TEKSTİL VE KONFEKSİYON
VOL: 30, NO. 4
DOI: 10.32710/tekstilvekonfeksiyon.675352

A Study on Coating with Nanoclay on the Production of Flame Retardant Cotton Fabrics

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ABSTRACT

In this study, 100% cotton fabrics' flame retardant properties were improved using commercial nanoclay (Cloisite 20A), clay-based montmorillonite. Flame retardancy and thermal decomposition behavior of the samples were characterized by the vertical burning test, limiting oxygen index (LOI), and thermogravimetric analysis (TGA). The surface morphology of untreated and treated fabric was examined using a scanning electron microscope (SEM). Fourier-transform infrared spectroscopy (FTIR) analysis was carried out for Cloisite 20A, untreated, and coated fabrics. The test results showed that the coating treatment, even at low nanoclay concentration, is enough to have a considerable flame retardant effect. This result was attributed to the barrier effect of the nanoclay.

ARTICLE HISTORY
Received: 15.01.2020
Accepted: 09.12.2020

KEYWORDS

Cotton, Nanoclay, Coating, Burning test, LOI, SEM, TGA, FTIR

1. INTRODUCTION

Fires are dangerous events that cause material damages and loss of life if they cannot be stopped. The increasing population in the world increases the risk of fire. Moreover, fire has become one of the most critical issues, especially in public places [Liu et al., 2011; Cordner et al., 2013; Gao et al., 2015]. The demand for the production of protective materials with high fire resistance increases because most of the products in our environment are highly flammable [Holder et al. 2017]. Due to its soft, comfortable, and breathable properties, cotton fiber is a prevalent and widely used natural fiber in the textile industry. Cotton fibers are always preferred because of their natural structure, no risk to health, and easy processibility [Du et al. 2011; Yuan et al. 2010]. Therefore, it is mostly used to produce garments, upholstery fabrics, tents, pillowcases, towels, and linens. However, cotton is a flammable fiber [Zhang et al., 2017; Başyiğit and Kut, 2018]. The cotton fibers have an LOI of 18.4% [Ghoranneviss and Shahidi 2014] so that even a tiny spark is sufficient for the fibers to burn, and the flame spreads rapidly. For this reason, numerous studies have been carried out to improve the combustion behavior of such highly preferred cotton fibers [Gao et al., 2015; Carosio et al., 2012]. The flame-retardant agents are applied to cotton fabrics by using different methods [Zhang et al. 2017; Shahidi and Ghoranneviss 2014]. Although there are many commercial flame-retardant products, the numbers of environmentally friendly ones have limited [Holder et al., 2017]. At this point, clay minerals come to popular with their environmentally friendly properties, and they are used in the production of flame-retardant textiles [Ghosh 2011; Uddin 2008]. There are many studies on flame retardant textiles [Gao et al. 2015; Başyiğit 2018; Shah et al. 2017; Guo et al. 2017; Majka et al. 2017; Makhlouf et al. 2017; Rehan et al. 2018; Chowdary and Kumar 2015] by various methods such as melt-spinning [Bhat et al. 2008], layer by layer [Holder et al. 2017; Qiu et al. 2017], sol-gel [Zhang et al. 2017] and plasma [Shahidi and Ghoranneviss 2014].

Clay minerals are generally considered nanomaterials, as they possess layers with thickness and inter-layer spaces both within the nanoscale range, so the term ‘clay minerals’ is often used interchangeably with ‘nanoclay’. There is increasing evidence to suggest that nanomaterials are different from their bulk counterparts in terms of their physicochemical and toxicological properties. The increase in clay materials, particularly in food, agriculture, animal feed, environmental remediation, and medicine, will inevitably increase the environmental and human exposure to different clay materials. Clay minerals are layered substances consisting of sheets of silicate tetrahedra (SiO_4) and octahedra (containing Al, Mg, and Fe). Natural clay minerals are built of layered structural units with a layer thickness of approximately one to a few nanometres and lateral dimensions varying from 30 nm to several microns,

To cite this article: *Kertmen N, Dalbaşı ES, Körlü A, Özgüney AT, Yapar S. 2020. A Study On Coating with Nanoclay On the Production of Flame Retardant Cotton Fabrics. Tekstil ve Konfeksiyon, 30(4), 302-311.*

which gives a ratio of length to a thickness greater than 1000 [Zhu and Njuguna 2014].

Clays and clay minerals have been evaluated for diverse potential applications, as pollutant adsorbents for sustaining the environment and their use in human and veterinary medicine. They have large adsorption capacities, excellent mechanical and chemical properties [Yapar et al., 2015]. Through the replacement of interlayer metal cations of montmorillonite with quaternary alkylammonium salts, the hydrophobicity is increased [Erkan et al. 2010], the interlayer space is expanded [Schumann et al. 2014], and thus the organo-montmorillonite obtained, allowing it to be used in a wide range of technological applications [Ruiz-Hitzky et al. 2010].

The clay minerals are composed of silicate and alumina layers containing metal oxides and cations [Zeng et al. 2005]. These layers parallel to each other and located at a distance of about 1 nm, and their structures have varying ions and OH groups and the clays in the crystalline structure generally have Van der Waals bonds between the layers [Zeng et al. 2005; Mittal et al. 2018]. Clay minerals can be found in 3 different types as 1:1 and 2:1 [Zhang et al. 2017] depending on the ratio of silica and alumina layers [Mittal et al. 2018; Azeez et al. 2013]. Montmorillonites, a clay mineral of type 2:1 is highly advantageous clays due to its wide surface area, morphological structure, abundant presence, ecological nature and low cost [Uddin 2008; Yelkovan et al. 2014].

In order to be used in some industrial applications, clays must have an organophilic structure which is dispersed in organic phases. The conversion of clays to organoclay occurs by a simple displacement reaction. After the reaction, the surface of the clay gains organophilic properties by using alkyl ammonium and alkyl phosphonium cations [Visakh 2015].

Montmorillonites are widely used in the textile industry. They have (Na, Ca) (Al, Mg)6(SiO10)3(OH)6-nH_2O formula [Ghosh 2011]. Because they have average surface energy, they can be modified more easily than other clay types [Visakh 2015; Cao et al. 2014]. Montmorillonites have recently come to the forefront with their environment-friendly flame retardant properties in the textile industry. There are many studies about using montmorillonite clays to improve textiles' thermal properties [Gao et al. 2015; Shahidi and Ghoranneviss 2014; Bourbigot et al. 2002; Li et al. 2010]. Montmorillonite clays form a protective layer during the combustion process, slow the evaporation of the flammable gas released during the combustion and block the oxygen transfer to prevent heat transfer and thus disrupt the combustion cycle [Gao et al. 2015].

Nanoclays are nanoparticles of layered mineral silicates organized into several classes such as montmorillonite (MMT), bentonite, kaolinite, hectorite, and halloysite on chemical composition and morphology. The most commonly used layered silicate in polymer nanocomposites is MMT, which has encouraged much improvement in the mechanical, thermal, flammability, and barrier properties of polymers due to its high aspect ratio and large surface area, extraordinary modulus, and nanoscale dispersion [Norouzi et al. 2015]. The layered silicates enhance the flame retardancy properties of polypropylene textile articles. The use of nanoclay and polyhedral oligomeric silsesquioxanes in polyurethane coating applied to polyester and cotton reduces peak heat release [Rault et al. 2015]. The additives such as a nano additive made of synthetic clay montmorillonite and two polyhedral oligomeric silsequioxanes are incorporated into the polyurethane resin [Devaux et al. 2015].

In this study, flame retardant properties of 100% cotton woven fabrics were tried to be improved by using commercial nanoclay (Cloisite 20A) which is a montmorillonite based organoclay. Cloisite was also used in the other studies targeting the flame retardancy. For instance, it has been applied to polyethylene terephthalate (PET) polymer [Fabia et al. 2020], polyethylene terephthalate fiber and nanocomposites in studies conducted to date. Yelkovan and et al. (2014) applied Cloisite to PET polymer. In that study, Cloisite and PET polymer were combined with melt blending method in terms of twin screw extruder [Yelkovan et al. 2014]. Devaux and et al. (2002) applied Cloisite to polyurethane resins (PU) nanocomposites [Devaux et al. 2015]. Unlike the studies reported in the literature, in this study, cloisite was applied directly to the cotton fabric. In particular, it is intended to provide a flame retardant effect in technical textile fabrics that are not washed. Flame retardancy and thermal decomposition behavior of the samples were characterized by the vertical burning test, limiting oxygen index (LOI), and thermogravimetric analysis (TGA). The surface morphology of untreated and treated fabrics was examined using a scanning electron microscope (SEM). Fourier-transform infrared spectroscopy (FTIR) analysis was carried out for Cloisite 20A, untreated and coated fabrics. The obtained results were evaluated and discussed.

2. MATERIAL AND METHOD

2.1 Material

The physical properties of 100% cotton woven fabrics (desized, scoured and bleached) used for experiments are given in Table 1.

Table 1. The physical properties of fabrics used in coating experiments

Specifications		
Fiber type		100% Cotton
Fabric construction		Plain
Fabric weight (g/m^2)		154.7
Yarn density	Warp density	42
(threads/cm)	Weft density	28

In this study, nanoclay called Cloisite 20A (Figure 1) was used as a flame retardant material supplied by Feza Kimya Company. It is montmorillonite modified with a quaternary ammonium salt. The thickener (Alginate SMT T, high viscosity sodium alginate) and wetting agent (Biomegapal D40) were supplied from CHT Company and Bozzetto Company respectively.

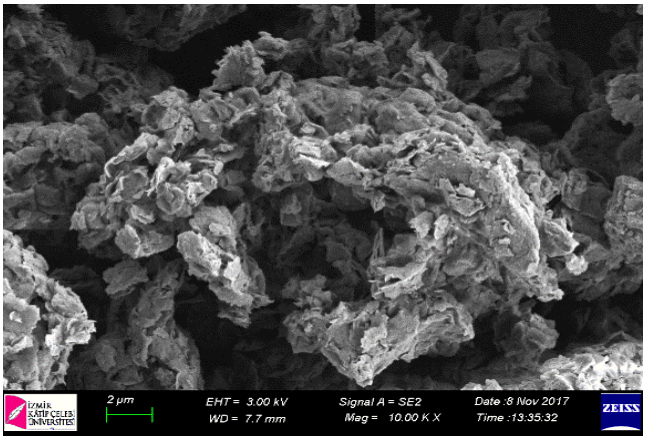


Figure 1. SEM image of the Cloisite 20A nanoclay (magnified 10000 times)

2.2 Method

The fabrics were coated by paste containing Cloisite 20A (Table 2), alginate and wetting agent (at 2 g/kg concentration). Alginate SMT T was used to prepare thickener paste by using at a 4% (w/v) concentration and the paste was mixed for 5 minutes after the adding Cloisite 20A and wetting agent. The coating treatment was carried out by a laboratory type coating machine (Mathis AG). After coating, the fabric samples were dried at 100°C for 6 minutes in a laboratory-type stenter (Ataç 40 GK). In the coating method, only one surface of fabric was coated and the used knife was over an endless rubber band. The thickness coating (the gap between fabric and knife), was 2 mm.

Table 2. Applied recipes in coating treatments

Code	Chemical concentration(g/kg)
	Cloisite 20A
UT*	-
A	2.5
B	5
C	10
D	15

*Untreated fabric

2.3. Characterization and the flame retardant effect determination

Cloisite 20A and the untreated and coated cotton fabric samples were subjected to Scanning Electron Microscopy (SEM), thermogravimetric (TGA) and FTIR analyses for characterization. Vertical burning and Limiting Oxygen Index (LOI) tests were conducted to determine of the flame-retardant effect coating.

The surface morphology of nanoclay and uncoated and coated cotton fabrics was observed by a scanning electron microscope (SEM, Carl Zeiss 300VP**)** with an accelerating voltage of 15 kV. The samples were pre-coated with gold, using a sputter coater (Quorum Q150 RES).

Thermogravimetric analyses were conducted to determine the thermal properties of the nanoclay and uncoated and coated cotton fabrics. The samples were tested by using a TA TGA-STD Q600 thermal gravimetric analyzer operating under nitrogen atmosphere. The samples of 5-6 mg was heated from room temperature to 600°C at a heating rate of 10 °C/min under nitrogen atmosphere at a flow rate of 60 ml/min.

FTIR measurements of the nanoclay, uncoated and coated cotton fabrics of were carried out by a Thermo Scientific Nicolet IS50 infrared spectrometer using KBr pellet technique in the range of 4000-450 cm^{-1} with a resolution of 4 cm^{-1}.

The burning tests of the coated fabrics were performed by SDL Atlas-M233B vertical burning test device according to BS 5438:1989 standard. After the test, the fabrics' char width and length were measured [BS 5438 standard, 1989].

LOI values of the coated cotton fabrics were measured according to method using a limiting oxygen index chamber [ASTM D 2863 standard, 1997].

3. RESULTS AND DISCUSSION

3.1 SEM analysis

Figure 2 and Figure 3 SEM photographs of the untreated and coated cotton fabrics; Sample A and Sample D were given for 100x and 1000x magnifications.

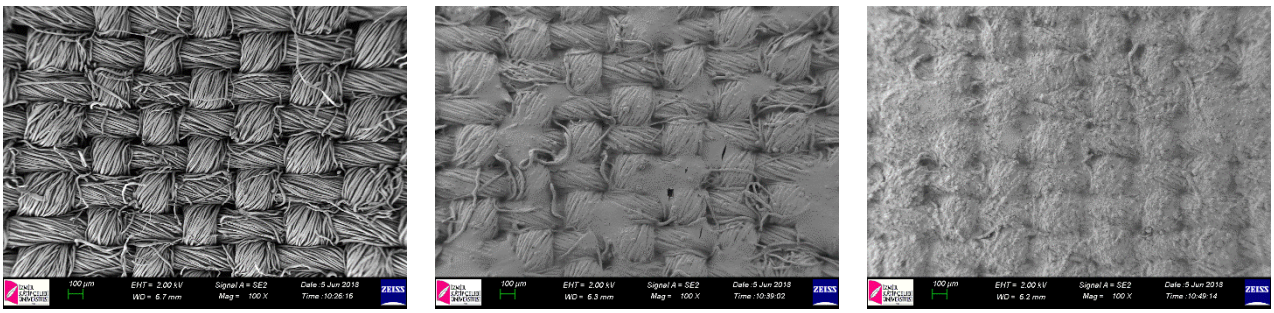
A close examination of the Figure 2 revealed that the yarns at the surface of Sample A were partially covered whereas the surface of the other sample coated using a higher amount of Cloisite 20A is relatively homogenous. In the case of higher magnification, the coverage of the yarns with a film made of alginate and Cloisite 20A was distinguished. While the yarns under the film layer were observed in Sample A, Sample D's surface was covered with a continuous and relatively homogeneous coating without leaving any trace of the fabric's yarns nanoclay particles were also more visible.

3.2 Thermogravimetric analysis

Figure 4 illustrated TGA and DTA graphs of Cloisite 20A. Table 3 showed the thermal decomposition temperatures and residues of Cloisite 20A.

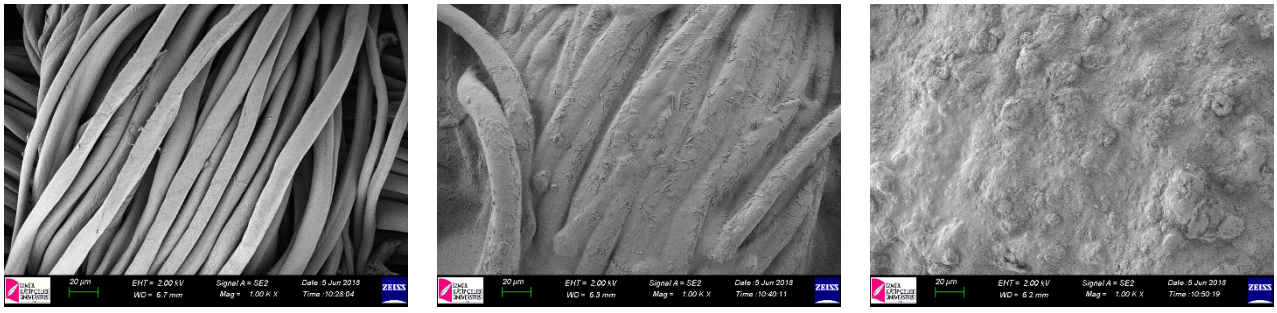
As shown in Figure 4, Cloisite 20A has a broad peak in a temperature range changing from 199.39°C to 482.60°C and maxima at 309.12°C. The corresponding weight losses were 1.84%, 32.15% and 13.34%, respectively. The end of the test, the total weight loss of nanoclay was 39.85%.

Figure 5 illustrated TGA graphs of untreated and coated fabrics (sample A and sample D).



UT A D

Figure 2. SEM photographs of the untreated and coated cotton fabrics (100x magnifications)



UT A D

Figure 3. SEM photographs of the untreated and treated cotton fabrics with Cloisite 20A (1000x magnifications)

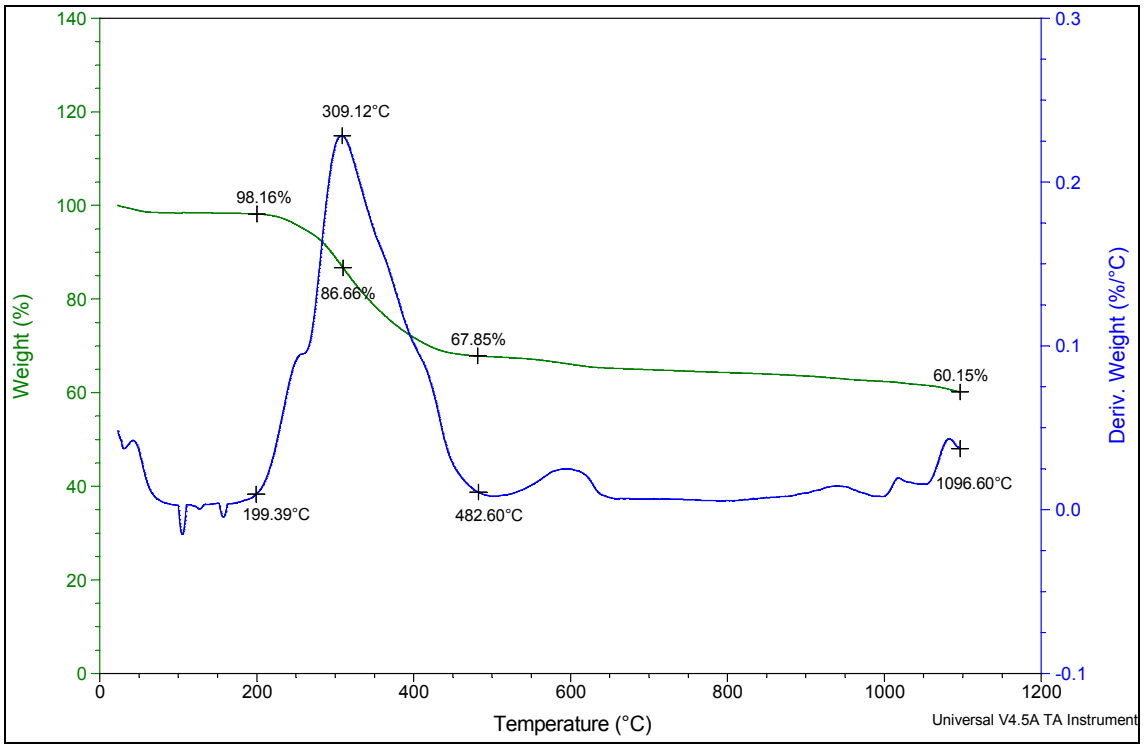


Figure 4. TGA and DTA graphs of Cloisite 20A

Table 3. Thermal decomposition temperatures and residues of Cloisite 20A

Material	Initial decomposing temperature (°C)	Decomposition end temperature (°C)	The residue (%)				Maximum peak point (°C)
			199.39°C	309.12°C	482.60°C	1096.6°C	
Cloisite 20A	199.39	482.60	98.16	86.66	67.85	60.15	309.12

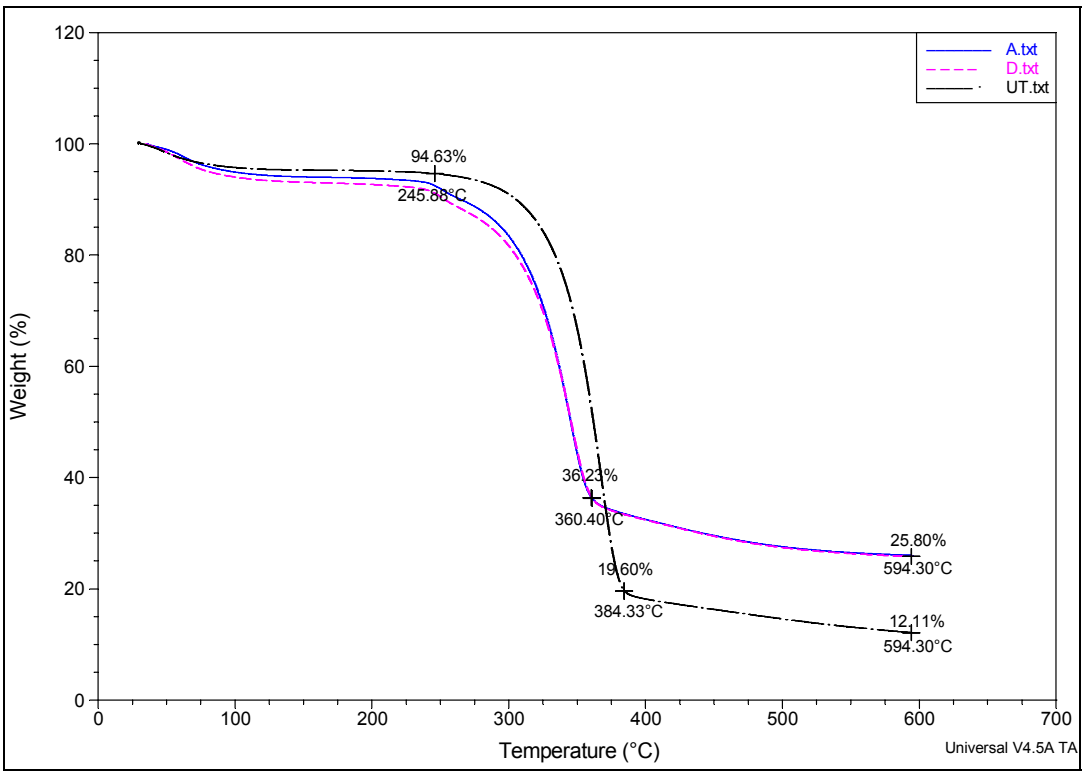


Figure 5. TGA graphs of untreated and coated fabrics (sample A and D)

The weight losses of untreated and coated fabrics were observed in a temperature range between 200°C and 600°C. As shown in Figure 5, two regions were observed in the temperature range studied. The first region covers 200°C-400°C temperature range. A considerable weight loss was observed in this range, and the weight loss in the second region is gradual. This range involves pyrolysis temperature of cotton fabric (250-270°C), the critical temperature (350°C) at which a spark causes a sudden burning due to the high ratio of flammable gases and then the spontaneous ignition temperature (400°C) when energized [Zhu et al. 2004; Zhu and Li 2011].

Table 4 showed the thermal decomposition temperatures and residues of untreated and coated fabrics.

The total weight losses were 87.89%, 74.20% and 74.20% for untreated fabric, Sample A and Sample D, respectively. The weight losses of coated samples were the same, when they were compared. Therefore, it was concluded that low clay concentration (sample A, 2.5 g/kg concentration) was even enough. It was found that as the temperature increased, the weight losses also increased rapidly. Consequently, the coated cotton fabrics' degradation reaction rates with nanoclay were slower than those of untreated fabric. Due to the clay mineral barrier effect, the enhancement of coated cotton fabrics' thermal stability was provided.

3.3 FTIR analysis

FTIR spectrum of Cloisite 20A is given in Figure 6. In the spectrum, the bands observed at 2923 cm^{-1}, 2851 cm^{-1} and 1471 cm^{-1} were assigned to antisymmetric and symmetric CH_2 stretchings and methylene scissoring vibration [Yapar 2009]. The other bands observed at 1653 cm^{-1}, 1117 cm^{-1} and 1013 cm^{-1} are typical for clay minerals and they represent OH deformation of water and Si-O stretchings, respectively [Madejová and Komadel 2001].

Table 4. Thermal decomposition temperatures and residues of untreated and coated fabrics

Material	Decomposition Temperature range		The residue (%)			Weight loss (%)
	Beginning (°C)	End(°C)				
UT	245.88	384.33	245.88°C 94.63	384.33°C 19.60	594.30°C 12.11	87.89
Sample A	245.88	360.40	245.88°C 94.63	360.40°C 36.23	594.30°C 25.80	74.20
Sample D	245.88	360.40	245.88°C 94.63	360.40°C 36.23	594.30°C 25.80	74.20

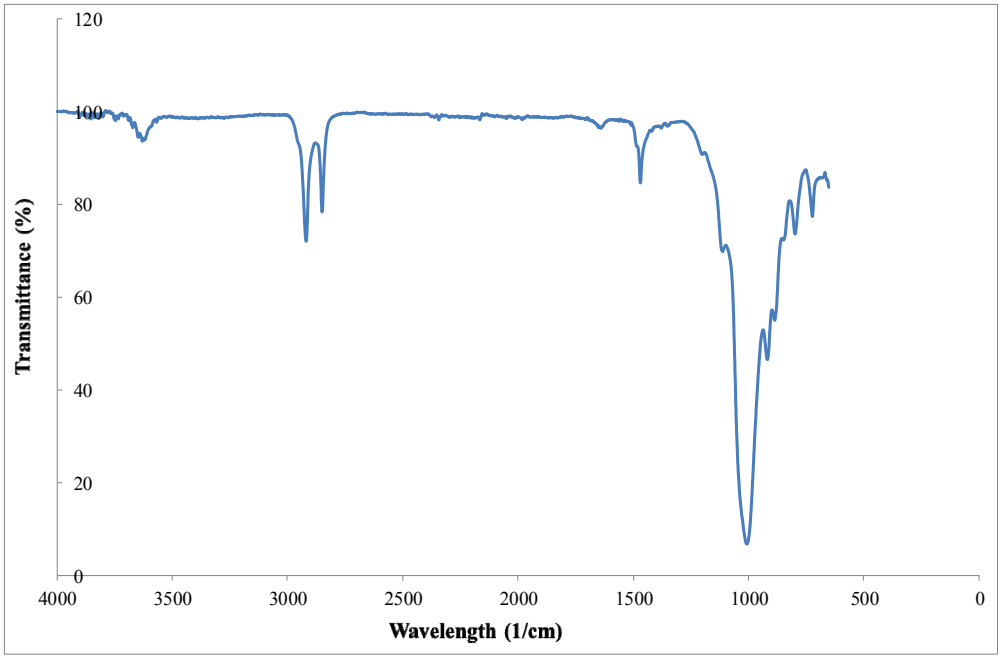


Figure 6. FTIR spectrum of Cloisite 20A

FTIR spectra of untreated and coated fabrics (sample A and sample D) are given in Figure 7 and the peak wavenumbers and bonds are given in Table 5. Due to the existence of the common structural groups such as -CH_2, the spectra has similar features; however, the typical bands given in Table 5 are distinguished. A close examination of the figure and the table reveals that the peak observed at 1653 cm^{-1} in Cloisite is shifted to a lower wavelength and the peaks at 1423 cm^{-1} and 1416 cm^{-1} observed in untreated fabric and in alginate spectra are disappeared and a new peak appears at 1402 cm^{-1}as a result of the interaction among the functional groups. The peaks at 1423 cm^{-1} and 1416 cm^{-1} were showed in Figure 7.

Table 5 showed FTIR analysis results of untreated, coated fabrics, Cloisite 20A and alginate.

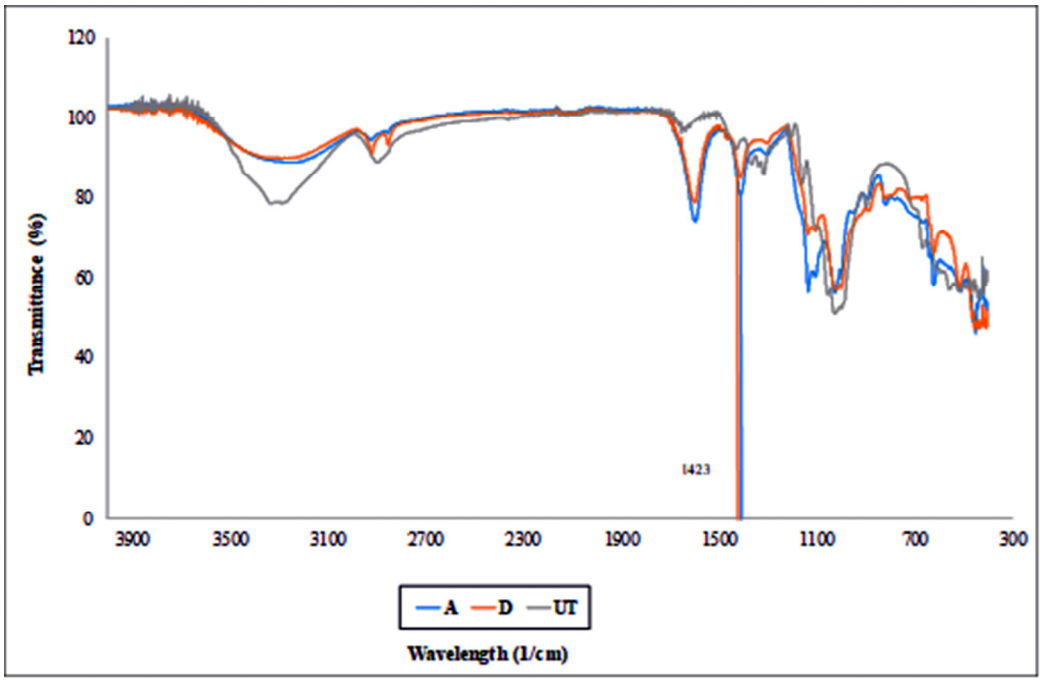


Figure 7. FTIR graphs of untreated and coated fabrics (sample A and sample D)

Table 5. FTIR results of Cloisite 20A, alginate, untreated and coated fabrics [Yapar 2009; Madejová and Komadel 2001; Sartori 1997]

Sample	Peak wavenumber (cm^{-1})	Bonds
UT	3326-3256	OH stretching
	2896	C-H symmetrical stretching
	1647	OH deformation
	1423	HCH and OCH in-plane bending vibration
	1314	CH_2 rocking vibration at C6
	1158	C-O-C symmetrical stretching
	1018	C-C, C-OH, C-H ring and side group vibrations
Sample A	2981-3503	OH stretching
	2934	antisymmetric CH_2 stretching
	2836	symmetric CH_2 stretching
	1595	OH deformation
	1402	HCH and OCH in-plane bending vibration and/or methylene scissoring vibration and/or symmetric stretching vibration
	1129	C-C and C-O stretching
	1098	Si-O stretching
	1037	Si-O stretching
Sample D	2981-3503	OH stretching
	2917	antisymmetric CH_2 stretching
	2838	symmetric CH_2 stretching
	1589	OH deformation
	1402	HCH and OCH in-plane bending vibration and/or methylene scissoring vibration and/or symmetric stretching vibration
	1126	C-C and C-O stretching
	1098	Si-O stretching
	1037	Si-O stretching
Cloisite 20A	3651	C-H symmetrical stretching
	2923	antisymmetric CH_2 stretching
	2851	symmetric CH_2 stretching
	1653	OH deformation of water
	1471	methylene scissoring vibration
	1117	Si-O stretching
	1013	Si-O stretching
	922	AlAlOH deformation
	893	AlFeOH deformation
Alginate	1610	O-C=O asymmetric stretching
	1416	O-C=O asymmetric stretching
	1125	C-C and C-O stretching

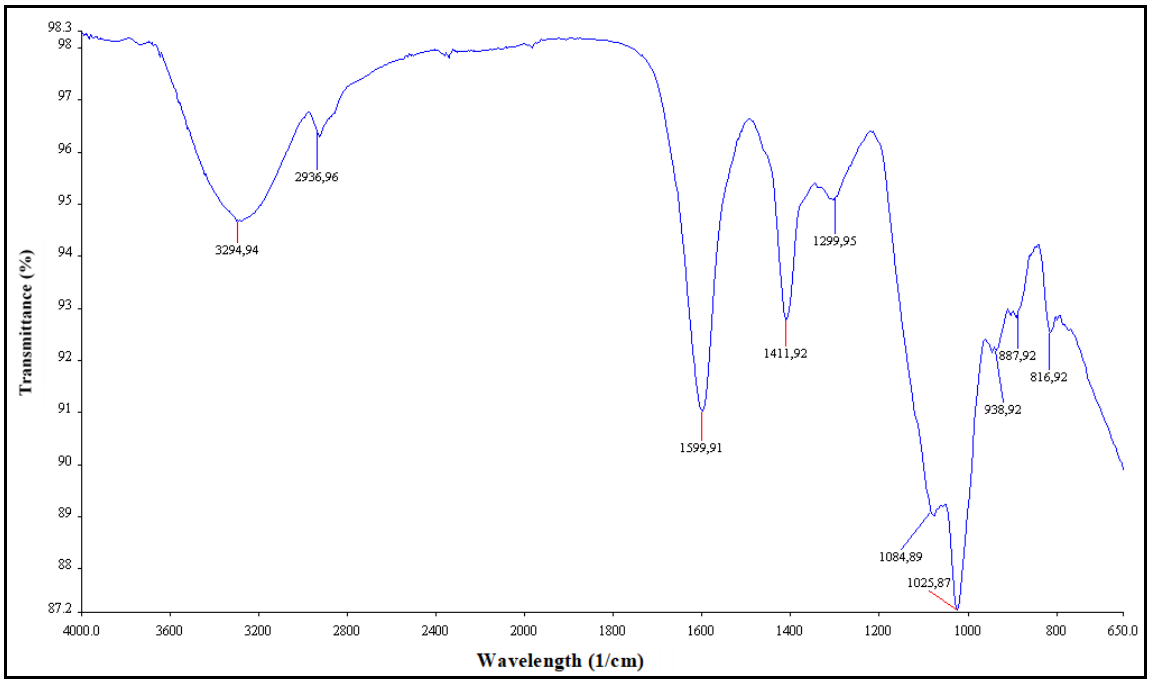


Figure 8. FTIR spectrum of alginate

FTIR spectrum of coated fabric with alginate is given in Figure 8. The bands observed at 1599 cm^{-1} and 1411 cm^{-1} were assigned to O-C=O antisymmetric stretchings in the spectrum. These bands are typical for Alginate.

3.4 Vertical burning test

The vertical burning tests showing the cotton samples' upward burning behavior were given in Figure 9 and Table 6.

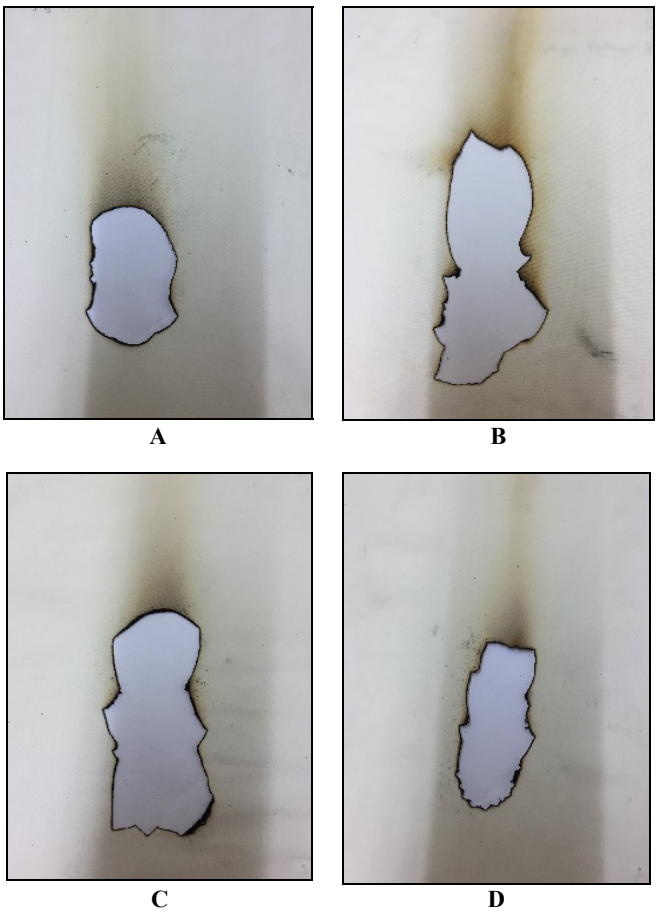


Figure 9. The images of coated cotton samples after vertical burning tests

Table 6. Flame retardant performance of the cotton samples

Code	Char Width (cm)	Char Length (cm)
UT	-	-
A	4.4	6.1
B	4.5	12
C	5.3	10.3
D	3.6	7.4

During the tests, the untreated fabric burned up, while the coated samples were burned locally, at which the flame contacted. As shown in Table 6, the differences between the samples' char lengths were more obvious than those of char widths. Compared to sample B and C, sample A and D had shorter char widths and shorter char lengths. As a result, all nanoclay concentration provided satisfactory flame retardant effect. In other words, ignition and burning did not continue after the flame contact. There is no linear relation between the increase in concentration and the flame retardant effect.

3.5 LOI test

According to the results of burning tests, the samples' flame-retardant performances exhibited no considerable differences; therefore, only two samples coated by using 2.5 g/kg and 15 g/kg nanoclay concentration were subjected to LOI tests. Table 7 showed LOI values of untreated and coated cotton fabrics.

Table 7. LOI values of untreated and coated cotton fabrics

Code	LOI value (%)
UT	18.2
A	25.1
D	24.4

It can be seen that LOI values of the coated samples were much higher than that of untreated sample. LOI values of sample A and untreated fabrics were 25.1% and 18.2%, respectively. With the increase of Cloisite 20A in the coating paste, the LOI value was not changed so much. Consequently, the coating treatment, even at low nanoclay concentration imparted a satisfactory flame-retardant effect to the cotton fabrics.

4. CONCLUSION

In this study, the flame-retardant properties of 100% cotton fabrics were improved using commercial nanoclay (Cloisite 20A) coatings. The coated samples were subjected to the burning test, SEM, FTIR, TGA analyses, and LOI tests. SEM analysis showed that the cotton yarns were partially or completely covered depending on the amount of nanoclay used. FTIR analyses indicated that the peaks observed on Cloisite and alginate spectra were shifted, and also a new peak has appeared on spectra as a result of the interaction among the functional groups. The test results showed that the coating treatment, even at low nanoclay concentration, is enough to have a considerable flame-retardant effect. This result was attributed to the barrier effect of the nanoclay.

Clays and clay minerals have been evaluated for diverse potential applications, as pollutant adsorbents for sustaining the environment and their use in human and veterinary medicine. They have large adsorption capacities, excellent mechanical and chemical properties. These clay minerals are essential for improving textile materials. In this study, the flame-retardant properties of cotton fabrics were improved using commercial nanoclay. Cloisite has been applied to polyethylene terephthalate polyethylene terephthalate fiber, and nanocomposites in studies conducted to date [Fabia et al. 2020; Devaux et al. 2015; Yelkovan et al. 2014]. In this study, Cloisite was applied directly to the cotton fabric with the coating method,

speedy. After applications, the tests showed that the coating treatment with nanoclay on cotton fabrics had a considerable and satisfactory flame retardant effect. In other words, ignition and burning did not continue after the flame contact.

Acknowledgement

This work was supported by Ege University Scientific Research Projects Coordinator in Turkey with the project number 16 MÜH-077. The authors wish to thank by Ege University Scientific Research Projects Coordinator.

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