POLİTEKNİK DERGİSİ

JOURNAL of POLYTECHNIC

ISSN: 1302-0900 (PRINT), ISSN: 2147-9429 (ONLINE)
URL: http://dergipark.gov.tr/politeknik

Functionalization of textile materials with nanoclay incorporation for improved characteristics

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Bu makaleye şu şekilde atıfta bulunabilirsiniz(To cite to this article): Göcek İ., "Functionalization of textile materials with nanoclay incorporation for improved characteristics", ***Politeknik Dergisi***, 22(2): 509-522, (2019).

Erişim linki (To link to this article): http://dergipark.gov.tr/politeknik/archive

DOI: **10.2339/politeknik.508592**

İyileştirilmiş Özellik Elde Edilmesi Amacıyla Tekstil Malzemelerinin Nanokil Katkısı ile Fonksiyonelleştirilmesi

Araştırma Makalesi / Research Article

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(Geliş/Received : 04.05.2018 ; Kabul/Accepted : 06.09.2018)

ÖZ

Tekstil endüstrisi, tüketici taleplerini karşılayabilmek için yeni teknolojiler üzerine araştırmalar yapmaktadır. Günümüzde, üretim, terbiye ve kaplama işlemleri esnasında nanokompozit yapılar elde edilmesiyle tekstillere çok işlevlilik veya özel işlevler sağlanması için nanomalzeme uygulamaları öne çıkmaktadır. Bu çalışmada, özellikleri iyileştirilmiş fonksiyonelleştirilmiş nanokompozit kumaş elde edilmesi amacıyla, farklı pamuklu kumaşların yapısına terbiye teknikleri yoluyla nano ölçekli parçacıklardan nanokiller katılmıştır. Testlerin analiz edilmesinden sonra, nanokil ile işlem görmüş pamuklu kumaşların işlem görmemiş kumaşlara göre daha iyi alev geciktiricilik özelliğine ve ısıl kararlılığa sahip olduğu ve yıkamadan sonra işlevselliğin devamlılığının sağlandığı aynı zamanda da iyileştirilmiş kopma mukavemetine sahip olduğu gözlenmiştir.

Anahtar Kelimeler: Pamuklu kumaş, nanokil katkısı, alev geciktiricilik, yıkamaya dayanım, yanma davranışı.

Functionalization of Textile Materials with Nanoclay Incorporation for Improved Characteristics

ABSTRACT

Textile industry has been seeking for new technologies to meet consumer demands. Nowadays, nanomaterial applications during manufacturing, finishing and coating processes to produce nanocomposite structures has come into prominence for acquiring multifunctionality or special functions for textiles. In the current study, nano-scaled particles namely nanoclays were incorporated in the structure of different cotton fabrics via finishing techniques to develop functionalized nanocomposite fabric with improved characteristics. After analyzing the tests, cotton fabrics treated with nanoclay were found to possess better flame-retardant characteristics and thermal stability compared to the untreated ones with the durability of the functionality against washing as well as improved tensile strength.

Keywords: Cotton fabric, nanoclay incorporation, flame retardancy, durability to washing, burning behavior.

1. INTRODUCTION

Cotton, which is one of the most commonly used natural fiber in wide range of textile products, is preferred due to its outstanding characteristics including smooth handle and softness, hydrophilicity, sufficient breathability, high strength, durability, nonallergenic structure, good dyeability, regeneration, biodegradability and eco-friendliness [1-7]. Therefore, cotton is widely used for the production of apparel, home-textiles, furnishings and some industrial products such as tarpaulins, industrial threads and medical supplies [4,5]. However, due to its subsistent structure, textiles made of cotton fiber confront some problems associated with yellowing, wrinkling, photo-degradation and vulnerability to bacteria and mildew [1,3]. Moreover, due to its chemical composition, cotton is prone to flammability which can cause immediate combustion leading to flames and fire and even it is known to be more combustible than its synthetic counterparts [2,4,6,7]. Today, in addition to comfort-related properties of textile products, textile industry has focused on development and production of multifunctional textiles possessing self-cleaning ability, antibacterial and nonallergenic properties, durability to photo-degradation, UV protection capability and flame-retardant characteristic. Furthermore, lately, owing to the environmental concerns regarding the production of synthetic fibers from crude oil, natural fibers especially cotton has become one of the most desired textile fibers. Therefore, the textile industry and the customers choose using smart natural textiles over synthetic textiles [3].

Recently, development and manufacturing of multifunctional fabrics made of cotton with high added-value have been attracting great attention in research projects and industry. Utilization of nanomaterials on cotton fabrics helps to improve inherent characteristics of cotton by the introduction of new functionalities to the final product including antimicrobial properties, abrasion

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resistance, gas barrier, protection to UV radiation, chemical resistance or reactivity, hydrophobicity or hydrophilicity, dyeability, self-cleaning, water repellency and flame retardancy [1, 3, 4, 7-10]. Numerous nanomaterials such as metal and metal oxide nanoparticles including silver, copper, MgO, ZnO, TiO2 and others including carbon nanofibers and nanotubes, nanosilica, chitosan, hydroxyapatites, nanoclays have been employed to functionalize cotton for achieving better performance in many ways from the final product. However, amongst all, natural clay minerals have been drawing the most interest in research and development studies and have been shown to have great potential for being applied to many different fields in textile industry [1, 3, 7-33]. Therefore, owing to their distinctive characteristics and cost-effectiveness, many studies have been focusing on the application of nanoclays such as attapulgite, saponite, laponite, vermiculite, mica, hectorite, smectite, kaolin and montmorillonite to textiles [1, 3, 9, 10, 12, 13, 15-18, 21, 25, 27, 32, 34, 35]. In many previous studies, application of nanoclay minerals on cotton substrates were performed using different procedures and methods and investigated in terms of various functionalities such as flammability, super hydrophobicity, thermal and mechanical properties [6-10, 12, 15, 20]. In one study, montmorillonite was applied on cotton textile substrate via a commercial exhaustion dyeing-like process in order to obtain controlled release and flame retardancy, and the process was evaluated before and after laundering for washing fastness, binding stability and resistance to washing [1]. In some studies, layer-by-layer process and other coating techniques were employed to deposit polymer-clay nanocoatings on cotton substrates for different aims such as flame retardancy, super hydrophobicity and self-cleaning property [4, 5, 7, 8, 12, 20]. Moreover, in other studies, finishing processes based on impregnation method and washing was used to incorporate different nanoclays such as attapulgite, montmorillonite, organically modified montmorillonites in cotton substrates to improve their antibacterial and antifungal activity, UV resistance, mechanical properties, thermal performance and flame retardancy [3, 6, 9-11, 36].

The cellulosic material, cotton with a low limiting oxygen index and low combustion temperature is a highly combustible material. Owing to the rapid burn just after ignition and fast flame spreading over the surface, textiles made of cotton have potential to result in fatal burns just in a few seconds of ignition [5, 6]. Currently, the risk of fire and the danger incurred by the flammable structure of cotton can be eliminated or at least minimized by numerous flame-retardant treatments i.e. sol-gel technology, surface chemical grafting, nanoparticle adsorption, different coating techniques applied onto textiles which result in enhancement of the flame-retardant characteristics of cotton products and thereby fire safety regulations can be fulfilled as well as the use of cotton in textile products can be diversified. Furthermore, with the use of flame retardants, the combustion process can be decelerated and there will be time both for the people to escape from uncontrolled fire and save their lives and for the firefighters to put out the fire before it results in severe hazard to lives and resources [2, 4, 5, 16, 37, 38]. Mainly, flame retardants used in these treatments can be categorized into four different groups which are inorganic, halogenated organic, organophosphorus, and nitrogen-based. However, recent environmental and health-related concerns regarding utilization of these chemical treatments including many chemicals on textile products have brought out a need for eco-friendly alternatives which promoted innovative research and development [4, 6, 30, 35, 39-41]. Although halogenated and boron-containing additives are one of the most commonly used flame-retardants with high effectiveness, halogenated flame retardants have been shown to be toxic and flame retardants containing boron are not durable to aqueous washing [5]. Phosphorus-based flame retardants are known to be the most commercially useful ones owing to their durability to repetitive washing, ability to decrease volatile fuel, pyrolysis temperature and afterglow and ability to augment carbonaceous char [5]. As an alternative eco-friendly material to current flame-retardants lately, nanoclays especially montmorillonite (MMT) have been used with polymeric materials in different coatings and in the production of nanocomposites, and incorporated in cellulosic fibers through surface modification, coating and finishing techniques since they have been shown to decrease flammability and pile up heat resistance and thermal stability even at very small amounts of clay [5-7, 17-20, 22, 24 -33, 35, 37-51]. Nanocomposite textiles made of different synthetic fibers produced with nanoclays have been found to perform better in terms durability to fire compared to their counterparts made of pristine synthetic fibers [5, 18, 25, 27, 32, 34, 48]. Moreover, for some of the nanocomposite coatings of cotton fabrics, polyhedral oligomeric silsesquioxane (POSS), carbon nanotubes and MMT clays have been used as flame retardants. However, due to complex two-stage synthesis and high cost, POSS and carbon nanotubes have limited potential to be used in commercial products. On the other hand, combustion process of polymer and clay systems have been propounded to include a layer of protective charred ceramic surface formed in the course of polymer ablation, which has been demonstrated to decelerate the volatilization of combustible gas, prevent oxygen penetration resulting in reduced gas permeability, disrupt heat transfer and hinder degradation [5, 6, 18, 22, 24-27, 30, 38, 41, 48, 51, 52]. Therefore, at present, many studies have been concentrating on enhancing the flame retardancy of cotton products by the help of nanoclay utilization [4-7, 9, 10, 12, 20, 38].

Since today, providing multifunctionality or special functions for textiles is a requirement to satisfy customer expectations, for this goal, novel technologies that have the potential to lead to innovations have been investigated so far. Therefore, in this study, it was aimed

to produce a multifunctional cotton fabric by the treatment with the nanoclay Nanomer I.44P which was preferred due to its antibacterial activity previously demonstrated in the scientific literature [53]. Furthermore, the fabrics treated with the nanoclay Nanomer I.44P can be acknowledged as environmentally friendly since throughout the treatment no hazardous chemicals were used and the fabrics treated were made of natural and biodegradable fiber cotton [1, 3]. In addition to this, montmorillonite nanoclays are biodegradable and completely generated from naturally occurring resources which implies their environmentally friendliness [6, 10, 11, 19]. Especially, the nanoclay Nanomer I.44P is known as environmentally friendly flame retardant [24, 54]. On the other hand, the method used in the study is compatible with the conventional textile processes which means that the nanoclay Nanomer I.44P can be easily used in the textile industry for treating cotton fabrics via textile finishing processes improving the manufacturability of the product. In the study, after the nanoclay particles were successfully incorporated in the structure of three different types of cotton fabrics through finishing techniques for functionalization, the treated fabrics were evaluated in terms of homogeneity of the nanoclay distribution over the fabric surface, flame retardancy and burning behavior, durability of the functionality to washing and the change in tensile strength.

2. EXPERIMENTAL WORK

2.1. Materials

Three different types of plain weave 100% cotton fabrics in raw, conventional (desized and scoured) and optical brightened (desized, scoured and optical brightened) forms were purchased to be treated with the nanoclay and analyzed in terms of their fabric construction and basis weight as mass per unit area (Table 1).

Acetone and Ethyl alcohol were purchased from Riedel-de Haën and Merck, respectively. They were exploited to wash off contaminations from all of the fabric samples. Moreover, acetone was also used to clean the glass equipment by removing possible contaminations existing.

Distilled water was obtained in the laboratory by the utilization of Veolia Water Solutions and Technologies ELGA Pure Lab Option DV35 LA620. Distilled water was used to prepare the solutions with nanoclay, to wash the fabric samples just after immersing them in acetone, ethyl alcohol and tap water before the treatment with the solutions in order to remove any remaining contaminations and to remove excessive amount of nanoclay on the fabric surface that was not incorporated into the fabric structure after the completion of the process in the Gyrowash.

The nanoclay Nanomer® I.44P, which is surface modified montmorillonite clay containing 35-45 wt% dimethyl dialkyl (C14-C18) amine was purchased from Sigma Aldrich and it was used to prepare the nanoclay solutions for the treatment of the fabric samples. It is known to have good heat stability, electrochemical property and antibacterial activity [53, 55].

2.2. Methods

2.2.1. Preparation of the treating bath

The solutions to be applied on the fabric samples were prepared with 1 wt% nanoclay using distilled water. Firstly, nanoclay was distributed in distilled water utilizing a hot plate with magnetic stirring effect by applying heat for 1 hour and the temperature was kept at around 60 to 63 °C. Wisd Laboratory Instruments WiseStir MSH-20A was used as a magnetic stirrer and hot plate in order to homogeneously stir the solution with the application of heat and distribute nanoclays in distilled water.

Afterwards, the solutions were ultrasonicated by the help of Hielscher UP400S ultrasonicator for totally 1 hour with consecutive quadruple 15 minute-intervals and 2 minute-breaks in between the process intervals in order to obtain homogeneously distributed nanoclay particles in all over the solution by hindering the agglomerates both to form and precipitate at the bottom of the beaker and moreover in order to obtain separated nanoclay stacks by the help of sound waves with the amplitude of 65% and cycle of 0.8. Therefore, ultrasonicator was used in order to prevent formation of nanoclay agglomerates in the solution and obtain homogenously distributed nanoclay particles.

2.2.2. Preparation of the fabric samples

The fabrics were cut into small pieces whose dimensions were determined depending on the size constraints of the containers of the Gyrowash machine which was as well sufficient enough for the sample sizes required by the techniques of characterization and the standards of the chemical and physical tests.

The fabric samples that were cut into small pieces from the three types of fabrics were immersed firstly, in acetone and then, ethyl alcohol in 1000 ml separate beakers. After the both immersions, they were washed with tap water and lastly, immersed in distilled water in order to remove any remaining contaminations.

Table 1. Fabric structural properties

Types of Cotton Fabrics	Fabric Density		Fabric Basis Weight (g/m^2)
	Warp (warp/cm)	Weft (weft/cm)	
Raw	46	36	1.3738
Optical Brightened	52	45	1.4132
Conventional	68	62	0.7065

In order to make fabric structural analysis i.e. fabric density and fabric basis weight on the three different fabric types, those without nanoclay treatment were conditioned at 65 ± 4 % relative humidity and 20 ± 2 ºC temperature for 48 hours in the laboratory.

2.2.3. Treatment of the fabric samples

After the fabric samples were decontaminated, they were immersed in the prepared solutions with 1 wt% nanoclay in distilled water that were previously poured into the containers of the James H Heal Gyrowash with 4 containers. The liquor ratio was methodically adjusted as 1:40. The fabric samples were treated with this instrument for 1 hour at 60 °C by utilizing 25 steel balls in each container for mechanical agitation in order to be incorporated with nanoclays. A similar treatment with different nanoclays using a rotary drum washer was demonstrated in the literature [36].

Once the processing in the Gyrowash was completed, the fabric samples were taken out of the containers and right after that each sample was separately dipped up 5 times subsequently in distilled water inside different 1000 ml beakers to remove excessive amount of nanoclay on the fabric surface that was not incorporated into the fabric structure. Then, each of them were squeezed, laid on the racks of the oven that was heated up to 70 °C and left there for 30 minutes to be dried while being cured for providing bonding between nanoclay and cotton. An oven Thermo Scientific Heraeus T6 that can be heated up to 250 °C with the capacity of 57 L and interior depth of 386 mm was utilized for this purpose. After the process was over, the fabric samples were taken out of the oven and flat-dried by keeping at ambient temperature in atmospheric conditions over night.

To make the weight analysis and examine the tensile strength of the processed fabrics, conditioning was done at 65 ± 4 % relative humidity and 20 ± 2 ºC temperature for 24 hours before the testing processes.

2.3. Tests and Characterization

2.3.1. Fabric density and basis weight analysis

For the determination of fabric density in warp and weft directions and fabric basis weight, the standards TS 250 EN 1049-2 (Textiles-Woven Fabrics-Construction-Methods of Analysis-Part 2 Determination of Number of Threads Per Unit Length) and TS 251 (Determination of Mass Per Unit Length and Mass Per Unit Area of Woven Fabrics) were used, respectively. The fabric basis weight was analyzed before and after the treatment with the nanoclay to ensure that the nanoclay particles were incorporated and existed in the fabric structure. On the other hand, it was also analyzed before and after the washing process to determine the durability of the fabric samples against washing in terms of loss and remaining amounts of nanoclay in the fabric structure.

2.3.2. Fourier transform infrared spectroscopy (FTIR-ATR)

The Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance (FTIR-ATR) was used for analyzing the bond structure and bonding energy of the surfaces of the fabric samples treated with the nanoclay and hence, for getting information about the molecular structure and existence of bonds in the certain regions to identify the types of chemical bonds. Perkin Elmer Spectrum 65 FTIR-ATR Spectrometer was utilized in order to examine the presence and distribution of the nanoclay particles on the cotton fabric samples functionalized with the nanoclay. The FTIR-ATR spectra were taken at 64 scans in each analysis from 5 different regions of the surface of the cotton fabric samples in order to understand whether the nanoclay particles were incorporated and distributed evenly on the whole fabric surface after the treatment with the nanoclay and whether the nanoclay particles existed and stayed homogenously distributed in the fabric structure after washing.

2.3.3. Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS)

SEM micrographs were taken from the raw cotton fabric samples to observe whether the nanoclay particles were incorporated into the fabric structure and how they were distributed over the fabric surface after the treatment with the nanoclay and to visually demonstrate the presence of nanoclay particles and their distribution over the surface of the fabric sample after washing. For the morphology analysis of the untreated raw cotton fabric sample, nanoclay treated raw cotton fabric sample and its washed counterpart, Tescan Vega3 scanning electron microscope (SEM) operating at 10 kV was used. Before SEM analysis, gold/palladium sputtering which forms electrically conductive thin coating on the surface of the samples was conducted for each of them. This thin layer of gold/palladium hinders charging, lowers thermal damage, and enhances secondary electron emission, which are helpful for scanning electron microscopy. Quorum SC7620 sputter coater with a deposition rate of 0-10 nm/min having multi sample holder, completely automatic control and high resolution fine coating was employed for gold/palladium sputtering process.

A chemical microanalysis characterization method, Energy Dispersive Spectroscopy (EDS) was employed in combination with scanning electron microscopy for the characterization of the elemental composition of the raw cotton fabric samples before and after the treatment with the nanoclay to demonstrate the presence of nanoclay particles in the structure of the fabric samples. The EDS system of EDAX was used in conjunction with the scanning electron microscope.

2.3.4. Tensile strength test

James Heal Titan 710 Strength Test Machine was used for the assessment of the tensile strengths of the cotton fabric samples before and after the treatment with the nanoclay particles in order to observe if any alteration as a decrease or as an improvement occurred owing to the treatment. The cotton fabric samples were tested in warp and weft directions with the cross-head speed of 100 mm/min according to the standard TS EN ISO 13934-1 (Textiles- Tensile properties of fabrics- Part 1:

Determination of maximum force and elongation at maximum force using the strip method).

2.3.5. Vertical flame test

The burning behavior and flammability properties of the cotton fabric samples were analyzed with the vertical flame test in accordance with the standard TS 5775 EN ISO 6940 (Textile fabrics - Burning behavior - Determination of ease of ignition of vertically oriented specimens). The test was conducted before and after the treatment with the nanoclay particles in order to determine the effect of nanoclay incorporation into the fabric structure in terms of the change in the burning behavior and flammability properties of the fabric samples. In addition to this, the fabric samples were exposed to this test before and after the washing process to reveal the durability of the treatment against washing in terms of the change in the burning behavior and flammability properties of the fabric samples.

2.3.6. Thermogravimetric analysis (TGA)

The thermal decomposition behaviors of the nanoclay treated and untreated cotton fabrics were monitored and their thermal stability was determined using thermogravimetric analysis. TGA was conducted on a TA Q-600 Thermogravimetric Analyzer (TA Instruments) in the temperature range of 50-600 °C, at the heating rate of 10 °C min-1 in the presence of N2.

2.3.7. Analysis of durability against washing

For the determination of durability against washing, washing process was performed in accordance with the standard TS EN ISO 105-C06 (Textiles - Test for colour fastness - Part C06: Colour fastness to domestic and commercial laundering). After this process, the fabric samples were line-dried at ambient temperature in atmospheric conditions over night and conditioned as in the previous conditioning process. Finally, the fabric samples were analyzed in terms of their weights before and after washing to observe if any change in the fabric weight in terms of nanoclay amount occurred owing to the washing process. The FTIR-ATR spectra were taken from 5 different regions of the surface of the fabric samples before and after washing to show the presence of nanoclay particles in all over the fabric structure remained after washing process. Moreover, SEM micrographs were taken for the raw cotton fabric samples before and after the washing process to visually demonstrate the existence of nanoclay particles and their distribution over the fabric samples after washing. The fabric samples were subjected to the vertical flame test before and after washing to determine if there was any change in their burning behavior and flammability properties.

3. RESULTS AND DISCUSSION

3.1. Basis Weight Analysis

Fabric basis weight was analyzed for all the types of cotton fabric samples before and after the treatment with the nanoclay Nanomer I.44P. According to the analysis, the fabric basis weight was found to increase for all of the cotton fabric samples after the treatment as can be observed in Table 2 indicating the incorporation of the nanoclay particles in the cotton fabric samples.

3.2. Fourier Transform Infrared Spectroscopy (FTIR-ATR)

Comparison of the FTIR spectra of the nanoclay, untreated Raw Cotton Fabric sample and Raw Cotton Fabric sample treated with the nanoclay can be seen in Figure 1 for further investigation in order to comprehend the changes in the peaks of the FTIR spectrum of the Raw Cotton Fabric after the nanoclay incorporation.

The FTIR spectrum of the nanoclay Nanomer I.44P can be seen in Figure 1. The characteristic peaks of the nanoclay Nanomer I.44P were obtained at 2917, 2848, 1467, 1115, 1021, 914, 887, 623 and 519 cm^{-1} wavenumbers. While the hydrogen bonds were observed at about 2887-2919 cm^{-1} and 992-999 cm^{-1}, the peaks at 2924 cm^{-1} and 2848 cm^{-1} indicated the stretching C-H aliphatic bonds. The stretching O-H bonds can be seen in the transmittance band in between 3594 cm^{-1} and 3735 cm^{-1} [55].

The FTIR spectrum of the untreated Raw Cotton Fabric samples can be observed in Figure 1. The characteristic peaks of the Raw Cotton Fabric were obtained at 723, 1017, 1054, 1101, 1160, 1242, 1337, 1408, 1713, 2899, 2973, 3279 and 3331 cm^{-1} wavenumbers. The vibration at around 1733 cm^{-1} is ascribed to C=O stretching vibration originating from esters or amides [56-58]. This vibration was obtained at 1713 cm^{-1}. O-H bending vibration of water molecules was obtained around 1627 cm^{-1}. The strong transmittance band in between 3000 cm^{-1} and 3600 cm^{-1} can be ascribed to O-H stretching vibration [56-58]. Two vibrations which are ascribed to intermolecular hydrogen bonds and intra-molecular hydrogen bonds were attained in this band at 3279 and 3331 cm^{-1} wavenumbers, respectively [56-58]. The vibration at 1534 cm^{-1} which possibly indicates proteins or amino acids can be ascribed to NH_2 deformation [56-58]. However, this vibration was located with a peak at 1505 cm^{-1}. C-O stretching of acetyl group was observed at 1368 cm^{-1} [56-58]. The vibrations observed at 1337, 1315 and 1211 cm^{-1} can be attributed to OH in plane bending [56-58]. The vibration occurred at 1242 cm^{-1} can be ascribed to C=O stretching or NH_2 deformation [56-58]. The vibration which can be ascribed to C-O-C

Table 2. Basis weights of the fabric samples before and after the treatment with the nanoclay

Cotton Fabric Samples	Fabric Basis Weight (g/m^2)	
	Before the Treatment	After the Treatment
Raw	1.3738	1.4293
Optical Brightened	1.4132	1.4980
Conventional	0.7065	0.7421

stretching mode of the pyranose ring appeared at 1204 cm^{-1} [56-58]. The vibration which appeared at 900 cm^{-1} can be ascribed to β-linkage [56-58]. The anti-symmetric bridge C-O-C stretching vibration and anti-symmetric in-plane ring stretching vibration were located at 1160 cm^{-1} and 1101 cm^{-1}, respectively [56-58]. While the vibrations located at 1054 cm^{-1} and 1017 cm^{-1} can be ascribed to C-O stretching mode, the ones at 1000 cm^{-1} and 985 cm^{-1} can be ascribed to C-O and ring stretching modes [56-58]. The vibration at 710 cm^{-1} which can be ascribed to CH_2 rocking vibration in cellulose and the vibrations at 2918 and 2850 cm^{-1} which can be ascribed to $–CH_2$ asymmetric vibrations possibly originating from the presence of wax substances on the surface of the primary cell wall were obtained at 723 cm^{-1} and 2973 cm^{-1} and 2899 cm^{-1} [56-58].

Some peaks mainly at 3331, 1713, 1242, 1054 and 723 cm^{-1} wavenumbers for the untreated Raw Cotton Fabric sample were found to disappear which was caused by the nanoclay Nanomer I.44P addition to the structure of the cotton fabric when the FTIR spectra of the untreated Raw Cotton Fabric sample and the sample treated with the nanoclay Nanomer I.44P were compared (Figure 1). Moreover, some small shifts and/or intensity changes were obtained for the remaining peaks (Figure 1). Therefore, a very similar FTIR spectrum with the spectrum of the nanoclay Nanomer I.44P was obtained with a few slight differences for the treated Raw Cotton Fabric sample (Figure 1). It can be concluded that all of these differences were caused by the nanoclay addition to the fabric structure and were the sign of successfully imparted nanoclay Nanomer I.44P to the structure of the cotton fabric.

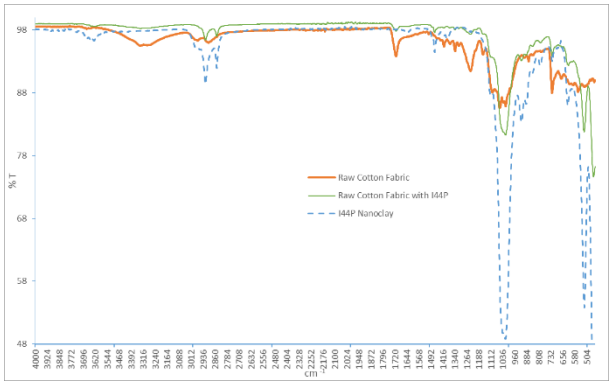


Figure 1. FTIR spectra of the Raw Cotton Fabric, Raw Cotton Fabric treated with Nanomer I.44P and the nanoclay Nanomer I.44P

Comparison of the FTIR spectra of the nanoclay, untreated Optical Brightened Cotton Fabric sample and Optical Brightened Cotton Fabric sample treated with nanoclay can be seen in Figure 2 for further examination to understand the changes in the peaks of the FTIR spectrum of the Optical Brightened Cotton Fabric after the nanoclay incorporation.

The FTIR spectrum of the untreated Optical Brightened Cotton Fabric samples can be observed in Figure 2. The characteristic peaks of the Optical Brightened Cotton Fabric were obtained at 661, 892, 985, 1000, 1031, 1055, 1110, 1160, 1315, 1337, 1371, 1428, 2892, 3276 and 3329 cm^{-1} wavenumbers. The strong transmittance band in between 3000 cm^{-1} and 3600 cm^{-1} can be ascribed to O-H stretching vibration [59]. Two vibrations which are ascribed to intermolecular hydrogen bonds and intra-molecular hydrogen bonds were attained in this band at 3276 and 3329 cm^{-1} wavenumbers, respectively [59]. The vibration at around 2898 cm^{-1} is ascribed to CH_2 and CH_3 stretching vibration [59]. This vibration was obtained at 2892 cm^{-1}. O-H bending vibration of absorbed water molecules was obtained around 1627 cm^{-1}. The vibrations at 1426, 1362, 1334 and 1314 cm^{-1} can be ascribed to C-H and CH_2 bending vibrations [59]. However, these vibrations were located with the peaks at 1428, 1371, 1337 and 1315 cm^{-1}. The anti-symmetric bridge C-O-C stretching vibration of glycosidic ether in cellulose and hemicellulose and C-C ring breathing vibration were located at 1110 cm^{-1} and 1160 cm^{-1}, respectively [59]. C-OH bond of secondary alcohol was observed at 1055 cm^{-1} [59]. The vibration which can be ascribed to C-O stretching mode of cellulose and hemicellulose appeared at 1031 cm^{-1} [59]. The vibration which was located at 892 cm^{-1} can be attributed to β-Glycosidic linkage [59].

Some peaks mainly at 2892, 1000, 985, and 892 cm^{-1} wavenumbers for the untreated Optical Brightened Cotton Fabric sample were found to disappear which were ascribed to the nanoclay Nanomer I.44P addition to the structure of the cotton fabric when the FTIR spectra of the untreated Optical Brightened Cotton Fabric sample and the sample treated with the nanoclay Nanomer I.44P were compared (Figure 2). On the other hand, some new peaks appeared at 2920, 2848, 895 and 911 cm^{-1} wavenumbers in the FTIR spectrum of the Optical Brightened Cotton Fabric sample treated with the nanoclay Nanomer I.44P (Figure 2). Moreover, some small shifts and/or intensity changes were obtained for the rest of the peaks (Figure 2). Therefore, some similarities occurred in between the FTIR spectrum of the treated Optical Brightened Cotton Fabric sample and that of the nanoclay Nanomer I.44P (Figure 2). All of these differences in between the untreated and treated Optical Brightened Cotton Fabric samples were attributed to the nanoclay inclusion to the fabric structure and indicated the successfully imparted nanoclay Nanomer I.44P to the structure of the cotton fabric.

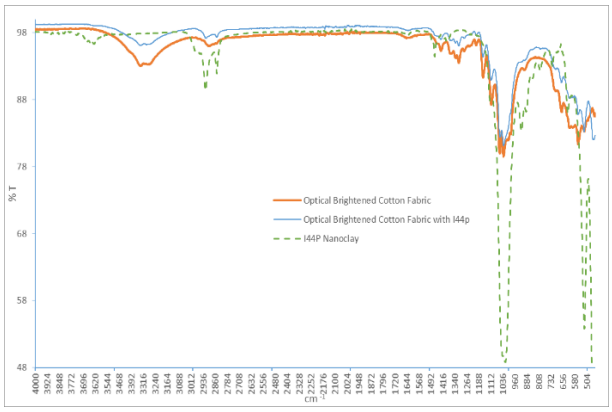


Figure 2. FTIR spectra of Optical Brigthened Cotton Fabric Optical Brightened Cotton Fabric treated with Nanomer I.44P and the nanoclay Nanomer I.44P

Comparison of the FTIR spectra of the nanoclay, untreated Conventional Cotton Fabric sample and Conventional Cotton Fabric sample treated with the nanoclay is shown in Figure 3 for further exploration to observe the alterations in the peaks of the Conventional Cotton Fabric because of the nanoclay incorporation.

The FTIR spectrum of the untreated Conventional Cotton Fabric samples can be observed in Figure 3. The characteristic peaks of the Conventional Cotton Fabric were obtained at 685, 900, 983, 999, 1028, 1053, 1109, 1161, 1207, 1279, 1315, 1334, 1363, 1425, 1630, 2893, 3275 and 3335 cm^{-1} wavenumbers. The strong transmittance band in between 3000 cm^{-1} and 3600 cm^{-1} can be ascribed to O-H stretching vibration [60]. Two vibrations which are ascribed to intermolecular hydrogen bonds and intra-molecular hydrogen bonds were attained in this band at 3275 and 3335 cm^{-1} wavenumbers, respectively [60]. The vibration which can be ascribed to C-H stretching vibration appeared at 2893 cm^{-1} [60]. O-H bending vibration of water molecules absorbed by cellulose was obtained around 1630 cm^{-1} [60]. The vibration located at 1455 cm^{-1} can be ascribed to OH in plane bending [60]. The vibration at around 1420 cm^{-1} is ascribed to CH_2 scissoring vibration at C(6) [60]. However, this vibration was located with a peak at 1425 cm^{-1}. C-H bending vibration was observed at 1363 cm^{-1} [60]. The vibrations observed at 1334 and 1315 cm^{-1} can be attributed to OH in plane bending and CH_2 wagging, respectively [60]. The vibration occurred at 1279 cm^{-1} can be ascribed to CH bending [60]. OH in plane bending vibrations were located at 1247 and 1207 cm^{-1} [60]. The asymmetric C-O-C stretching vibration and C-O stretching vibrations appeared at 1161 cm^{-1} and 1109 and 1053 cm^{-1}, respectively [60]. The vibrations which appeared at 999 and 900 cm^{-1} can be attributed to C-O valence vibration at C(6) and C-O valance vibration in cellulose I and II [60].

Some of the peaks mostly at 2893, 999, 983, and 900 cm^{-1} wavenumbers for the untreated Conventional Cotton Fabric sample were found to disappear which were attributed to the nanoclay Nanomer I.44P addition to the structure of the cotton fabric when the FTIR spectra of the untreated Conventional Cotton Fabric sample and the sample treated with the nanoclay Nanomer I.44P were compared (Figure 3). However, some new peaks appeared at 2919, 2852, 898 and 911 cm^{-1} wavenumbers in the FTIR spectrum of the Conventional Cotton Fabric sample treated with the nanoclay Nanomer I.44P (Figure 3). Furthermore, some small shifts and/or intensity changes were obtained for the rest of the peaks (Figure 3). Thus, some similarities occurred in between the FTIR spectrum of the treated Conventional Cotton Fabric sample and that of the nanoclay Nanomer I.44P (Figure 3). The aforementioned differences in between the untreated and treated Conventional Cotton Fabric samples were ascribed to the nanoclay inclusion to the fabric structure denoting the successful impartation of the nanoclay Nanomer I.44P to the structure of the cotton fabric.

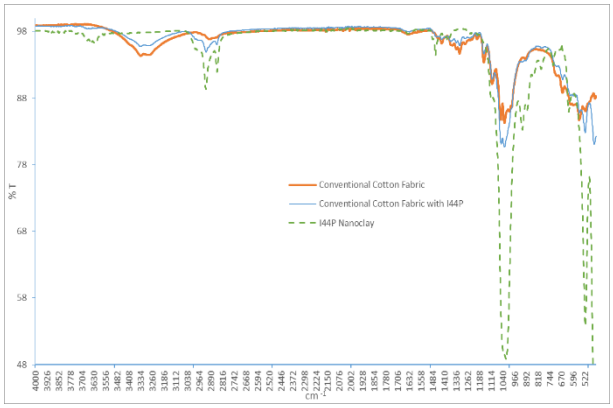


Figure 3. FTIR spectra of the Conventional Cotton Fabric, Conventional Cotton Fabric treated with Nanomer I.44P and the nanoclay Nanomer I.44P

Since the nanoclay Nanomer I.44P was detected in every region of the treated fabric samples that were characterized by FTIR Spectroscopy from 5 different regions for each, it can be deduced that the nanoclay particles were present and homogenously dispersed over the surface of the cotton fabric samples after the treatment with the nanoclay implying that the nanoclay incorporation in the cotton fabric structure was successfully accomplished.

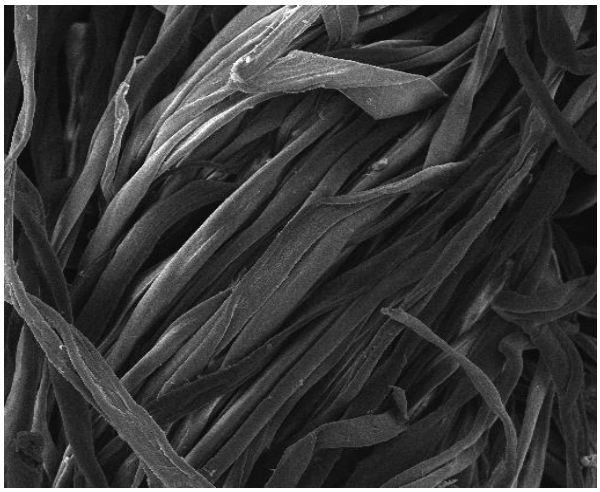
3.3. Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS)

SEM micrographs of the untreated Raw Cotton Fabric sample and its treated counterpart with nanoclay can be observed in Figure 4a and 4b, respectively. Presence of nanoclay particles can be apparently seen on all over the surface of the cotton fibers in the structure of the treated fabric sample. Moreover, the distribution of nanoclay particles in the fabric structure was found sufficiently homogenous and it is also obvious from the figure that nanoclay particles penetrated into the interfaces in between the fibers in the fabric structure. On the other

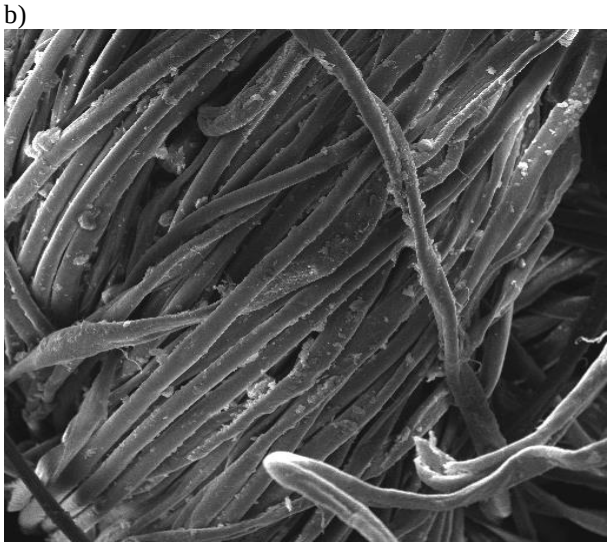
hand, the pristine structure of the cotton fibers can be recognized in the structure of the untreated fabric sample.

EDS spectra of the untreated and treated Raw Cotton Fabric samples are shown in Figure 4c and 4d, respectively. In the EDS spectrum of the untreated cotton fabric sample, it is clear that the elemental composition only consisted of C and O elements which constitute the chemical structure of cellulose showing that the fabric sample was only composed of cellulose, since it was made of cotton, and did not include any other substance which was nanoclay in this case. However, in the elemental composition, EDS spectrum of the treated cotton fabric sample prominently exhibited not only the peaks of C and O elements constituting the chemical structure of cellulose but also the peaks of silicon (Si), aluminum (Al), iron (Fe) and calcium (Ca) elements taking part in the formation of montmorillonite nanoclay. Therefore, in addition to the other characterization techniques (FTIR and SEM) employed in the current study, EDS analysis also demonstrated the existence of nanoclay particles in the fabric sample treated with the nanoclay I.44P.

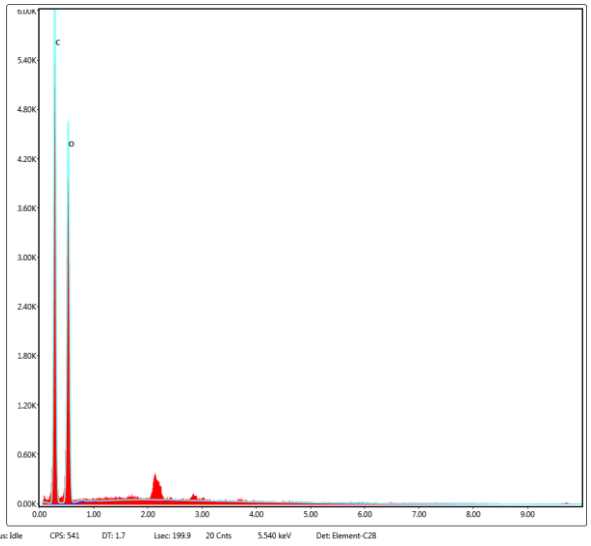
a)



b)



c)



d)

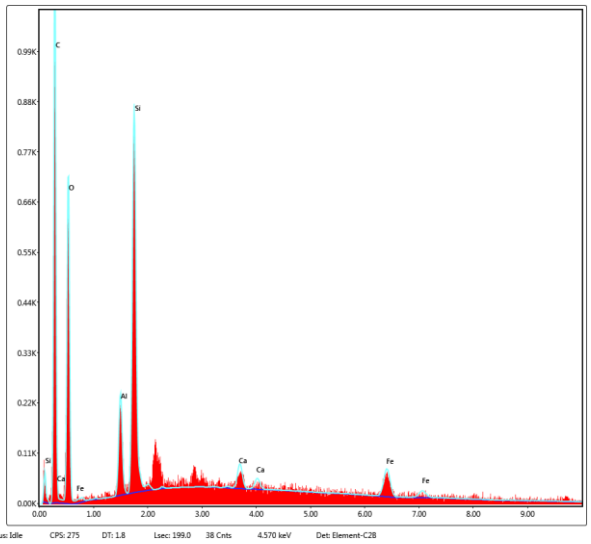


Figure 4. SEM-EDS analysis results of the Raw Cotton Fabric sample a) SEM micrographs before the treatment with the nanoclay (400X magnification) b) SEM micrographs after the treatment with the nanoclay (400X magnification) c) EDS Spectrum before the treatment with the nanoclay d) EDS Spectrum after the treatment with the nanoclay

3.4. Tensile Strength Test

According to the results obtained for the tensile strength test performed in both weft and warp directions before and after the treatment with the nanoclay particles (Table 3), it is obvious that the tensile strength values of all of the cotton the fabric samples in both weft and warp directions were not affected negatively by the treatment with the nanoclay particles however, they were even found to be higher indicating the positive effect of the nanoclay incorporation into the cotton fabric samples which is also supported by the other studies in the literature. In the previous work, polymeric nanocomposites prepared with montmorillonite and other

Table 3. Tensile strengths of the fabric samples before and after the treatment with the nanoclay

Cotton Fabric Samples	Warp				Weft			
	Before		After		Before		After	
	Tensile Strength (N)	Std. Dev.	Tensile Strength (N)	Std. Dev.	Tensile Strength (N)	Std. Dev.	Tensile Strength (N)	Std. Dev.
Raw	417.25	15.51	479.00	13.91	276.60	11.67	283.74	9.44
Optical Brightened	439.75	12.23	451.00	16.98	349.20	9.98	371.50	9.72
Conventional	271.80	15.31	277.25	16.39	238.00	10.63	246.00	15.97

nanoclays were used to coat surfaces of cotton and cotton blend fabrics and some level of improvement in tensile strength was reported to be obtained for the treated fabrics [5-7, 61]. On the other hand, organo-montmorillonite was used for washing of denim garments in a conventional washing machine for the production of old-look garments neither with previous desizing nor post-chemical softening. Washing and finishing with nanoclay was found to have no effect on the mechanical properties of the denim fabrics [10]. Moreover, discoloration of indigo dyed denim garment was done by using enzymes and montmorillonite based nanoclay in a conventional washing machine and in addition to many properties tensile strength was evaluated, as well. Treatment with nanoclay particles were found to have no negative effect on the fabric tensile strength [62].

3.5. Vertical Flame Test

Considering the results of the vertical flame test performed to determine the burning behavior and flammability properties of the three different types of cotton fabrics after the treatment with the nanoclay Nanomer I.44P nanoclay (Table 4), average ignition time values were found to be improved with the nanoclay incorporation denoting that all of the fabrics acquired flame retardancy characteristics with the change in their burning behavior. More rapid burning with a brighter and powerful flame was observed for the untreated fabric samples compared to their treated counterparts. Similar findings of improved flammability and change in the burning behavior of fabrics in accordance with the vertical flame test have been reported in the literature for the fabrics treated with different finishing and coating solutions including nanoclays [4-6].

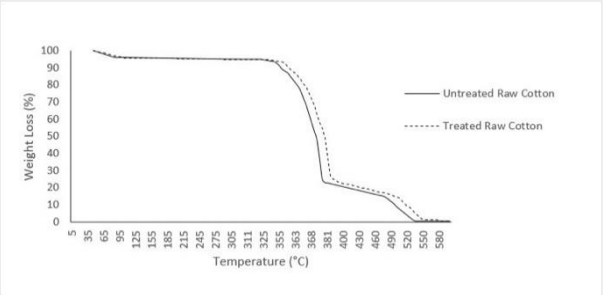
Table 4. Average ignition times of each of the fabric samples before and after the treatment with the nanoclay

Cotton Fabric Samples	Average Ignition Time (sec)	
	Before the Treatment	After the Treatment
Raw	3	4
Optical Brightened	3	5
Conventional	3	4

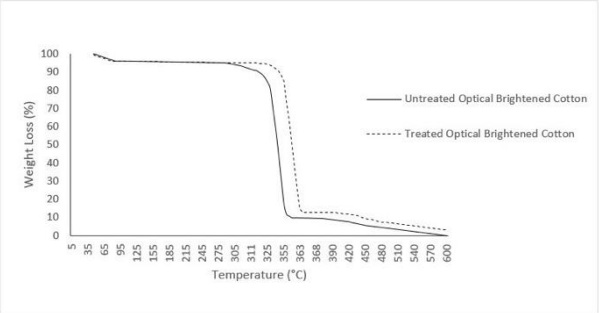
3.6. Thermogravimetric Analysis (TGA)

Untreated raw cotton fabric was found to begin to degrade over 310 °C and encounter two decomposition stages between 300 °C and 400 °C and between 400 °C and 600 °C. At 600 °C, 1wt % residue char was found to be left (Figure 5a). However, its treated counterpart was demonstrated to leave more residue at 600 °C with increased decomposition temperatures in both of the decomposition stages (Figure 5a). On the other hand, optical brightened and conventional cotton fabric samples treated with nanoclays exhibited stability against heat with lower mass loss and lower decomposition rate compared to their untreated counterparts (Figure 5b and 5c). Similar findings have been reported in the scientific literature regarding nanoclay loaded cotton fabrics via different methods [1, 2, 9, 10, 18]. According to these studies, nanoclay particles settled on the surface of the fibers alter the flammability characteristics of the nanoclay treated fabric samples with higher amount of residual ashes compared to the untreated ones. Furthermore, as it is indicated, due to the mineral structure of nanoclay including Al, Si, Fe, Ca etc., enhanced char formation occurs and a kind of heat barrier begins to develop over the surface of the fibers, which lead to increase in the decomposition temperature of the cotton fabric samples.

a)



b)



c)

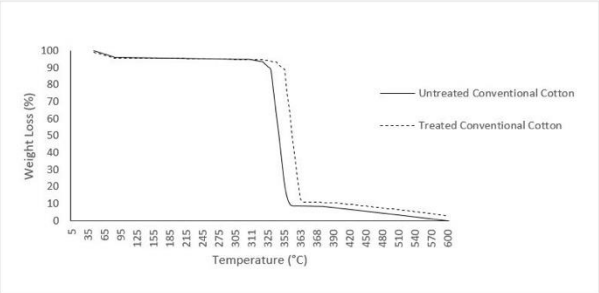


Figure 5. Weight loss as a function of temperature for cotton fabrics a) Raw b) Optical Brightened c) Conventional

3.7. Durability against Washing

In the literature, durability of the functionality of fabrics treated with finishing or coating solutions of nanoclays against washing have been considered performing the washing cycles according to different standard methods [1, 11, 36] and the fabrics washed after the treatments were found to have reasonable durability levels owing to the remaining nanoclays in the fabric structure.

3.7.1. Basis weight analysis

In order to reveal the durability of the treatment with the nanoclay Nanomer I.44P applied to the fabric samples, the fabric basis weight was analyzed for all types of cotton fabric samples after the treatment with the nanoclay and after the washing process that was performed subsequent to the treatment with the nanoclay. As a result of this analysis, although the fabric basis weight was determined to inconsiderably decrease for all of the cotton fabric samples after the washing process (Table 5), it was still considerably higher than that of the cotton fabric samples before the treatment with the nanoclay particles denoting the durability of the treatment with the nanoclay particles (Table 2).

Table 5. Basis weights of the fabric samples before and after the treatment with the nanoclay

Cotton Fabric Samples	Fabric Basis Weight (g/m^2)	
	After the Treatment	After Washing
Raw	1.4293	1.4132
Optical Brightened	1.4980	1.4570
Conventional	0.7421	0.7219

3.7.2. Fourier transform infrared spectroscopy (FTIR-ATR)

From the FTIR spectra of the nanoclay treated samples of the Raw Cotton Fabric, Optical Brightened Cotton Fabric and Conventional Cotton Fabric it can be clearly observed that similar peaks at around the same wavenumbers were obtained for the fabric samples before and for their counterparts after the washing process (Figure 6, 7 and 8) indicating the presence of the remaining nanoclay particles in the fabric structure after washing. Furthermore, since the FTIR-ATR spectra were taken from 5 different regions of the surface of the each fabric samples before and after washing and in every one of them the nanoclay Nanomer I.44P was clearly detected, it can be concluded that the nanoclay remained in all over the surface of the cotton fabric samples with a homogenous dispersion even after washing implying the durability of the treatment against washing.

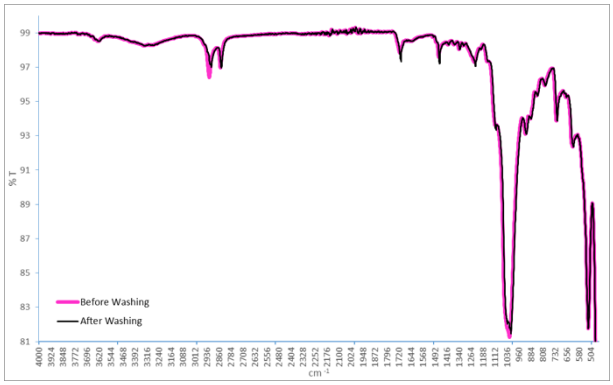


Figure 6. The FTIR spectra of the Raw Cotton Fabric sample treated with the nanoclay Nanomer I.44P before and after washing

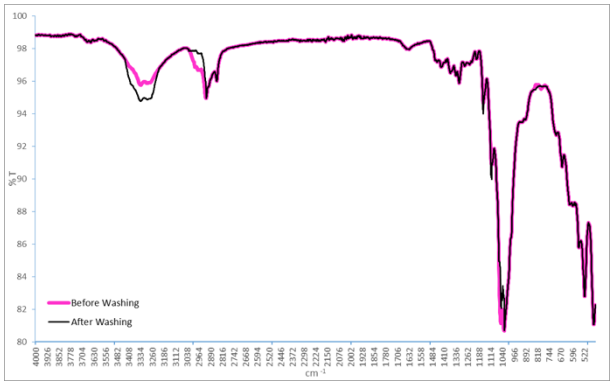


Figure 7. The FTIR spectra of the Optical Brightened Cotton Fabric sample treated with the nanoclay Nanomer I.44P before and after washing

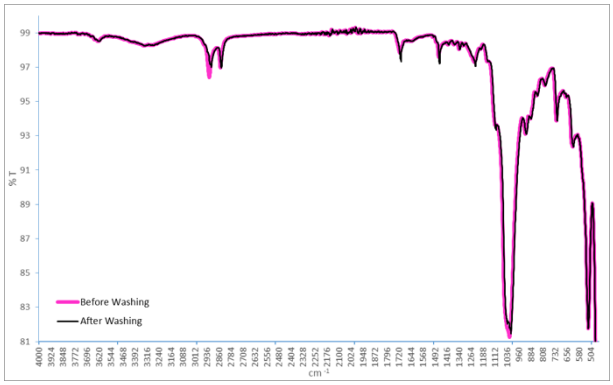


Figure 8. The FTIR spectra of the Conventional Cotton Fabric sample treated with the nanoclay Nanomer I.44P before and after washing

3.7.3. Scanning electron microscopy (SEM)

As can be seen from the SEM micrograph of the Raw Cotton Fabric sample that was washed after the treatment with the nanoclay (Figure 9), nanoclay particles were still found to be existing and distributed evenly on all over the surfaces of the fibers in the fabric structure. Moreover, from the figure, it is also apparent that nanoclay particles penetrated into the interfaces in between the fibers in the fabric structure and was not removed from the fabric structure with the effect of washing. Therefore, it can be once more deduced with this characterization technique that the treatment has durability against washing.

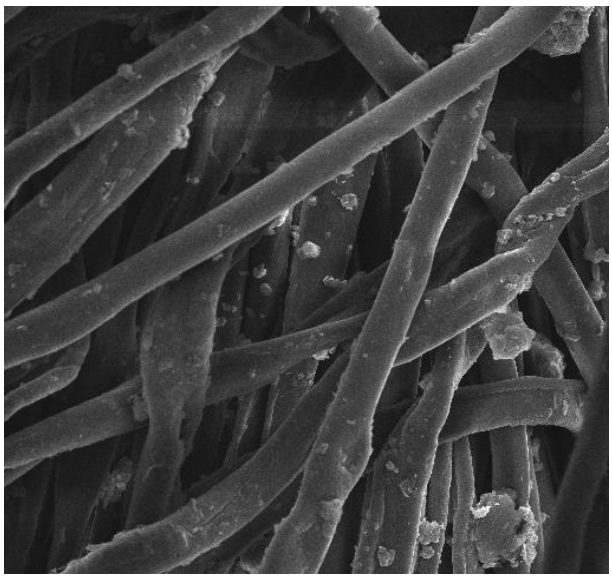


Figure 9. SEM micrographs of the Raw Cotton Fabric sample after washing (800X magnification)

3.7.4. Vertical flame test

When the results of the vertical flame test conducted for the investigation of the burning behavior and flammability properties of the cotton fabrics treated with the nanoclay particles before and after washing were considered (Table 6), no change was observed in the average ignition time values of the three different types of cotton fabrics after washing indicating that none of the fabrics lost their flame retardancy characteristics with the washing process. Hence, the treatment the fabrics were subjected to was found durable to washing.

Table 6. The average ignition times of each of the treated fabric samples before and after washing

Cotton Fabric Samples	Average Ignition Time (sec)	
	After the Treatment	After Washing
Raw	4	4
Optical Brightened	5	5
Conventional	4	4

4. CONCLUSIONS

Recently, textiles are required to be made multifunctional or have special functions to meet customer expectations. Thus, in the current study, cotton fabrics were functionalized with the incorporation of nanoclay particles via finishing techniques. The nanoclay Nanomer I.44P was preferred in this study owing to its antibacterial activity since the antibacterial characteristic of Nanomer I.44P has been reported [53]. Moreover, the fabrics treated with Nanomer I.44P can be acknowledged as environmentally friendly products since throughout the treatment no hazardous chemicals were used and the fabrics treated were made of natural and biodegradable fiber cotton. In addition to this, montmorillonite nanoclays are biodegradable and completely generated from naturally occurring resources as well as, Nanomer I.44P is known as environmentally friendly flame retardant. On the other hand, since the method used in the study is compatible with the conventional textile processes, Nanomer I.44P can be easily used in the textile industry for treating cotton fabrics via textile finishing processes improving the manufacturability of the product. After the treatment, the fabrics were assessed in terms of homogeneity of the nanoclay distribution over the fabric surface, flame retardancy, thermal stability, the change in tensile strength and durability of the functionality to washing. According to the results,

• All of the fabrics were demonstrated to have homogeneously distributed nanoclay particles over their surface by the basis weight analysis and FTIR spectroscopy.

• The fabrics were shown to possess lower flammability by the vertical flame test denoting that nanoclay incorporation had contributed to their burning behavior with flame retardancy.

• The fabric samples treated with nanoclays exhibited stability against heat with lower mass loss and lower decomposition rate compared to their untreated counterparts according to TGA implying the enhancement in their thermal stability.

• There was no decrease in the tensile strength of the fabrics implying that the treatment with the nanoclay particles did not affect the tensile strength in a negative way instead, enhanced it.

• Durability of the treatment against washing was analyzed by the basis weight analysis, FTIR spectroscopy and vertical flame test and the treatment was found durable to washing with no loss in flame retardancy.

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