partially attacked].

Table 7. Acid resistance data [20% H_2SO_4] of Polyurethane amides resins [PUALO and PUARO]

Resin	Air –Dried films Immersion period days												Stoved –Dried films Immersion period days											
Name	1		6		12		18		24		30		1		6		12		18		24		30	
	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O
PUA 0.5	E X	EX	E X	EX	EX	EX	EX	EX	EX	EX	P	G	E X	EX	EX	EX	EX	EX	EX	EX	EX	EX	EX	G
PUA 1.0	E X	EX	E X	EX	EX	EX	EX	EX	EX	EX	P	G	E X	EX	E X	EX	EX	EX	EX	EX	EX	EX	G	P
PUA 1.5	E X	EX	E X	EX	EX	EX	EX	EX	G	G	P	G	E X	EX	EX	EX	EX	EX	EX	EX	EX	EX	G	P
PUA 2.0	E X	EX	E X	EX	EX	EX	EX	EX	G	G	P	G	E X	EX	EX	EX	EX	EX	EX	EX	EX	EX	G	F

EX: Excellent, almost no change . G: good. P: Poor [complete film failure]. F: fair [partially attacked].

Table 8. Alkali resistance data [10% NaOH] of Polyurethane amides resins [PUALO and PUARO]

Resin	Air –Dried films Immersion period days												Stoved –Dried films Immersion period days											
Name	1		6		12		18		24		30		1		6		12		18		24		30	
	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O
PUA 0.5	E X	EX	G	G	G	G	P	P	F	F	F	F	E X	G	G	G	G	G	G	G	P	P	F	F
PUA 1.0	G	G	G	G	P	P	P	P	P	F	F	F	G	G	G	G	P	P	G	G	P	F	F	F
PUA 1.5	G	G	G	G	P	P	P	P	G	P	F	F	E X	G	G	G	P	P	P	P	P	P	F	F
PUA 2.0	G	G	G	G	P	P	P	P	G	G	F	F	G	G	G	G	P	F	P	P	F	P	F	F

EX: Excellent, almost no change . G: good. P: Poor [complete film failure]. F: fair [partially attacked].

Table 9. Solvent resistance data [Benzene /turpentin] of Polyurethane amides resins [PUALO and PUARO]

Resin	Air –Dried films Immersion period days												Stoved –Dried films Immersion period days											
Name	1		6		12		18		24		30		1		6		12		18		24		30	
	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O
PUA 0.5	E X	EX	E X	EX	EX	EX	EX	EX	EX	EX	P	G	E X	EX	EX	EX	EX	EX	EX	EX	EX	EX	EX	G
PUA 1.0	E X	EX	E X	EX	EX	EX	EX	EX	EX	EX	P	G	E X	EX	E X	EX	EX	EX	EX	EX	EX	EX	G	P
PUA 1.5	E X	EX	E X	EX	EX	EX	EX	EX	G	G	P	G	E X	EX	EX	EX	EX	EX	EX	EX	EX	EX	G	P
PUA 2.0	E X	EX	E X	EX	EX	EX	EX	EX	G	G	P	G	E X	EX	EX	EX	EX	EX	EX	EX	EX	EX	G	F

EX: Excellent, almost no change . G: good. P: Poor [complete film failure]. F: fair [partially attacked].

Table 10. Coating Properties of treated Polyurethane amides resins [PUALO and PUARO]

Resin No	Film Thickness				Scratch Test				Adhesion Test				Stripping Test				Pinhole Test				Gloss at 60^0				Flexibility Bend test			
	A		S		A		S		A		S		A		S		A		S		A		S		A		S	
	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	R.O	L.O	RO	L.O	R.O	L.O	R.o
PUA 0.5	20	20	20	20	>1.0	>1.0	>1.0	>1.0	4B	3B	5B	4B	Pass	pass	Pass	Pass	Pass	Pass	Pass	Pass	80	85	81	86	Pass	Pass	Pass	Pass
PUA 1.0	20	20	21	21	>1.0	>1.0	>1.5	>1.0	5B	4B	5B	5B	Pass	pass	Pass	Pass	Pass	Pass	Pass	Pass	83	88	85	90	Pass	Pass	Pass	Pass
PUA1.5	20	20	20	20	>1.0	>1.0	>1.5	>1.0	5B	4B	5B	5B	Pass	pass	Pass	Pass	Pass	Pass	Pass	Pass	85	90	87	95	Pass	Pass	Pass	Pass
PUA2.0	20	20	20	20	>1.0	>1.0	>1.0	>1.0	4B	4B	5B	4B	Pass	pass	Pass	Pass	Pass	Pass	Pass	Pass	90	95	94	100	Pass	Pass	Pass	Pass

a :Air dried films **s : Stoved dried film**

3.5 Evaluation of treated cotton fabrics by modified polyurethane amide resin MPUALO

3.5.1 Chemical characterization of untreated and treated cotton fabric

3.5.1.1 FTIR Spectrum Analysis

FTIR spectroscopy is one of the state-of-the-art techniques for characterizing any natural substance or synthetic compound with respect to the identification of functional groups. The functional groups of the samples were determined using FTIR spectroscopy as shown in Figure 5a shows the IR spectra of virgin cotton, pure Amino Silicon, and MPUALO-cotton fabric. Cotton showed the characteristic peaks of cellulose:OH stretching at 3273 cm^{-1} , CH stretching at 2900 cm^{-1} , adsorbed water at 1650 cm^{-1} , asymmetric C-C stretching at 1144 cm^{-1}, and C-O stretching at 1044 cm^{-1}.

In the case of the Amino Silicone, in Figure 5b main peaks were CH_3 asymmetric and symmetric stretching at 2963 and 2905 cm^{-1} , respectively, Si[CH_3] symmetric bending at 1258 cm^{-1} , Si-O- Si symmetric and asymmetric at 1074 and 1007 cm^{-1} , respectively, and CH_3 rocking at 783 cm^{-1} . It is expected that one would also detect peaks at 1731 and 1673 cm^{-1}, corresponding to - NH and -NH2 vibration bands. The inability to detect these peaks is attributed to the fact that the molar content of the amino/amine functional groups is quite minute [~nano-molar] compared to the silicone polymer chain [42] or even if they are detected in the pure silicone compound they disappear upon reacting with hydroxyl groups on fiber surfaces forming trace amounts of ammonia gas .The infrared spectrum of cotton coated with a mixture of PU and Amino Silicone showed the bands of the three components. Two shifts were observed in the extended spectral regions of OH/N-H and the methylene vibration. Figure 5 c. compares the OH/N-H stretch of cotton and MPUALO-cotton fabric.

The difference between the two spectra [a and c] [PUALO-Si cotton fabric minus the untreated cotton fabric spectrum] highlighted the presence of a band at approximately 3405 cm^{-1}. This is a typical value for N-H and OH that interact strongly by H bonds indicating that the hydroxyl groups of cotton and the polyurethane groups of PU can interact through this type of secondary bonds. In addition, a shift of ~29 cm^{-1} was observed between the methylation vibration mode of silicon in pure silicon and silicon with cotton and MPUALO, as shown in Figure 5a, b and c.

3.5.2 Morphological characterization of untreated and treated cotton fabric

3.5.2.1 Scanning Electron Microscopy [SEM]

The surface morphology of cotton fabric was studied without any chemical treatment and used as an environmentally friendly surface. It can be seen from Figure 6a that the untreated cotton fabric appears as a typical twisted and wrinkled structure [43] due to its longitudinal fibrous structure, which, combined with the presence of porosity, creates a large surface area to interact with MPUALO molecules and enhance absorption. Figure 6b clearly shows the accumulation of MPUALO [PUALO -Si [70-30] %] molecules on the surface of cotton fabrics which proves that the surface of the adsorbent was completely changed, the pore sizes decreased and this indicates that MPUALO was successfully adsorbed on the surface of cotton fabrics.

3.5.2.2 Energy-dispersive spectroscopy X-ray [EDX]

EDX analysis was used to clarify the qualitative elementals composition of cotton fabric before and after modification by [a Quanta FEG 250 Czcch Republic]. According to the X- ray spectroscopy, the chemical composition [by wt %] of untreated cotton fabric was 47.79 for carbon and 52.21 for oxygen. Furthermore, the chemical composition [by wt %] of MPUALO-cotton fabric was 41.11 for carbon, 39.20 for oxygen, 8.57 for nitrogen and 11.12 for Silicon as shown in "Figure 7a,b " Based on the noticeable differences in weight percent between untreated cotton fabric and MPUALO-cotton fabric, it can be concluded that the chemical structure of untreated cotton fabric was changed due to the effective binding of polyurethane and Amino Silicone molecules on the pores of untreated cotton fabric [44].

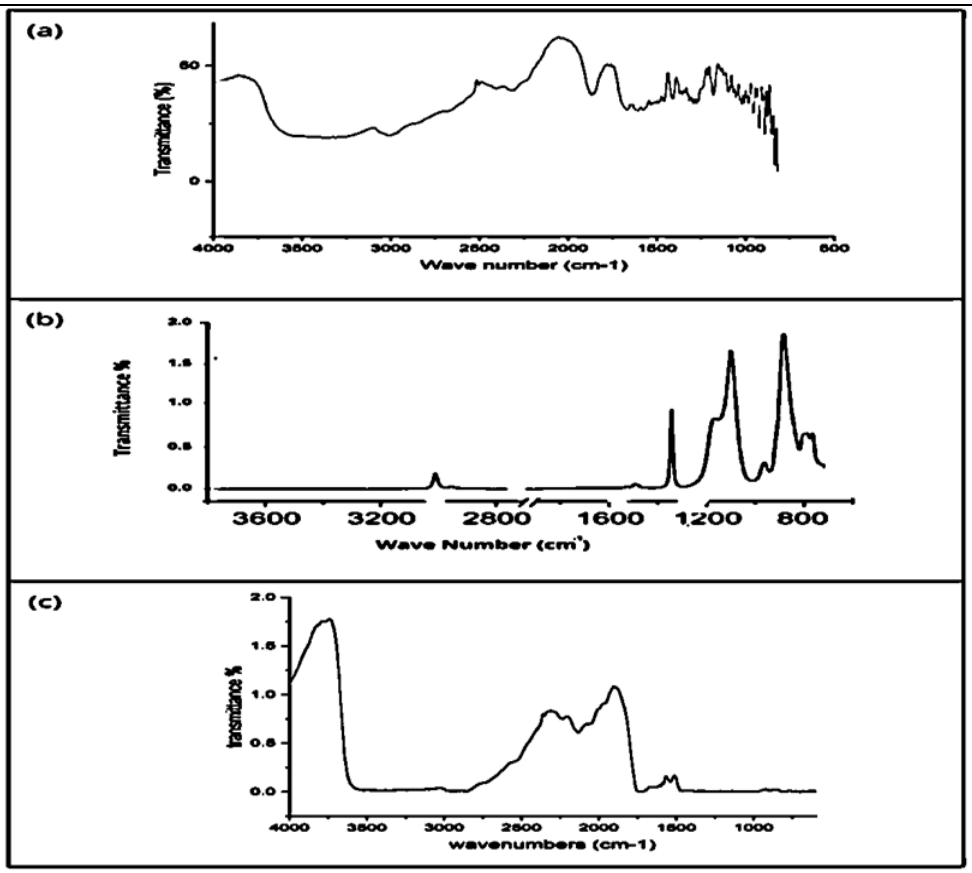


Fig. 5. FTIR spectra of [a] untreated cotton fabric, [b] Amino Silicone fluid and [c] treated MPUALO-cotton fabric

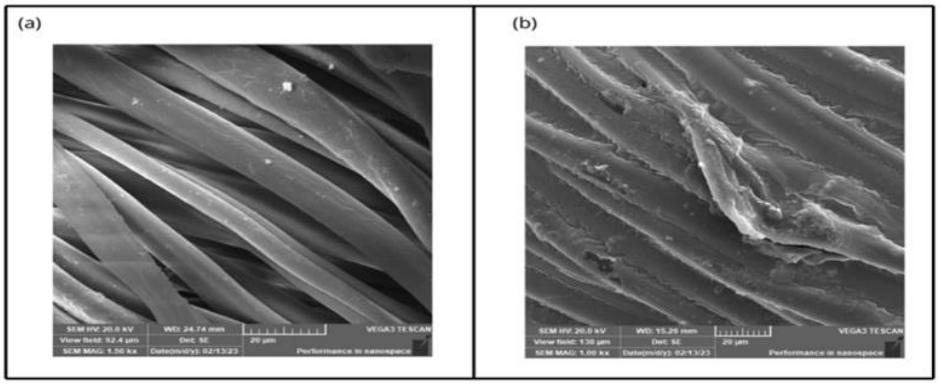


Fig. 6. SEM image of [a] untreated cotton fabric and [b] treated MPUALO-cotton fabric

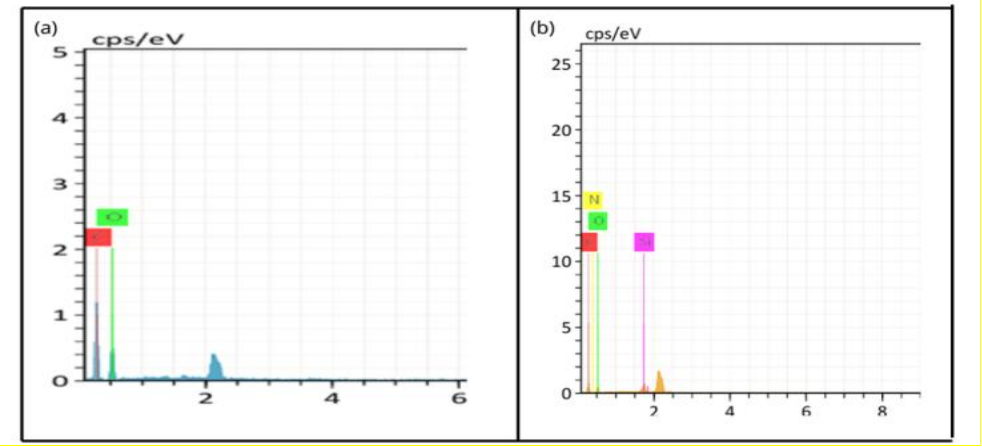


Fig. 7. EDX analysis of [a] untreated cotton fabric and [b] MPUALO-cotton fabric.

3.5.3 Mechanism of bonding between the surface of untreated cottonfabrics, Polyurethane Amide resin and Amino silicone fluid

Based on this analysis, it is very likely that there are hydrogen bonding interactions between cellulose OH groups and amine groups of silicone liquid and amine groups in polyurethane, cellulose OH groups and OH groups of aliphatic polyurethane chains and between amine groups of silicone liquid and OH groups of polyurethane [45]. These chemical reactions are shown in Scheme 2.

3.5.4 Physical properties of untreated and treated cotton fabrics with modified Polyurethane Amide resin MPUALO

3.5.4.1 Wettability test [water absorption]

Wetting by wicking is an important factor in determining the hydrophobic properties of treated fabrics. Table 11 and Figure 8 show the water absorption percentages of untreated and treated cotton fabrics. From the experimental results, it was found that the water absorption rates of all treated cotton fabrics decreased significantly compared to untreated cotton fabrics from 45.00 % to 6.21 % respectively. This is due to the fact that polyurethane covers the surface of the fiber and prevents the hydrophilic group in the fiber. The greater the amount of polyurethane [46].

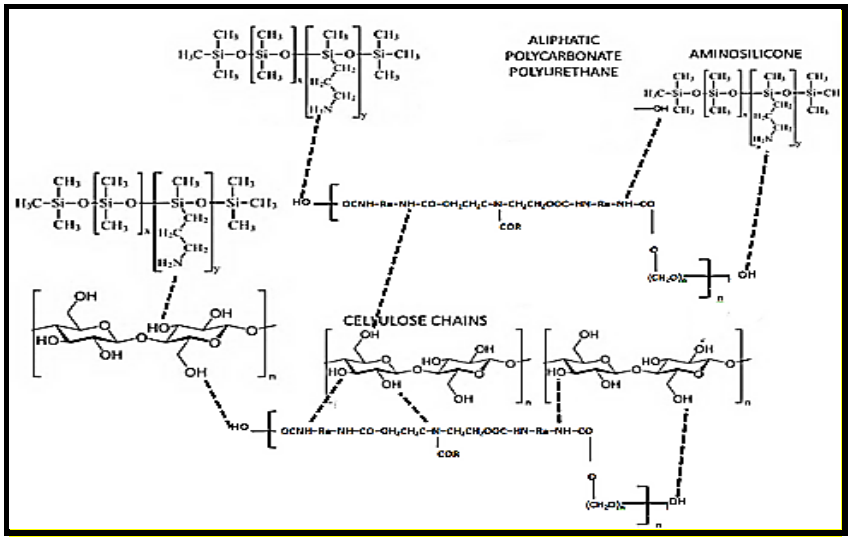
Reduced water absorption of coated fabrics, due to the increased water content and cross- linking density and due to the hydrophobic nature of PUALO. Therefore, as the PUALO content increases, the cross-link density increases and the polymer structure becomes more rigid and dense and the possibility of the presence of water molecules penetrating the MPUALO-cotton fabric decreases.

3.5.4.2 Spray Test

The spray test determines the resistances of the cotton fabrics by water. All treated cotton fabrics are appreciably better than untreated cotton fabrics in all compositions [47]. Among them, 80-20 % [C_4] and 90-10% [C_5] composition of treated cotton fabrics has the highest rating. In both cases, it can be noted that the water resistance is increased when the amount of Amino Silicone used is reduced. To get the desired degree of repellency, the amount of Amino Silicone used must be especially controlled in this study. The more decrease the water absorption percentage, the more increase the spray rating as shown in Table 11 and Figure 9.

3.5.4.3 Contact angle measurement

Contact angle is the angle between the solid surface and the water surface. On a hydrophobic surface, the contact angle is greater than 90° and a water droplet tends to form on the surface. On the other hand, if the surface is hydrophilic, the contact angle is less than 90° and the water droplet tends to spread out and wet the surface. In this research, the digital images were used to measure the contact angle at 60 sec [48]. First, contact angles are intended for untreated cotton fabrics measurement. It is observed that the water droplet seeps into the fabric within 5 to 10 seconds and thus the contact angle of untreated cotton fabric is zero.
According to the contact angle measurements, the water resistance effects of the treated cotton fabrics are obtained. The contact angle value is greater than 90° these treated fabrics thus retain their hydrophobic effect as shown as in Table 11 and Figure 10. Moreover, it was also found that the chemical compositions affect the repellent effect. In this research, the greater the amount of polyurethane used, the greater the contact angles of the treated cotton fabric.



Scheme 2. Schematic representation of the potential hydrogen bonding interaction between the surface of cotton fabric, Polyurethane Amide resin and Amino Silicone fluid.

3.5.4.4 Water vapor permeability

Breathability is the ability of a material to transmit

moisture steam or sweat through it. It is one of the basic performance criteria for modern textile industries because it explains the comfort level of the material and fabric. For clothing to be breathable, it must be designed to maintain a balanced posture automatically under different environmental conditions and body movements without reducing evaporation moisture resulting from sweat. PU has gained popularity because of its ability to exert decent strength, liquid penetration resistance and breathability .To evaluate the breathability of treated cotton fabrics, water vapor permeability [WVP] was measured [49]. The average WVP of untreated cotton fabric is calculated to be ~ **7.8 x10^{-4}** [g [m d Pa]-1]. This value corresponds to the permeability of the starting material [untreated cotton fabric], which is considered highly breathable. The average measurement uncertainty was within 0.1x10^{-4} [g [m d Pa]-1] .After hydrophobic treatments, all fabrics analyzed indicated WVP values very close to the original fabric [untreated cotton fabric] due to the lack of filling of the voids or pores between the fibrils [see Figure 11] as shown in Table 11.

The processing of cotton fabrics by MPUALO enhances vapor transport through the molecular mechanism of absorption - diffusion and desorption, in which water vapor molecules are absorbed by the polymer, diffused through the bulk and fabric fibers, transported to the other side, and finally released into the environment due to the hydrophilic fragments in the polyurethane [50].

3.5.4.5 Elongation %

The amount of stretch or stretch that the fiber accepts is referred to as elongation. Elongation at break is the amount of stretch a fiber can endure before breaking. From Figure12 it can be seen that the elongation at break [%] was affected by the treatment of cotton fabric with MPUALO, as it decreased with the increase of PU as a result of the increased cross-linking density content of PU and the hydrogen bonds formed [51.

3.5.5 Evaluation of antibacterial activity of untreated and treated cotton fabrics

Textiles are often attacked by microbes, resulting in decreased aesthetics, unpleasant odor and the possibility of infection by pathogenic microbes. To resist such attacks, antibacterial activity has become one of the essential functional properties of outdoor textile products, especially those used as protective textiles [52].

The antibacterial activity of coated cotton was evaluated against S. aureus and E. coli bacteria, and the results are presented in Figure11. The quantitative test results for the evaluation of the antibacterial activity of the aforementioned six cotton fabric samples are shown in Figure 13. It is easily noticed that the untreated cotton sample [C_0] shows clear growth of bacteria, which reflects that almost all the bacteria were alive after 24 hours with zero R % indicating that the untreated cotton fabric by itself does not inhibit the bacterial activity. Sample 2 [C_1] scored a R% value of 94.81 for S. aureus followed by 93.75 for E. coli due to the different cell walls' constitutions of both bacteria , higher values of antibacterial activity against S. aureus and E.coli were recorded when compared to the untreated cotton fabric [C_0].

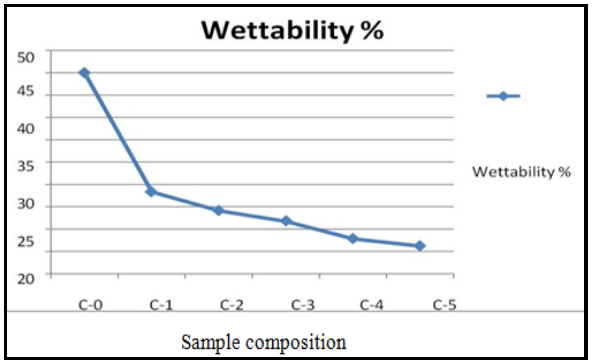


Fig. 8: Wettability test of untreated and treated cotton fabric

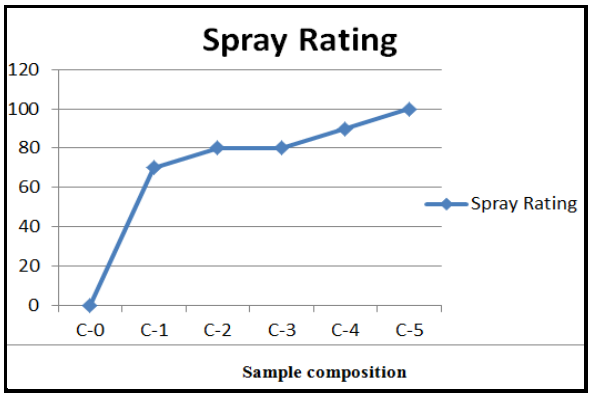


Fig.9. Spray rating of untreated and treated cotton fabric

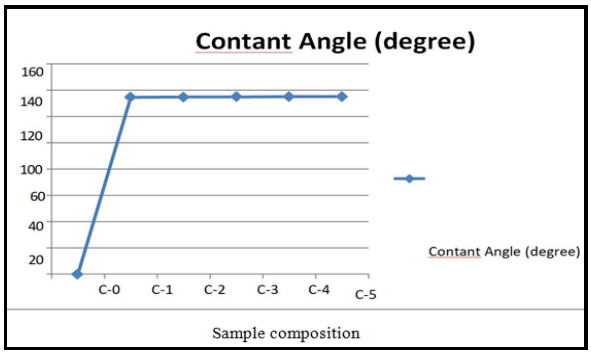


Fig. 10. Contact angle of untreated and treated cotton fabric

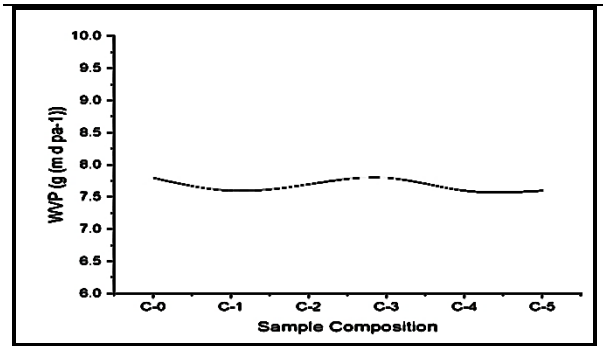


Fig.11: Water vapor permeability [WVP] of untreated and treated cotton fabric [x 10^{-4}]

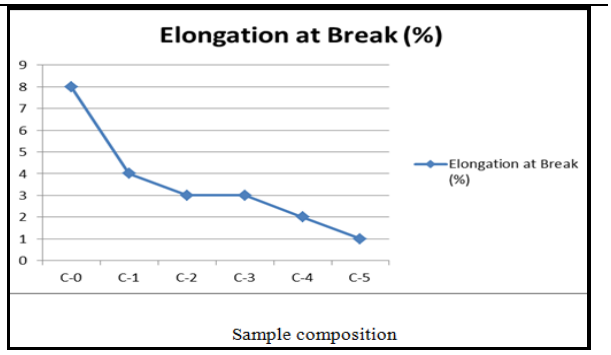


Fig. 12. Elongation at break [%] of untreated and treated cotton fabric

Table 11 : Physical properties of untreated and treated cotton fabric

Sample Code	Wettability %	Spray rating %	Contact angle	WVP[g[mdpa]$^{-1}$]	Elongation at break%
C_0	45.00	Zero	Zero	$7.8x10^{-4}$	8
C_1	18.34	70	134.50^0	$7.6\ x10^{-4}$	4
C_2	14.12	80	134.75^0	$7.7x\ x10^{-4}$	3
C_3	11.75	80	134.83^0	$7.8x\ x10^{-4}$	3
C_4	7.83	90	135.01^0	$7.6x\ x10^{-4}$	2
C_5	6.21	100	135.10^0	$7.6x\ x10^{-4}$	1

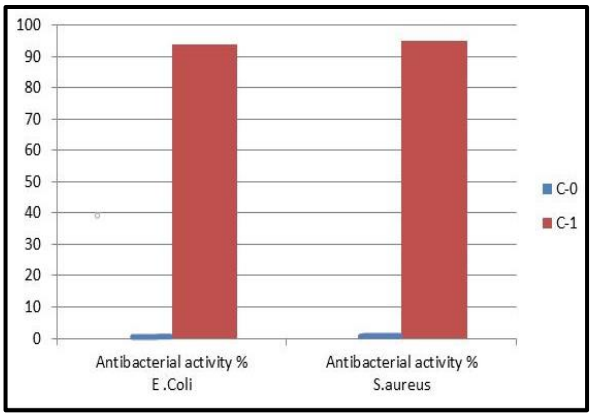


Fig. 13. Antibacterial activity of untreated and treated cotton fabrics towards *E.coli* and *S. aureus.*

4. Conclusion

PU has gained great importance in functional textile fields due to its cost-effective nature, mass production capabilities, and interesting physical and chemical properties. The environmentally friendly synthesis steps were easily carried out at a much lower temperature [lower energy consumption] and without any liquid or gaseous waste. This research focused on transferring the hydrophobic properties of the fabric to cotton by forming a continuous thin layer that protects the cotton fibers from abrasion, improves air permeability, and provides antimicrobial and anti-dust properties. The results obtained indicated that the treated cotton fabric remained hydrophobic and had the ability to shed water droplets. The results showed that the treated cotton fabrics had water contact angles exceeding 134 degrees, with the water absorption of the treated cotton fabrics decreasing from 45.00 % to 6.21%. The treated cotton fabrics were shown to be breathable with vapor permeability levels of 7.6 x 10^{-4} g [m day Pa]$^{-1}$ which was similar to untreated cotton fabrics. Furthermore, the surface appearance, elemental analysis, and functional groups of untreated and treated cotton fabrics were studied using FTIR, SEM, and EDX. This sustainable approach can therefore be easily expanded to process fabrics of heritage value; as well as cotton-based commercial textiles, as a valuable therapeutic alternative.

References

1. Amit. G, Bharatkumar. Z and Ketan. K., Novel applications of castor oil based polyurethanes: a short review, Polymer Science Series b .57[4], 292–297, [2015].

2. Roger. G, Jr., Mary .A, Leanne. C, Rosal .G, Ruda.B, Felrose.P, Applegen.I, Evalyn .C, Kaye.J, Kassandra .J,Tejas, Edison.A , Gerard. D, Roberto.M, and Arnold, A valorization of agricultural rice straw as a sustainable feedstock for rigid polyurethane/Polyisocyanurate foam production, Lubguban American Chemical Society. 9, 13100−13111, [2024].
3. Yingbin .S, Jialiang .H, Zhenxing .X, Xing .Z, Changqing F. and Chaoqun Z. ,Synthesis and characterization of vegetable oil based polyurethanes with tunable thermomechanical performance , Industrial Crops and Products.132,163-171, [2019].
4. Moyeenuddin .A, Polyurethanes from vegetable oils and applications: a review, Journal of polymer research, 25 [8], 165, [2018].
5. Abhijit D., Prakash M. , A brief discussion on advances in polyurethane applications , Advanced Industrial and Engineering Polymer Research , 3 [3], 93-101, 2020.
6. Giulia M. , Muhammad Z. , Jose A. , Eleonora B. , Elisabetta Z. , Athanassia A. and Ilker S. , Hydrophobic treatment of woven cotton fabrics with polyurethane modified aminosilicone emulsions, Applied Surface Science 490, 1024-1034 , [2019].
7. Hnin L. and Swe H., Effect of polyurethane finish on hydrophobic properties of cotton fabric, International Journal for Innovative Research in Multidisciplinary Field, 5, [9], 188-191, [2019].
8. Ahmed G. , Nourhan M. , Nehad G. , Nadeen K. , Sohaila S., Neaama A., and Eman , Polyurethane [PU] in textile finishing process, J. Text. Color. Polym. Sci., 21[1], 173-186, [2024].
9. Wang J., Han F., Liang B. and Geng G., Hydrothermal fabrication of robustly super hydrophobic cotton fibers for efficient separation of oil/water mixtures and oil-in water emulsions, Journal of Industrial and Engineering Chemistry , 54, 174–183, 2017.
10. Lee J., Kim D, and Kim Y., High-performance recyclable and super hydrophobic oil absorbents consisting of cotton with a polydimethylsiloxane shell, Journal of Industrial and Engineering Chemistry, 35,140–145. [2016].
11. Sasaki K., Tenjimbayashi M., Manabe K., and Shiratori S., Asymmetric superhydrophobic/superhydrophilic cotton fabrics designed by spraying polymer and nanoparticles, ACS Applied Materials & Interfaces, 8, 651–659, [2016].
12. Huang J., S.H., M.Z., Wang L. , Xing T., Chen G., Liu.X., Al-Deyab S., Zhang K., Chen T and Lai Y., Robust superhydrophobic TiO@fabrics for UV shielding, self-cleaning and oil–water separation, Journal of Materials Chemistry , A. 3, 2825– 2832, [2015].
13. Liu Q., Huang J., Zhang.J., Hong Y., Wan Y., Wang Q., Gong M., Wu Z and Guo C., Thermal, water proof, breathable, and antibacterial cloth with a nanoporous structure, ACS Appl. Mater. Interfaces, 10, 2026–2032, [2018].
14. Jeyasubramanian K., Hikku G., Preethi A., Benitha V, and Selvakumar N., Fabrication of water repellent cotton fabric by coating nano particle impregnated hydrophobic additives and its characterization, Journal of Industrial and Engineering Chemistry, 37, 180–189, [2016].
15. Martin W. , Natalie F., Lubos H., Armin Go., Elmar M and Andrea E. , Improved abrasion resistance of textile fabrics due to polymer coatings , Journal of Industrial Textiles, 49[5] ,572–583, [2019] .
16. Wenwen L., Yufa S. , Bin H. and Xiangdong Z., Synthesis and application of polyurethane-modified silicone as finishing agent for cotton fabric , Fibers and Polymers, 19[7] 1394-1401 ,2018.
17. Wanchao F., Yanhui Z., Guanghui X., Meiqi H. and Xiangdong L., Wear-resistant cotton fabrics modified by PU coatings prepared via mist polymerization, Journal of Applied Polymer Sciences , 133[7] , [2016].
18. Shazia T., Mohammad Z., Abdul J and Khalid M., Properties of the modified cellulosic fabrics using polyurethane acrylate copolymers, Carbohydrate Polymers, 94 [2], 866-873, [2013].
19. Sidra, Tabasum S., Zia K. , Parveen B. and Shahid M., Polyurethane dispersions prepared from vegetable oil and their application as textile finishes , Textile Research Journal , 92[23] ,2834-2847 [2022].
20. Delebecq E., Pascault J., Boutevin B and Ganachaud F., On the versatility of urethane/urea bonds: reversibility, blocked isocyanate, and nonisocyanate polyurethane, Chem. Rev, 113, 80–118, [2012].
21. Sridaeng D., Sukkaneewat B., Chueasakol N and Chantarasiri N., Copper- amine complex solution as a low- emission catalyst for flexible polyurethane foam preparation, e-Polym., 15[2], 119–126,[2015].
22. Test for Acid Value, in Annual Book of American Society for Testing and Materials Standards, American Society for Testing and Materials. Philadelphia, ASTM: D1639–90, [1996].
23. Standard Test Method for Hydroxyl Value of Fatty Oils and Acids. ASTM International. ASTM D1957-86 [2001]
24. Paquot C. and Houtfenne A.,"Standard Methods for the analysis of oils, fats and derivatives"7th ed.P.88, [1987].
25. Official and Tentative methods of the American oil chemists society 3rd ed. including additions and revisions American oil chemistis society 508, [1979].
26. Grdner H.A. and Sward G.G,"Physical and Chemical Examination of paints", Varnishes and Laquers"9th ed. P.422, [1946].
27. Heaton N., "Outline of paint Technology ", 3rd ed .P.358, [1956].
28. Standard Test Method for Water and Alkali Resistances, Philadelphia, ASTM:D1647-89
29. Standard Test Method for Water and Alkali Resistances, Philadelphia, ASTM:D1647-89
30. Standard Test Method for Solvent Resistance, Philadelphia, ASTM:D 1647-59

31. Standard Test Method for Film Hardness by Pencil Test, Philadelphia, ASTM:D 3363–92a
32. ASTM method, D 522-93, [Reapproved 2001].
33. ASTM method, D 1005-95a.
34. American Petroleum Institute, Recommended Practice 5 L 2 [RP5L2] Third Edition, May 31, 1987 [Reaffirmed January 1 , [1994].
35. Standard Test Method for Adhesion, Philadelphia, ASTM: D 3359-95 [1995]
36. Santos C.D., Zukerman S., Imamura and pm,"chemical transformation of abietic acid to new chiral derivatives" Journal Braz.Chem. Soc., 14, 998-1004, [2003].
37. Mazzon G., Zanocco I., Zahid M. , Bayer I., Athanassiou A., Falchi L., Balliana E. and Zendri E., Nanostructured coatings for the protection of textiles and paper, 180–188, [2017].
38. Hnin l., Soe and Swe H. , Effect of polyurethane finish on hydrophobic properties of cotton fabric , International Journal for Innovative Research in Multidisciplinary Field , 5 [9], 188-191, [2019] .
39. Giulia M., Muhammad Z., Jose A., Eleonora B. , Elisabetta Z. , Athanassia A., Ilker S., Hydrophobic treatment of woven cotton fabrics with polyurethane modified aminosilicone emulsions, Applied Surface Science , 490 [1] , 331-342, [2019].
40. Partha S., Tanvir M. , Avik K., Saiful He. and Solaima B. , Polyurethane [PU] based multifunctional materials: Emerging paradigm for functional textiles, smart, and biomedical applications, Journal of Applied Polymer Science, 139[38] e52832, [2022].
41. Giulia M., Muhammad Z. , Jose A., Eleonora B. , Elisabetta Z., Athanassia A and Ilker S, Hydrophobic treatment of woven cotton fabrics with polyurethane modified aminosilicone emulsions, Applied Surface Science , 490 [1], 331-342, [2019]
42. Wei Y., Zheng C., Chen P., Yu Q., Mao T., Lin J., Liu L., Synthesis of multiblock linear polyether functional amino silicone softener and its modification of surface properties on cotton fabrics, Polymer Bulletin, 76 ,447–467, [2019].
43. Zahid M., Heredia-Guerrero A., Athanassiou A., and Bayer I., Robust water repellent treatment for woven cotton fabrics with eco- friendly polymers, Chemical Engineering Journal, 319, 321–332, [2017].
44. Sugii M., Ferreira F., Müller K., Lima D., Groppo F., Imasato H., Rodrigues-Filho U., Aguiar F., Physical, chemical and antimicrobial evaluation of a composite material containing quaternary ammonium salt for braces cementation, Materials Science and Engineering: C., 73, 340–346,[2017]
45. Heredia-Guerrero J., Ceseracciu L., Guzman-Puyol S., Paul U., Alfaro-Pulido A., Grande C., Vezzulli L. ,Bandiera T. ,Bertorelli R., Russo D., Athanassiou A and Bayer I., Antimicrobial, antioxidant, and waterproof RTV silicone-ethyl cellulose composites containing clove essential oil, Carbohydrate Polymers, 192 ,150–158,[2018].
46. Mazzon G., Zanocco I., Zahid M., Bayer I.,Athanassiou A., Falchi L., Balliana E. and Zendri E., Nanostructured coatings for the protection of textiles and paper, 11,180–188, [2017].
47. Hnin L. and Swe H. , Effect of polyurethane finish on hydrophobic properties of cotton fabric , International Journal for Innovative Research in Multidisciplinary Field , 5 [9], 188-191 ,[2019].
48. Rahman M., Lijing W. and Robert A. and Jie D. , Polyurethane–superabsorbent polymer-coated cotton fabric for thermo-physiological wear comfort, Journal Mater Sci., 54,9267– 9281, [2019].
49. Tedeschi G., Guzman-Puyol S., Paul U., Barthel M., Goldoni L., Caputo G., Ceseracciu L., Athanassiou.A and Heredia- Guerrero.J, Thermoplastic cellulose acetate oleate films with high barrier properties and ductile behaviour, Chemical Engineering Journal, 348,840–849, [2018].
50. Badr A. and El-Nahrawy A., Moisture properties of raised 3-thread fleece fabric knitted with different face and fleecy yarns, Alexandria Engineering Journal, 55, 2881–2892, [2016].
51. Delhoma C., Wanjuraband J. and Hequet E., Cotton fibre elongation: a review, The Journal of the Textile Institute, 115, 1-12, [2022].
52. Jay R., Nidhi G., Vimal S. and Dholakiya B. , A review on polyurethane based multifunctional materials synthesis for advancement in textile coating applications, Journal of Polymer Research, 31[3] , [2024].