Çukurova Üniversitesi Mühendislik Fakültesi Dergisi, 37(2), ss. 351-366, Haziran 2022
Cukurova University Journal of the Faculty of Engineering, 37(2), pp. 351-366, June 2022

Investigation of Flame Retardancy Effect of Licorice Root Extract on Cotton and Cotton-Polyester Blended Fabrics

Aslıhan KORUYUCU[*1] ORCID *0000-0002-8443-5188*
Fehmi Çağlar BALABAN[2] ORCID *0000-0002-5968-4764*

[1]*Namık Kemal University, Çorlu Faculty of Engineering, Department of Textile Engineering, Tekirdağ*
[2]*Zorluteks Tekstil, Kırklareli*

Geliş tarihi: 06.01.2022 Kabul tarihi: 30.06.2022

Atıf şekli/ How to cite: KORUYUCU, A., BALABAN, F.Ç., (2022). Investigation of Flame Retardancy Effect of Licorice Root Extract on Cotton and Cotton-Polyester Blended Fabrics. Çukurova Üniversitesi, Mühendislik Fakültesi Dergisi, 37(2), 351-366.

Abstract

In this study; licorice root, which is a sustainable natural material with a low environmental waste load, is used as an alternative fire retardant (FR) material. Flammable retardancy properties of 100% cotton and 50% cotton-50% polyester blended woven fabrics were researched by using licorice root and commercial organic phosphorus-nitrogen and phosphorus including compounds. Flame retardancy and thermal decay behaviour of the cotton and cotton/polyester blended fabric samples were qualified by the vertical burning test, limiting oxygen index (LOI), thermogravimetric analysis (TGA) and scanning electron microscope (SEM). The findings revealed that licorice root extracts enhanced the thermal behavior of the cotton and cotton/polyester blended fabrics after padding and coating processes. The practices increased the amount of oxygen demand for combustion in the environment and besides they did not change the morphological properties of the fabric samples. As a result, the usage of licorice root extracts considerably improved the fabric's flammability under test.

Keywords: Licorice root, Burning test, LOI, SEM, TGA

Meyan Kökü Ekstraktının Pamuk ve Pamuk-Poliester Karışımlı Kumaşlarda Güç Tutuşurluğa Etkisinin İncelenmesi

Öz

Bu çalışmada; çevre atık yükü düşük ve sürdürülebilir doğal malzeme olan meyan kökü alternatif FR materyali olarak kullanılmıştır. %100 pamuklu ve %50 CO/%50 PES karışım dokuma kumaşların alev geciktirici özellikleri meyan kökü ve ticari organik fosfor-nitrojen ve fosfor içeren bileşikler kullanılarak iyileştirilmiştir. Pamuk ve pamuk/poliester karışım kumaş numunelerinin termal bozunma davranışı dikey yanma testi, limit oksijen indeksi (LOI) ve termogravimetrik analizi (TGA) ile karakterize edilmiştir. Ham ve uygulanmış kumaşın yüzey morfolojisi taramalı elektron mikroskobu (SEM) kullanılarak

[*]Corresponding author (Sorumlu yazar): Aslıhan KORUYUCU, *adelituna@nku.edu.tr*

incelenmiştir. Sonuç olarak; meyan kökünden elde edilen ekstraktlarla yapılan emdirme ve kaplama işlemlerinin pamuk ve pamuk/poliester karışımlı kumaşların termal dayanım özelliklerinde iyileşme sağlamıştır. Kumaşların alev alması için ortamda bulunması gereken oksijen miktarında olumlu yönde artış sağladığı, kumaş morfolojisinde olumsuz herhangi bir etkiye sebep olmadığı tespit edilmiştir. Sonuç olarak, meyan kökü ekstraktlarının kullanılması kumaşın alev alabilirliğinin önemli ölçüde artmasına neden olmuştur.

Anahtar Kelimeler: Meyan kökü, Yanma testi, LOI, SEM, TGA

1. INTRODUCTION

Textile is widely applied to clothing, knitwear and home textiles because of outstanding softness and breathability. However, due to its greatly flammability, it was essential and crucial to impart the flame retardancy to fabrics [1].

There are many factors that influence the flammability of textiles. These factors include composition of the fibers, the presence of certain finishes, the geometry or position of the material; the temperature and the existence of oxygen, the extent of heat and material modification and the existence or absence of flame retardants. Various fibres react differently to a flame exposure [2].

To guarantee human safety, textiles can be treated with different flame (fire) retardants (FR). These are chemicals that reduce the flammability of the material to which they are applied [3]. Fire-retardant materials do not burn; however, these materials show certain physical and chemical modifications after the removal of a flame source [3].

Flame retardants including phosphorus (P), nitrogen (N) and silicone (Si) elements appeal to lots of attention, because of their perfect flame resistance and insignificant influence on the natural properties of materials [5-7]. Licorice includes mineral salts (such as calcium, phosphorus, sodium, potassium, iron, magnesium, selenium, manganese, zinc, copper and silicone) [4]. By adding the suitable fire-retardant elements, phosphorus and silicone, the resulting coating can supply the emphasising material with good flame properties. Phosphorus and silicone elements have been brought out because of their perfect carbonization and flame retardancy [8]. Phosphorus-including compounds are emphasized to be among the most influence exerting flame retardants, as illustrated in many current studies [9-11]. This kind of FRs is qualified by their great influence grade of flame retardancy. They can alter the chemical reactions of decay; they produce a surface layer of protective char during fire before the unburned structure materials begin to decompose [12-14]. Silicone-including compounds are emphasized to be one of the “environmentally friendly” flame retardant materials. In spite of the fact that some certain studies have proved, they themselves do not have enough flame retardant properties to fulfill practice necessities, when they are used in addition to phosphorus-including flame retardant, there is certain synergistic influence between them [15,16].

Flame retardancy (FR) specification is desirable in various conventional textile applications such as home textiles, apparel as well as technical textile practices in order to protect consumers from unsafe textile materials. Flame-retardant coatings can be applied in many fields, such as building construction, electrical practices, textiles, electronics and transportation [17,18]. Being the most used fibers in these practices, cotton (CO) and polyester (PET or PES) are greatly flammable and they burn easily. The physical and chemical properties of cotton and polyester contrast greatly; cotton is hydrophilic, while polyester is hydrophobic. Reagents repelled by polyester are absorbed by cotton [1,19] .

Cotton is one of the perfect natural materials that has been widely used in many fields, particularly in textile industry such as carpets, curtains, and clothing [20,21]. Cotton fabrics have good hydrophilicity, softness, and hygroscopicity. Since it is greatly flammable, the flame-retardant cotton textiles have accepted significant attention from both industry and academia [22-25].

Conventional flame-retardant cotton textiles are mostly produced by the flame-retardant agents including halogens and phosphorus. However, the burning of the halogen flame-retardant generates a large amount of toxic gas, which leads to secondary pollution. Phosphorus flame-retardant has a inadequate surface treatment on the textile substrates due to the deficiency of suitable anchor groups for the fixation on the fiber surface [26].

Phosphorus and/or halogen compounds are among the fire retardants that confer good protection to polyester. Phosphorus compounds are produced for use with both cotton and polyester fibres [27]. These compounds act mainly in the solid phase and during heating. They generate phosphoric acid, which in turn reacts with the substrate to become a char producing a carbon layer [28,29]. By producing a carbon layer, these compounds prevent supply of oxygen and flammable gases which makes enhancement of flames difficult [30].

2. REVIEW OF LITERATURE

The naturally flammable materials with padding method to polyester fabric a flame retardant feature were reviewed by Ömeroğulları et. al. [30]. It was emphasized that a flammable substance is a naturally flammable substance depending on $CaCO_3$ made from limestone. There was a 39.5% increase in LOI (Limiting Oxygene Index) values and it was noticed that polyester fabric burned without dripping and melting during the burning test. Comparison was made with phosphonate based flame retardant material, which is frequently used for the production of flame retardant polyester fabric and it was detected to burn five times longer than the fabric treated with this substance [30].

The chitosan phosphate as a new way to generate environmentally friendly flammable cotton textiles were analyzed by El-Tahlawy et. al.[31]. It was underlined that chitosan amino groups became more reactive than cellulose hydroxyls, citrate salt facilitated the phosphorylation reaction. It was noticed that chitosan concentration from 0% to 2% increased cotton fabric’s flame retardancy. Increasing the amount of chitosan limited influence on thermal decay of the fabric has been achieved by increasing the chitosan concentration mostly 2% [31].

The herbal extracts were tried as a new way to generate environmentally friendly flammable cotton fabric; with the use of spinach leaf juice, which is an environmentally friendly natural product. Cellulosic fabrics that have a flame retardant feature were examined by Basak et. al. [32]. Spinach juice (SJ) was made alkaline and bleached, and then practiced to mercerized cotton fabric. LOI values of untreated control fabric and treated fabric were measured. The study proved that the treated fabrics had better flame retardancy properties than the control fabric. It was noticed that the LOI value increased 1.6 times after the SJ practice. It was also noticed that there was not much loss in LOI values after washing fastness [32].

The fulfillment of aqueous casein suspensions on flame retardancy by coating rotational pressures at different pH and concentrations on cotton fabrics were examined by Faheem et. al. [33]. As a result, in both alkaline and acidic environments, flame resistance increased with increasing casein concentrations. In terms of thermooxidative properties, the suspension, which is in an acidic environment, was notified to be in a better condition than the suspension in an alkaline environment. Better fulfillment was acquired from the suspension in acidic environment with the help of ammonia release easier than protonated casein.

Thermally stable and hygienic cotton fabric with the material acquired through the extraction of coconut shell were analyzed by Teli and Pandit [34]. In this study, cocos nucifera linn was practiced to cotton fabrics by padding in acidic, neutral and alkaline environments. Flammability properties were analyzed by LOI measurement and vertical combustion tests. All treated fabrics proved better flame resistance compared to untreated fabrics, and it was noticed that the practice in alkaline environment increased the LOI value by 72.2% or more.

The zinc borate (ZnB) was effectively used as a flame retardant for polyester and the results were analyzed by Üreyen et. al. [35]. In this study, zinc borate was used as a flame retardant, a smoke suppressant and an antitracking agent in several practices. In this work, the influence of ZnB on the flame retardancy of PET (poly (ethylene terephthalate) woven fabrics was analyzed. ZnB dispersion was mixed with low-produce aldehyde melamine resin based cross-linking agent and it was practiced to PET fabrics by pad-dry-cure method.

The purpose of current study is the production of licorice root extract macromolecules to be used as flame retardancy products that are harmless to the environment and also ecological. Therefore, in this study, naturally flammable macromolecules were practiced to 100% cotton and 50% cotton-50% polyester fabrics by using padding and coating methods.

Unlike the studies reported in the literature, licorice root was practiced to the cotton and cotton/polyester fabrics by using padding and coating methods. The thermal stability of samples was analyzed by TGA analysis with a heating rate of 20℃/min and the temperature range was differentiated from 32℃ to 900℃ under the atmosphere of air. SEM was employed to study the surface morphology of the padding and coating samples. Being a measure that enables an obvious assessment of flame protection properties is the limiting oxygen index (LOI) was calculated. The results were presented, evaluated and discussed.

3. MATERIALS AND METHODS

In this study, licorice roots to be extracted were supplied by considering the same batch and lot number. In the extraction process, 99% purity isopropyl alcohol was used as the solvent.

100% cotton and 50%-50% cotton/polyester fabrics were used in this study. The cotton and cotton/polyester fabrics had a plain weave, unit weight of 110.3 g/m², and had both weft and warp threads of 30/1 Ne. The structures and finishing process of the fabrics that will be subjected to padding and coating using extraction process. The flame retardant agents; Ruco-Flam NMT (organic phosphorus-nitrogen compounds), EOC FRD 41 BO (phosphorus compounds) are commercial flame retardant chemicals, and they were supplied by Rudolf-Duraner and EOC Group Company for the coating processes.

3.1. Method

Licorice roots with the same batch and lot number were supplied for extraction studies. Foreign products and chemical drugs on licorice roots were removed by pre-washing with distilled water. After pre-washing, the licorice root (10 g) was mixed with 300 mL distilled water. Licorice roots were kept in the oven at 75℃ for 24 hours after pre-washing and later dried. The materials were mechanically divided into small pieces by hand mixer after drying. Figure 1 shows the mechanical disintegration of licorice.

Figure 1. Mechanical disintegration of licorice

Three different analytical extraction methods can be used for licorice root extraction which were acid precipitation, alcohol and ammonia extraction [10]. In this study, isopropyl alcohol extraction method was used. Mechanically disintegrated materials were added separately into isopropyl alcohol with a purity of 99% according to the recipe given in Table 1. Isopropyl alcohol-licorice root solutions were mixed with a mechanical stirrrer at 900 rpm for 48 hours without contact with air.

Table 1. Extraction solution recipe

Used materials	Amount	Isopropyl alcohol (solvent) amount
Licorice root	5kg	20 liter

After mixing, the solutions were filtered once with Macherey-Nagel MN-GF-3 filter papers. The filtration process of isopropyl alcohol-licorice root solutions with filter paper was presented in Figure 2.

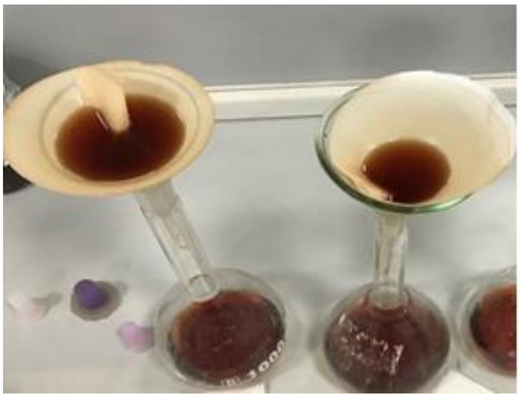

Figure 2. Filtration of isopropyl alcohol-licorice root solutions with filter paper

After filtration, the solutions were heated up to 85℃ to complete the extraction and to remove isopropyl alcohol. Extraction precipitate was obtained at the end of the evaporation progress. The acquired extraction precipitate was presented in Figure 3.

Figure 3. Extraction precipitate

The elemental composition of biomolecules obtained as a result of extraction of licorice were measured in Shimadzu EDX-8000 x-ray fluorescent spectrometer. Elemental analysis was performed by taking 30 g from the extraction sample. Elemental analysis of 1.5 mg Si and 0.6 mg P was acquired in 30 g of licorice root extract. Flame retardants containing phosphorus (P), nitrogen (N) and silicone (Si) elements attract plenty of attention, due to for their excellent flame resistance and slight influence on the natural properties of materials [36-38]. Certain researchers notified that the compound which consisted of P, N and Si elements could supply the polymer with better flame retardant specification [39]. Two flame retardant chemicals were used in pad-dry-cure system (Prowhite, horizontal padder and Ataç EV 250 oven) in order to optimize the amounts and to determine the influences of chemical agents on the functionalities of the textile structures.

100% cotton and 50%-50% cotton-polyester fabrics were padded with acrylate copolymer binders containing finishing bath using a laboratory padding and a coating machine. A wet pick-up ratio of 85% was used. After applying auxiliary chemicals in padding bath with a wet pick-up ratio of 85%. After padding and coating, the all samples were dried at 100℃ for 2 min and cured at 150℃ for 2 min.

The prepared recipes were given in Table 2. According to the recipes in Table 2, the preparation of licorice root solutions for the coating method could be between 1% and 5% [40].

According to the recipes in Table 2, the preparation of licorice root solutions for the padding method could be between 2.5% and 10% [41].

Table 2. The recipes applied to the samples

Component	Quantity (g/kg)
Licorice root extract	12 g
Citric acid monohydrate	0.6 g
Disodium hydrogen phosphate	0.6 g

Acetic acid (pH adjuster)	
Pure water	250 ml
pH	4
Component	**Quantity (g/kg)**
Ruco-Flam NMT	12g
Citric acid monohydrate	0.6 g
Disodium hydrogen phosphate	0.6g
Acetic acid (pH adjuster)	
Pure water	250 ml
pH	4
Component	**Quantity (g/kg)**
Licorice root extract	150g
Hard binder	200g
Soft binder(acrylic binder)	100g
Crosslinker	15g
Thickener	20g
Pure water	515g
Component	**Quantity (g/kg)**
ECO RFD 41 BO	150g
Hard binder	200 g
Soft binder (arcylic binder)	100 g
Crosslinker	15g
Thickener	20g
Pure water	515g

3.2. Determination of Flame Retardancy of Treated Fabrics

Surface morphology of the treated 100% cotton and 50%-50% cotton-polyester were tested by Fei Quanta Feg 250 scanning electron microscope (SEM).

The thermogravimetry evaluates the gradual mass loss of a specimen with regard to time at an amount of heating rate. It also signifies the influence of any flame retardant chemical on the pyrolysis of the polymer substrate [42]. The TGA of the polymers and licorice root extracts were performed by using Thermal Analyzer (TGA-Perkin Elmer Diamond). Tested samples for padding and coating were in 12 wt % and 150 wt %, respectively. The specimens were placed in platinium crucibles and subjected to a temperature ranging from 32 ℃ to 900℃ in N_2 gas with a heating rate of 20℃/min.

Flammability properties of the untreated and treated specimens were analyzed in vertical flammability. The vertical burning test was accomplished in the burning chamber according to the DIN 53906 standard. For LOI analysis, ASTM D2863 test method was used [43]. For each measurement, padded and coated cotton and cotton/polyester blend fabric samples were cut into strips of 52x140 mm.

4. RESULTS AND DISCUSSION

4.1. SEM Analysis

The changes in fiber geometry as a result of padding and coating application of films were qualified as magnification of 4000, shown in Figures 4, 5, 6 and 7, respectively. SEM was discussed to analyze the morphology of the untreated and treated fabrics. It was observed that the surface of the original fabric was smooth, as shown in Figures 4, 5, 6, 7(a). After further treatment with licorice root extract, circular substances emerged on the surface of the cotton and cotton/polyester fibers, which may be due to the attachment of the flame retardant; Figures 4, 5, 6, 7 (c). This is particularly noticed with different amounts of licorice root extract, 12 and 150 wt %, in Figures 4, 5, 6 ,7 (c), respectively. According to result in all SEM (c) images, surfaces of fabrics had certain impurities that could result from licorice root extracts. The existence of the char residues supported that the cellulose phosphate ester process via the reaction of hydroxyl groups of cellulose with phosphoric acid. The existence inorganic residues remained decay of flame retardant additives on fiber surfaces.

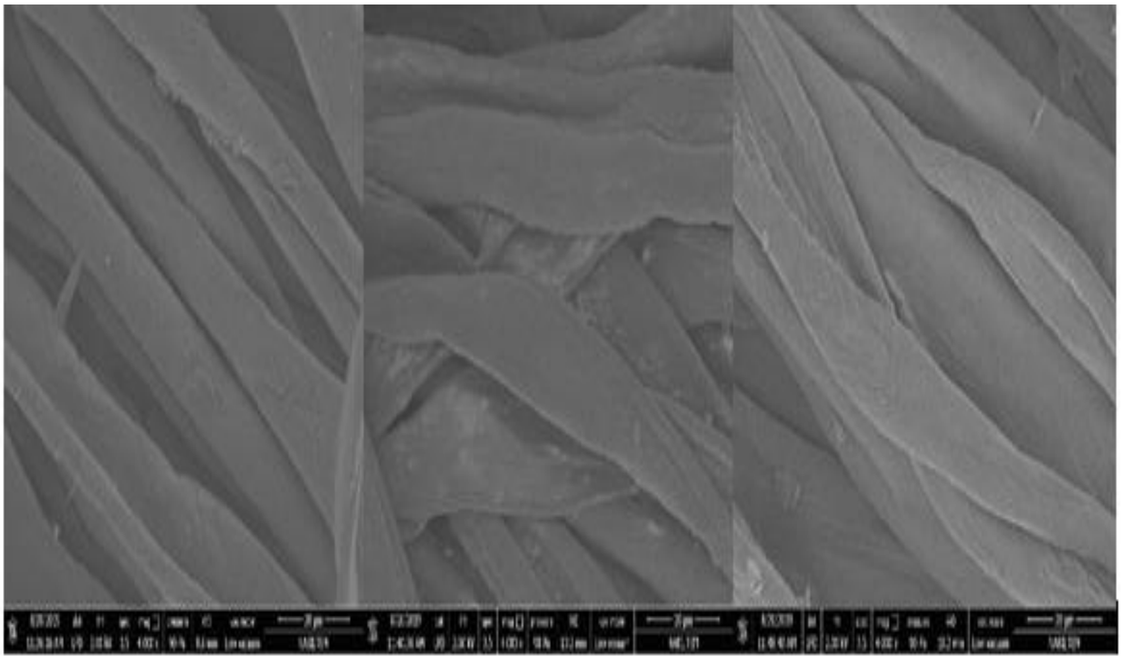

Figure 4. SEM images of unpadded cotton (a), padded with 12 g licorice root (c), padded with commercial flammable chemical (d)

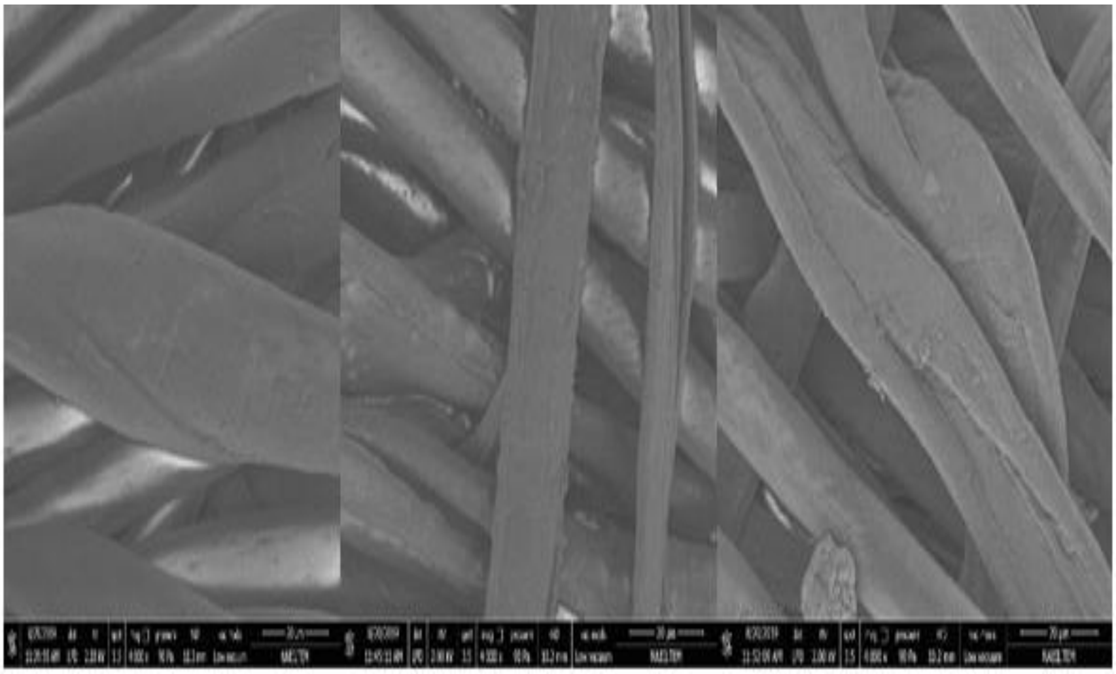

Figure 5. SEM images of unpadded Cotton/Polyester blend (a), padded with 12 g licorice root (c), padded with commercial flammable (d)

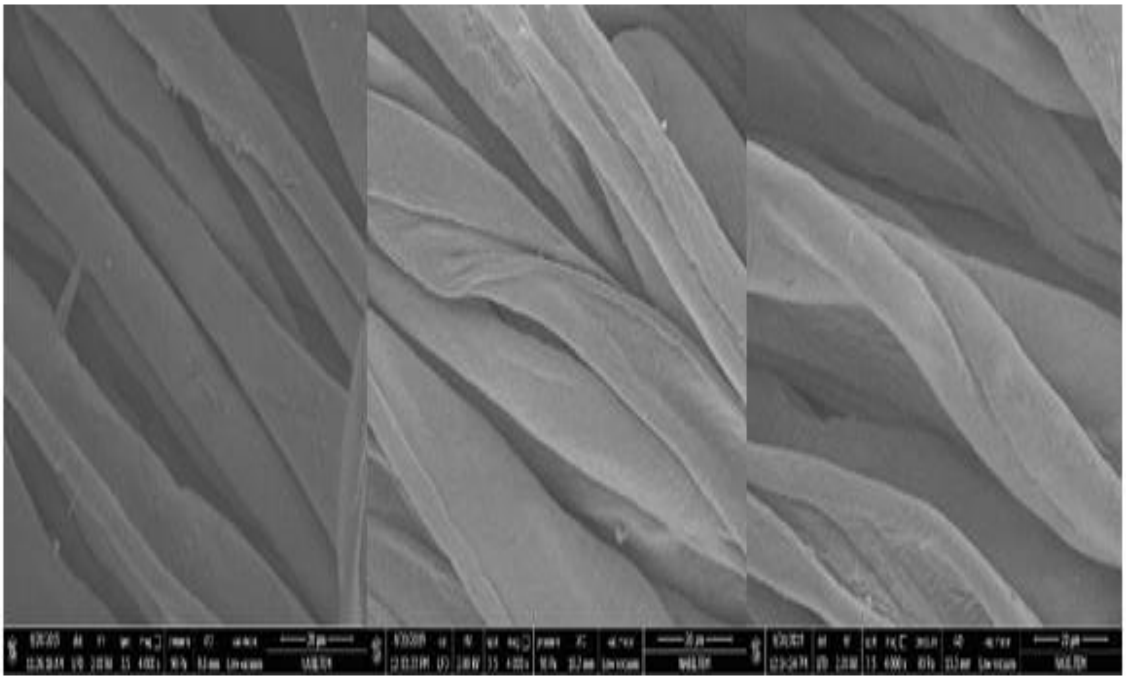

Figure 6. SEM images of uncoated cotton (a), coated with150 g licorice root (c), coated with commercial flammable chemical (d)

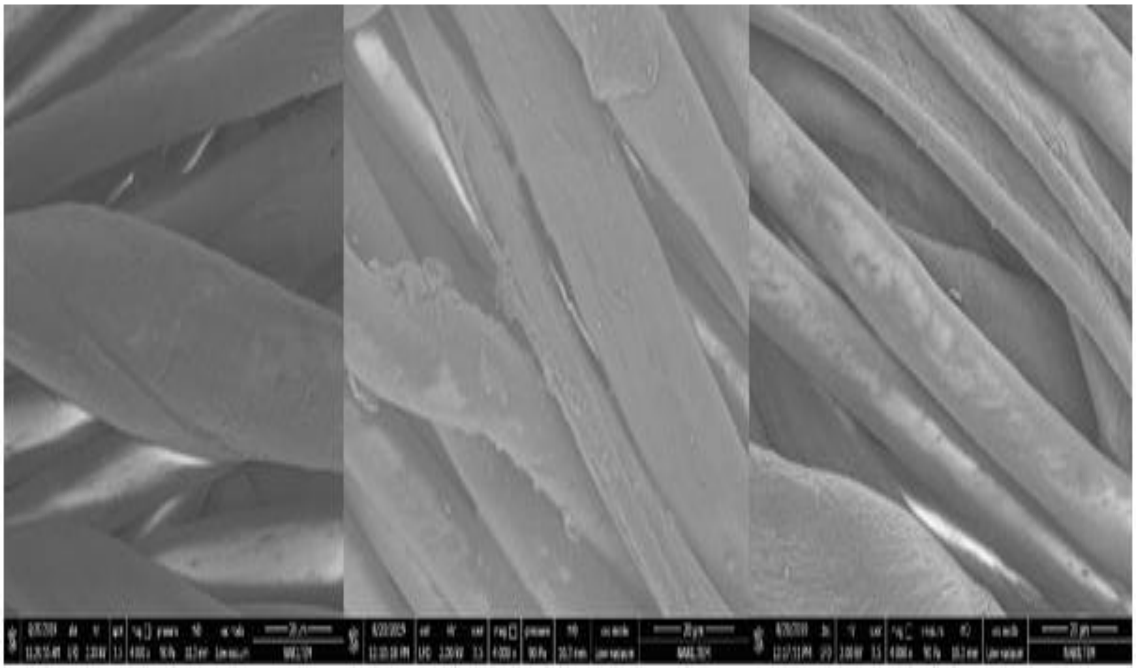

Figure 7. SEM images of uncoated Cotton/Polyester blend (a), coated with 150 g licorice root (c), coated with commercial flammable chemical (d)

Padding and coating processes with licorice root extract did not cause a serious change in the geometry of the 100% cotton and 50% cotton/50% polyester blended fibers. The interaction of licorice root extract with fiber was investigated by SEM. In SEM images; it was observed that the extraction products and commercial flame retardant chemicals were collected on the surface of the fibers.

4.2. Thermogravimetric Analysis (TGA)

Figures 8-11 show the TGA plots performed in N_2 and O_2 atmospheres of the cotton (A) and 50% cotton/50% polyester (B) woven fabrics at a heating rate of 20 ^oC/min.

The TGA arches of A and B specimens confirmed two levels of advancement. In the initial level at temperature over 300 ℃, the little mass loss occurred mainly due to the elimination of bound and unbound absorbed humidity from the cellulose polymer [42].

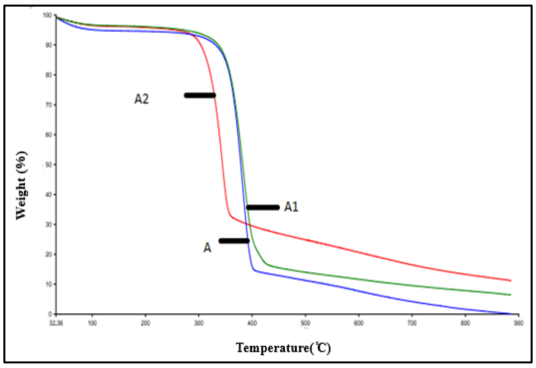

Figure 8. TGA arches of 100% cotton fabric (padding method) a-untreated [A] b-12 g. licorice root extract [A1] c-12 g. commercial flammable chemical [A2]

The TGA arch A, shows the beginning of decay at temperatures between 380 ℃ and 880℃, relying on the atmosphere (N_2 or O_2). The decay of cotton in N_2 is tracked by a second loss of mass that could be attributed to char pyrolysis up to 880℃ with a 14% of mass loss, outstanding to a final residue at 880℃ of 0%. An alike current in mass loss, decay was also noticed at the only untreated specimen.

From the TGA arch A, it was noticed that for the untreated sample, there was the single mass loss step at 380 ℃ and it completely degrades at 880 ℃.

From the TGA arch A2, it was noticed that for the commercial flammable chemical (organic phosphorus-nitrogen compounds) specimen was acquired with decay peak at 385℃ and with a mass loss of 31.239%. The final residue at 885℃ was 11.238%.

Moreover, the TGA curve (A2) proved the lower decay temperature and the higher char residues of 18% at 700 ℃, due to the mechanism of phosphorous-and triazine-including constituents and the synergistic influence of P and N elements [44].

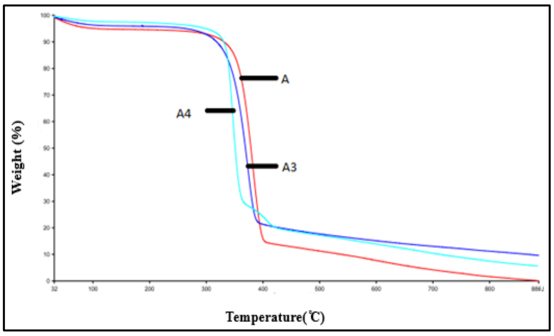

Figure 9. TGA arches of 100% cotton fabric (coating method)a-untreated [A] b-150 g. licorice root extract [A3] c-150 g. commercial flammable chemical [A4]

The TGA curve (Figure 9) (A3) shows the decay process of the licorice root extract treated fabrics. The mass loss step attributed to the decay of cotton until 410℃ (N_2) with a mass loss of 22%. The final residue at 886℃ was 9.633%.

Figure 9(A4) shows that the decay process of the commercial flammable chemical treated fabrics. The first mass loss step attributed to the decay of cotton until 380℃ (in N_2) with a mass loss of 27.873%. The decay of cotton in N_2 is tracked by a second loss of mass to 420℃ with a 19.412% of mass loss, outstanding to a final residue at continued up to 884 ℃. The final residue at 884℃ was 5.64%.

The practice of a flame retardant depend on licorice root extract just influences the thermal behaviour of the cotton woven fabric by increasing the beginning temperature of decay in N_2. Figure 8(A1) shows that the cotton fabric treated licorice root extract started to lose weight at 383.77 ℃. The TGA curve shows that the rate of weight loss arrived its peak at 410 ℃. About 14.933% of the mass was lost by this point. The final residue at 885℃ was 6.449%.

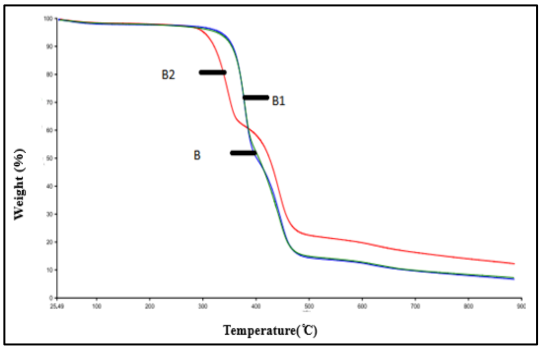

Figure 10. TGA arches of 50% CO/50% PES blended fabric (padding method) a-untreated [B] b-12 g.licorice root extract [B1] c-12 g. commercial flammable chemical[B2]

The TGA(B) (Figure 10) shows the beginning temperature of decay between 405 ℃ and 500 ℃ relying on the atmosphere (N_2). The TGA specifies the first mass loss step attributed to the decay of 50% CO/50% PES at 405 ℃ (48.5%) and 500℃ (14%) and the final residue at 884℃ was 6.562%.

The TGA(B1) analysis revealed that licorice root extract was mostly decomposed in the temperature range of 410℃-500℃ with two peaks and a maximum mass loss rate temperature of 410℃.

Figure 10 (B1) shows the decay process of the extract fabrics treated with licorice root. The first mass loss step attributed to the decay of cotton until 410℃ (in N_2) with a mass loss of 51.981%. The decay of cotton in N_2 is tracked by second loss of mass to 500℃ with a 14.908% of mass loss, leading to a final residue at continued up to 884℃. The final residue at 884℃ of 7.256%.

From the TGA arch (B2), it was noticed that the commercially flammable chemical specimen had two decays at 380℃ and 443.37℃. The first mass loss step was attributed to the decay at 380℃ with a 61.29% of mass loss, and the second loss of mass to 443.37 ℃ with 21.932%. The final residue at 884℃ was 12%.

The decay of cotton/polyester in N_2 is tracked by a second loss of mass to 510℃ with a 18% of mass loss, leading to a final residue at continued up to 884℃. The final residue at 884℃ was 8.737%.

From the TGA arch (B4), it was noticed that the commercial flammable chemical specimen had two decays at 380℃ and 490℃. The first mass loss step was attributed to the decay at 380 ℃ with a 61.93% of mass loss, and the second loss of mass to 490℃ with a 18%. The final residue at 884℃ was 11.939%.

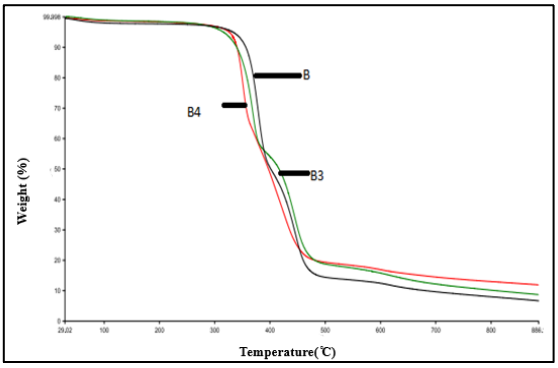

Figure 11. TGA arches of 50% CO/50% PES blended fabric (coating method) a-untreated [B] b-150g.licorice root extract [B3] c- 150g. commercial flammable chemical [B4]

Figure 11 shows the TGA plots(B3) performed in N_2 atmospheres of the 50% CO/50% PES samples. As temperature increases obvious endotherms were observed at 400℃ being mostly attributed to cotton/polyester. The first stage of decay is shown by a weight loss at about 400℃ (54.457%), probably due to partial decay of the polyester structure. The char amount is related to the grade of flame retardance [31]. 403℃-450℃ is the single step decay value of cotton/polyester samples, which show maximum weight loss interval at decay steps [45].

The decay of cotton/polyester in N_2 is tracked by a second loss of mass to 510℃ with a 18% of mass loss, leading to a final residue at continued up to 884℃.

From the TGA arch (B4), it was noticed that the commercial flammable chemical specimen had two decays at 380℃ and 490℃. The first mass loss step was attributed to the decay at 380℃ with a 61.93% of mass loss, and the second loss of mass to 490℃ with a 18%. The final residue at 884℃ was 11.939%.

The fabric with the most remaining mass for padding practice in cotton fabrics was acquired at the commercial flammable chemical application. In the coating method, licorice root extract was applied to the fabric. In cotton-polyester blended fabrics, the remaining mass for licorice root was the highest in the padding method, and the commercial flammable chemical proved the best influence in the coating method.

In this study, percent mass losses occured after the combustion test. In cotton fabric, mass loss decreases after padding with licorice root extraction. This is due to the presence of phosphorus in a small amount flammable retardant. It increases its effectiveness.

4.3. Vertical Burning Test

The vertical burning tests were given in Figures 12, 13 and in Table 3.

Figure 12. Samples of the untreated, padded and coated fabrics treated with licorice root after the vertical burning test: CO

Figure 13. Samples of the untreated, padded and coated fabrics treated with licorice root after the vertical burning test: CO/PES

Table 3. Flame retardant fulfillment of the cotton and CO/PES samples

Fabric Code	Char Length(cm)
CO A	-
CO A1	4
CO A2	5.8
CO A3	7.2
CO A4	12.5
CO/PES B	-
CO/PES B1	4.4
CO/PES B2	4.9
CO/PES B3	6.8
CO/PES B4	10.3

During the tests, the untreated fabric burned up, while the padded and coated cotton and CO/PES samples were burned locally, at which the flame contacted. Compared to sample A3 and B3, sample A1 and B1 had shorter char lengths. As a result, all licorice root concentration gave adequate flame retardant influence. There is no linear relation between the increase in concentration and the flame retardant influence.

The char lengths are shorter for A1 and B1 when compared to A3 and B3, although the licorice amount was lower. This was because the amounts of phosphorus in A3 and B3 were higher. Phosphorus element increases the flame retardant effectiveness. Structure and characterization of char depend on N,P and Si compound.

The flame retardant pyrolysis mechanism of cellulose fiber is differ to change the amount of flammable gases formed in a way that will decrease and increase that of non-flammable pyrolysis products, but exhibits lower decomposition temperatures. But flame retardant treatment lead to higher char yield compared to untreated cotton fabric [46]. Phosphorous based FR imparts flame retardancy to cellulose fiber by it speculiar mechanism [47]. Phosphorous compounds decompose to phosphoric acid, which catalyzes the cellulose dehydration reaction, and prevents flame retardant [46]. Phosphorus-based flame retardants have become the main focus as their decomposition products are less toxic and are considered ecological FR [47]. The combination of phosphorus and nitrogen has an excellent synergistic effect and high flame retardant efficiency.

By adding the appropriate fire retardant elements, as phosphorus and silicone (in licorice root), the resulting coating can provide the underlying material with good flame properties. Phosphorus and silicone elements have been developed because of their excellent carbonization and flame retardancy [48]. Phosphorus-containing compounds (in CO/PES blend fabrics) are qualified as among the most effective flame retardants, as indicated in many recent studies [49-51]. This kind of FRs is characterized by a highly efficient degree of flame retardancy. They can change the chemical reactions of decomposition; i.e, they form a surface layer of protective char during fire before the unburned structure materials begin to decompose [52-54].

Silicone-containing compounds are qualified as one of the “environmentally friendly” flame retardant materials. Although some studies proved that they themselves do not have sufficient flame retardant properties to meet application requirements; when they are used in addition to phosphorus-containing flame retardant, there is some synergistic effect between them [55,56].

4.4. LOI Test

The LOI, a measure of the flammability of a specimen, is specified as the minimum amount of oxygen in the oxygen/nitrogen mixture obliged to support the combustion.

As specified mostly, cotton is pure cellulosic in nature, catches flame rapidly describing an LOI value of 17.7%. The LOI value increased considerably after the application of licorice root and commercial flame retardant chemical to cotton and CO/PES blended fabrics by padding and coating method.

According to the results of the burning tests, the samples’ flame-retardant performances exhibited no considerable differences; therefore, only two samples padded and coated by using 12g/250g and 150g/1000g flammable chemical concentration were subjected to LOI tests, respectively. The LOI values of untreated, padded and coated cotton and CO/PES fabrics were given in Table 4.

Table 4. LOI values of untreated, padded and coated cotton and CO/PES fabrics

Fabric Code	LOI value (%)
A	17.7
A1	18.5
A2	18.7
A3	20.6
A4	21.4
B	17.5
B1	19.3
B2	19.6
B3	20.5
B4	22.5

It can be seen that LOI values of the coated samples were much higher than those of the padded sample.

LOI values of the treated licorice root sample A3(coated) and A1(padded) fabrics were 19.6% and 18.5%, respectively. The best LOI results for cotton fabrics in the coating method were acquired as commercially flammable chemical (A4)>licorice root extract (A3). With the increase of licorice root and commercial flammable concentration in the coating paste, the LOI value did not change very much. As a result, the coating process provide adequate flame-retardant effect to cotton fabrics even at 150g of natural and commercial flammable concentration.

It can be seen that LOI values of the commercial flammable chemical treated CO/PES samples were much higher than those of licorice root treated samples.

Phosphorous compounds (in CO/PES samples) influence the reactions taking place in the condensed (solid) phase. The flame retardant chemical is converted to phosphoric acid by thermal decay which extracts water from the pyrolysing polymer causing it to char (to produce a carbonaceous protective layer)[57].This process allows the decomposition of the polymer and reduces the amount and type of fuel precursor of volatiles. The presence of phosphorus in the formulation increase the fire resistance, LOI value and cause char formation.

This is evidently a positive influence in licorice root because a small amount of P-additive (0.6 % mg P) is enough to enhance the flame-retardant.

Also, when LOI results were taken into account, it seems like commercial compound addition is more effective in terms of flammable. Because the commercial compounds have more amounts of phosphorus in their formulations, they enhance the fire resistance and thus increase the LOI value.

5. CONCLUSIONS

In this study, the flame-retardant properties of 100% cotton and 50% cotton/50% polyester fabrics were researched by using ecological (licorice root) and commercial flame retardants by padding and coating methods. The padded and coated samples were subjected to the burning test besides SEM, TGA analyses and LOI tests. The dehydration and the char products formation in the presence of licorice root extracts and commercial flammable chemicals that were applied on cotton and cotton/polyester fabrics have been revealed in the TGA curves. After application, the tests proved that the coating treatment with licorice root on cotton and on cotton/polyester fabrics had partially considerable and adequate flame retardant effect. This result is related to the amount of P and Si elements in the structure of the licorice root. According to the limit oxygen index analysis, padding and coating processes had a positive influence on flammability. In other words, ignition and burning did not continue after the flame contact. Surface morphology of fiber char can give useful information about FR efficiency of especially licorice root and organic phosphorous-nitrogen based FRs. Thermal properties of untreated and treated samples can be researched to see effect of FR treatment and decomposition temperature and char amount.

Phosphorus (which was applied to CO/PES) is a thermodynamically stable high-polymer and is the most effective flame retardant when included in. It also partially reacts with certain polymers and enhances char formation.

6. ACKNOWLEDGEMENT

The study introduced here is a part of Fehmi Çağlar Balaban’s Master Thesis work at Graduate School of Natural and Applied Sciences, Namık Kemal University.

7. REFERENCES

1. Horrocks, A.R., B.K. Kandola, P.J., Davies, 2005. Developments in Flame Retardant Textiles. A Review Polymer Degradation and Stability, 88 (1), 3-12.
2. Golja, B., Šumiga, B., Boh, P., Bojana, Medved, J., Pušić, T., Tavčer, P., 2014. Application of Flame Retardant Microcapsules to Polyester and Cotton Fabrics. Material in Technologije, 48(1), 105-111.
3. Ceylan, Ö., Alongi, J., Landuyti, L.V., Fraches, A., Clerck, K.D., 2013. Combustion Characteristics of Cellulosic Loose Fibres. Fire and Materials, 37(6), 482-490.
4. Wang, Q., Qian, Y., Wang, Q., Yang, Y., Ji, S., Song, W., Ye, M., 2015. Metabolites Identification of Bioactive Licorice Compounds in Rats. Journal of Pharmaceutical and Biomedical Analysis, 115, 515–522.

5. Wang, N., Wu, Y., Mi, L., Zhang, J., Li, X., Fang, Q., 2014. The Affect of Silicone Shell on Double-layered Microcapsules in Intumescent Flame-retardant Natural Rubber Composites. J Therm Ana Calorim, 118, 349–357.

6. Zhou, T.C., He, X.M., Guo, C., Jian, Y., Dalian, L., Qun, Y., 2015. Synthesis of a Novel Flame Retardant Phosphorus/ nitrogen/ siloxane and its Application on Cotton Fabrics. Textile Research Journal, 85, 701–708.

7. Liao, F., Zhou, L., 2014. Synthesis of a Novel Phosphorus Nitrogen-silicon Polymeric Flame Retardant and its Application in Poly (Lactic Acid). Ind Eng Chem Res, 53, 10015–10023.

8. Masatoshi, I., Serizawa, S., 1998. Silicone Derivatives as New Flame Retardants for Aromatic Thermoplastics Used in Electronic Devices. Polymers for Advanced Technologies, 9, 593-600.

9. Cao, J.P., Zhao, X., Zhao, J., Zha, J.W., Hu G.H., Dang, Z.M., 2013. Improved Thermal Conductivity and Flame Retardancy in Polystyrene/poly (Vinylidene Fluoride) Blends by Controlling Selective Localization and Surface Modification of SiC. ACS Appl. Mater. Interfaces, 5, 6915-6924.

10. Liao, F., Zhou, L. Ju, Y., Yang, Y., Wang, X., 2014. Synthesis of A Novel Phosphororus-nitrogen-silicon Polymeric Flame Retardant and its Application in Poly (lactic acid). Ind. Eng. Chem. Res., 53, 10015-10023.

11. Lu, S.Y., Hamerton I., 2002. Recent Developments in the Chemistry of Halogen-free Flame Retardant Polymers. Progress in Polymer Science, 27(8), 1661-1712.

12. Liu, Y.L., Hsiue, G.H., Lan, C.W., Chiu, Y.S., 1997. Phosphorus-containing Epoxy for Flame Retardance: IV. Kinetics and Mechanism of Thermal Degradation. Polymer Degradation and Stability, 56(3), 291-299.

13. Liu, Y.L., Hsiue, G.H., Lan, C.W., Kuo, J.K., Jeng, R.J., Chiu, Y.S., 1997. Synthesis, Thermal Properties, and Flame Retardancy of Phosphorus Containing Polyimides. Journal of Applied Polymer Science, 63, 875-882.

14. Banks, M., Ebdon, J.R., Johnson, M., 1994. The Flame-retardant Effect of Diethyl Vinyl Phosphonate in Copolymers with Styrene Methyl Methacrylate Acrylonitrile and Acrylamide. Polymer, 35, 3470-3473.

15. Liu, Y.L., 2001. Flame-retardant Epoxy Resins from Novel Phosphorus-containing Novolac, Polymer, 42, 3445-3454.

16. Wu, C.S., Liu, Y.L., Chiu, Y.S., 2002. Epoxy Resins Possessing Flame Retardant Elements from Silicon Incorporated Epoxy Compounds Cured with Phosphorus or Nitrogen Containing Curing Agents. Polymer, 43, 4277-4284.

17. Horrocks, A.R., 2011. Flame Retardant Challenges for Textiles and Fibres: New Chemistry Versus. Polymer Degradation and Stability., 96, 377-392.

18. Kandola, B.K., Hull, T.R., 2009. Fire Retardancy of Polymers: New Strategies and Mechanisms. West Midlands: Royal Society of Chemistry, 456.

19. Horrocks, A.R., Price, D., 2008. Advances in Fire Retardant Materials., Elsevier.

20. Hou, A., Gang, S., 2013. Multifunctional Finishing of Cotton Fabrics with 3,3’, 4,4’-Benzophenone Tetracarboxylic Dianhydride: Reaction Mechanism. Carbohydrate Polymers, 95(2), 768-772.

21. Hou, A., Zhang, C., Wang, Y., 2012. Preparation and UV-protective Properties of Functional Cellulose Fabrics Based on Reactive Azobenzene Schiff Base Derivative. Carbohydr. Polym., 87, 284-288.

22. Pawlowski, K.H., Schartel, B., 2007. Flame Retardancy Mechanisms of Triphenyl Phosphate, Resorcinol Bis (Diphenyl Phosphate) and Bisphenol A Bis (Diphenyl Phosphate) in Polycarbonate/acrylonitrile-butadiene-styrene Blends. Polymer International, 56, 1404.

23. http://www.umweltdanten.de/publikationen/pdf /1988.pdf (on September 2008).

24. http://www.andrianos.com/fire-retardant.pdf (on October 2009).

25. Balaban, Ç.F., 2019. Bitkisel Atık Ekstraktlarıyla Yapılan Kaplama ve Emdirme İşlemlerinin Güç Tutuşurluk Üzerine Etkisinin İncelenmesi. Yüksek Lisans Tezi, Fen Bilimleri Enstitüsü, Namık Kemal Üniversitesi, Tekirdağ, Turkey, 60.

26. Chen, M.J., Shao, Z.B., Wang, X.L., Chen, L., Wang, Y.Z., 2012. Halogen-free Flame-retardant Flexible Polyurethane Foam with a Novel Nitrogen-phosphorus Flame Retardant. Ind. Eng. Chem. Res., 51(29), 9769-9779.

27. Horrocks, A.R., 1986. Flame-retardant Finishing of Textiles. Review of Progress in Coloration and Related Topics, 16(1), 62-101.

28. Alongi, J., Han, Z., Bourbigot, S., 2015. Intumescence: Tradition Versus Novelty. A Comprehensive Review., Prog. Polym. Sci. 51, 28–73, doi:10.1016/ j. prog polymsci.

29. Liang, S., Neisius, N.M., Gaan, S., 2013. Recent Developments in Flame Retardant Polymeric Coatings. Progress in Organic Coatings, 76(11), 1642-1665.

30. Ömeroğulları, Z., Kut, D., 2011. Investigation of Burning Behavior of Polyester Fabric with Using Natural Structured Flame Retardant Agent. Tekstil ve Konfeksiyon, 21(4), 364-368.

31. El-Tahlawy, K., 2008. Chitosan Phosphate: A New Way for Production of Ecofriendly Flame Retardant Cotton Textiles. Journal of the Textile Institute, 99(3), 185-191.

32. Basak, S., Samanta, K., Saxena, S., Chattopadhyay, S.K., Narkar, R., Mahangade, R., Hadge, G.B., 2015. Flame Resistant Cellulosic Substrate Using Banana Pseudostem Sap. Polish Journal of Chemical Technology, 11(1), 123–133.

33. Faheem, S., Baheti, V., Tunak, M., Wiener, J., Militky, J., 2017. Comparative Performance of Flame Retardancy, Physiological Comfortand Durability of Cotton Textiles Treated with Alkaline and Acidic Casein Suspension. Journal of Industrial Textiles, 48(6), 969-991.

34. Teli, M.D., Pandit, P., 2018. Coconut Shell Extract Imparting Multifunction Properties to Ligno-cellulosic Material. Journal of Industrial Textiles, 47(6), 1261-1290.

35. Üreyen, M., Kaynak, E., 2019. Effect of Zinc Borate on Flammability of PET Woven Fabric. Advances in Polymer Technology, (22), 1-13.

36. Wang, S., Sui, X., Li, Y., Li, J., Xu, H., Zhong, Y., Zhang, L., Mao, Z., 2016. Fabrication of Superhydrophobic Cotton Textiles with Flame Retardancy, Cellulose, 23, 1471-1480.

37. Chen, M.J., Shao, Z.B., Wang, X.L., Chen, L., Wang, Y.Z., 2012. Halogen-free Flame-retardant Flexible Polyurethane Foam with a Novel Nitrogen-phosphorus Flame Retardant. Ind. Eng. Chem. Res., 51(29), 9769-9779.

38. El-Tahlawy, K., 2008. Chitosan Phosphate: A New Way for Production of Ecofriendly Flame Retardant Cotton Textiles. Journal of the Textile Institute, 99(3), 185-191.

39. Zhong, H., Wei, P., Jiang, P., Wang, G., 2007. Thermal Degradation Behaviors and Flame Retardancy of PC/ABS with Novel Silicon-containing Flame Retardant., Fire Mater, 31, 411–23

40. Chen, C.H., Kuo, W.S., Lai, L.S., 2009. Rheological and Physical Characterization of Film-forming Solutions and Edible Films from Tapioca Starch/decolorized Hsian-tsao Leaf Gum, Food Hydrocoll., 23, 2132–2140.

41. Soderling, E., Karjalainen, S., Lille, M., Maukonen, J., Saarela, M., Autio, K., 2006. The Effect of Liquorice Extract-containing Starch Gel on the Amount and Microbial Composition of Plaque. Clin Oral Investig, 10, 108-13

42. Li, Q., Jiang, P.K., Su, Z.P., Wei, P., Wang, G.L., Tang, X.Z., 2005. Synergistic Effect of Phosphorus, Nitrogen, and Silicon on Flame-retardant Properties and Char Yield in Polypropylene. Journal of Applied Polymer Science, 96, 854-860.

43. ASTM D 2863-97, 1999. Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle Using an Oxygen Consumption Calorimeter. ASTM, West Conshohocken, PA.

44. Tesoro, G.G., Sello, S.B., Willard, J.J., 1969. Nitrogen-phosphorus Synergism in Flame-retardart Cellulose., Text. Res. J., 39, 180–190.

45. Atakan, R., Bical, A., Celebi, E., Özcan, G., Soydan, N., Saraç, A.S., 2019. Development of a Flame Retardant Chemical for Finishing of Cotton, Polyester and CO/PET Blends, Journal of Industrial Textiles,49(2),141-161.

46. Zhu, P., Sui, S., Wang, B., Sun, K., Sun, G., 2004. A Study of Pyrolysis and Pyrolysis Products of Flame Retardant Cotton Fabrics by DSC, TGA and PY-GC-MS. Journal of Analytical and Applied Pyrolysis, 71(2), 645-655.

47. Levchik, S.V., Weil, E.D., 2006. A Review of Recent Progress in Phosphorus-based Flame Retardants. J Fire Sci, 24, 345-364.

48. Siriviriyanum, A., O`rear, E.A., Yanumet, N., 2008. Self Extunguishing Cotton Fabric with Minimal Phosphorous Deposition. Cellulose, 15, 731-737.

49. Masatoshi, I., Serizawa, S., 1998. Silicone Derivatives as New Flame Retardants for Aromatic Thermoplastics Used in Electronic Devices. Polymers for Advanced Technologies, 9, 593-600.

50. Cao, J.P., Zhao, X., Zhao, J., Zha, J.W., Hu, G.H., Dang, Z.M., 2013. Improved Thermal Conductivity and Flame Retardancy in Polystyrene/poly (Vinylidene Fluoride) Blends by Controlling Selective Localization and Surface Modification of SiC. ACS Appl. Mater. Interfaces, 5, 6915-6924.

51. Liao, F., Zhou, L., Ju, Y., Yang, Y., Wang, X., 2014. Synthesis of a Novel Phosphororus-nitrogen-silicon Polymeric Flame Retardant and its Application in Poly (Lactic Acid). Ind. Eng. Chem. Res. 53, 10015-10023.

52. Lu, S.Y., Hamerton, I., 2002. Recent Developments in the Chemistry of Halogen-free Flame Retardant Polymers. Journal Progress in Polymer Science, 27, 1661-1712.

53. Liu, Y.L., Hsiue, G.H., Lan, C.W., Chiu, Y.S., 1997. Phosphorus-containing Epoxy for Flame Retardance. 4. Kinetics and Mechanism of Thermal Degradation. Polymer Degradation and Stability, 56, 291-299.

54. Liu, Y.L., Hsiue, G.H., Lan, C.W., Kuo, J.K., Jeng, R.J., Chiu, Y.S., 1997. Synthesis, Thermal Properties, and Flame Retardancy of Phosphorus Containing Polyimides. Journal of Applied Polymer Science, 63, 875-882.

55. Banks, M., Ebdon, J.R., Johnson, M., 1994. The Flame-retardant Effect of Diethyl Vinyl Phosphonate in Copolymers with Styrene Methyl Methacrylate Acrylonitrile and Acrylamide. Polymer, 35(16), 3470-3473.

56. Liu, Y.L., 2001. Flame-retardant Epoxy Resins from Novel Phosphorus-containing Novolac. Polymer, 42, 3445-3454.

57. Jarvis, C.W., Barker, R.H., 1978. Flammability of Cotton-polyester Blend Fabrics. In M. Lewin, SM Atlas and EM Pearce (Eds), Flame-retardant Polymeric Materials, 133-158. New York: Plenum Press.