Avrupa Bilim ve Teknoloji Dergisi
Sayı 17, S. 844-851, Aralık 2019

Araştırma Makalesi

www.ejosat.com ISSN:2148-2683

European Journal of Science and Technology
No. 17, pp. 844-851, December 2019

Research Article

Investigation of Flame Retardancy of Borax in Upholstery Leather Modified with Atmospheric Pressure Plasma

Safiye Meriç Açıkel[1*],

[1] İstanbul University-Cerrahpaşa, Vocational School of Technical Sciences, Leather Technology Programme, Büyükçekmece, İstanbul (ORCID: 0000-0002-1206-7726)

(İlk Geliş Tarihi 1 Kasım 2019 ve Kabul Tarihi 4 Aralık 2019)

(**DOI:** 10.31590/ejosat.641656)

ATIF/REFERENCE: Açıkel, S. M. (2019). Investigation of Flame Retardancy of Borax in Upholstery Leather Modified with Atmospheric Pressure Plasma. *Avrupa Bilim ve Teknoloji Dergisi*, (17), 844-851.

Abstract

Borax is in the class of inorganic chemicals and is used as flame retardancy in different industries. It has high ignition temperature, does not cause toxic gases during combustion and does not emit emissions that will pollute the environment. In this study, retanning process of leathers was made according to upholstery leather recipe and then the leathers were modified with argon gas containing atmospheric pressure plasma to increase the fixation of borax chemicals by surface modification effect of plasma. Then, 0, 30 g/L, 40 g/L, 50 g/L of borax solutions were applied to the modified leathers by padding technique and the leathers were finished by standard finishing recipe. Flame retardant property of leathers was determined by limit oxygen index (LOI) (ASTM D 2863-77) fire resistance test and TGA analysis. In addition, the treated leathers were characterized by FTIR, SEM and Hydrophilicity analyses. According to the obtained results, 30 g/L, 40 g/L, 50 g/L borax applied leather groups had 29.2%, 30.5% and 31.2% LOI values respectively, while control sample had 19.0%.

Keywords: Plasma, Leather, Borax, Flame Reterdancy, Upholstery

Atmosferik Basınç Plazma ile Modifiye Edilmiş Döşemelik Derilerde Boraks Kimyasalının Alev Geciktiricilik Özelliğinin Araştırılması

Öz

Boraks inorganik kimyasallar sınıfındadır ve alev geciktirici olarak farklı sektörlerde kullanılmaktadır. Boraks; yüksek tutuşma sıcaklığına sahiptir, yanma sırasında toksik gazlara neden olmaz ve çevreyi kirletecek emisyonlar yaymaz. Bu çalışmada, ilk olarak wet blue derilerin retenaj işlentisi yapılmış ve ardından finisajı yapılmamış deriler ilk olarak, boraks kimyasallarının fiksasyonunu arttırmak için atmosferik basınç plazması içeren argon gazı ile modifiye edilmiştir. Daha sonra 0, 30 g/L, 40 g/L, 50 g/L boraks çözeltisi padding tekniği ile modifiye edilmiş derilere uygulanmış ve deriler standart bir finisaj reçetesi ile mamul hale getirilmiştir. Derilerin alev geciktirici özelliği limit oksijen endeksi (LOI) (ASTM D 2863-77) alev dayanımı testi ve TGA analizi ile belirlenmiştir. Ek olarak, modifiye edilmiş deriler FTIR, SEM ve Hidrofilite analizleri ile değerlendirilmiştir. Elde edilen sonuçlarına göre, 30 g/L, 40 g/L, 50 g/L boraks uygulanmış deri gruplarının LOI değerleri sırasıyla %29.2, %30.5 ve %31.2 olarak tespit edilmişken kontrol numunesi için bu değer %19.0 olarak belirlenmiştir.

Anahtar Kelimeler: Plazma, Deri, Boraks, Alev Geciktirici, Döşemelik

---

* Corresponding Author: İstanbul University-Cerrahpaşa, Vocational School of Technical Sciences, Leather Technology Programme, Büyükçekmece, İstanbul, ORCID: 0000-0002-1206-7726, mericgokalp@gmail.com

1. Introduction

Flame Retardants can be classified as halogen containing and halogen-free products (Kaya, 1998; Açıkel, 2018a; Açıkel etc., 2017, Açikel, 2018). Borax and derivatives which are in the class of inorganic chemicals and are used for flame retardancy as well as in many fields such as agriculture, plastic, nuclear, glass and ceramics, textile, etc. The flame retardation effect of borax has been the subject of many studies, because borax has a high ignition temperature, does not cause toxic gases during combustion and does not emit emissions that will pollute the environment. Borax flame retardants act as a barrier by forming a glassy protective layer on the surface of the material. They cut off the contact of the burning material with oxygen and retard combustion of it (Açikel 2018b; Çakal etc., 2012; Akarslani 2015; Bozacı 2018; Gelgeç vd., 2019, Aydın, 2016). Plasma technology is often referred to as the fourth state of matter. Plasma is mostly comprised of positively charged ions, electrons and neutral particles. Occurred reactive particles are used for cleaning, cross-section, surface activation, corrosion, vaccination without changing main properties of material. This technology is widely used today in the textile industry to provide waterproofing, hydrophilic character, bleaching, dyeing, plasma polymerization, antimicrobial properties, addition of new reactive groups, adhesion enhancement, crosslinking, sterilization (Aslan etc., 2016; Acikel etc., 2013). Atmospheric pressure plasma application is more suitable for industrial production and low cost than other plasma pressures, and has more homogeneous and faster processing based on plasma density. Atmospheric pressure plasma processes can interfere with other gases such as oxygen and hydrogen in the air and can be converted into forms such as hydroxyl radical (OH), ozone (O^3), nitric oxide (NO), superoxide anion (O^{2-}) because of open systems (Kaygusuz etc., 2018; Koizhaiganova etc., 2017). These transformations can also reveal different synergistic effects on the surface of material. So in this study, firstly the leathers were modified by atmospheric pressure plasma treatment in order to better bond the borax chemical to the leather surface. After application of different concentration of borax chemical on the surface of the leather, combustion properties of the leathers were investigated.

2. Material and Method

2.1. Material

Wet blue cattle leathers were supplied from the leather company in Tuzla Leather Industrial Area. Boric acid (H_3BO_3) (99%, extra pure) and Borax ($Na_2B_4O_7.10H_2O$) (99%, extra pure) were purchased from Tekkim Ltd. Chemical Company (Turkey) (Figure 1.)

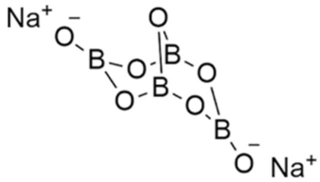

Figure 1. Molecular Structure of Borax

In the recipe of retanning process; Farben shine forel HT was used as nonionic Tencid, Tan Krom AB was used as Chrome Tannin, Alpine MX was used as Resin Tannin, Farben Retan N was used as Phenolic Syntan, Tara was used as Vegetal Tannin, Alpine Soft TK was used as synthetic oil, Farben Shine Grossöl ff was used as phosphoric ester oil, Alpine Soft SB was used as sulfite fish oil. In the finishing recipe; different chemicals were used, Pelle Curtecin PU 3234 (Farben b.v.) as polyurethane binder, Pelle Curial Binder OBN (Farben b.v.) as acrylic binder, Pelle Curtefill CP 5200 (Farben b.v.) as filler, Pelle Curtebind Lustre TE (Farben b.v.) as casein binder, Sarkol K Dark Brown (Sarchem b.v.) as Pigment, Pelle Curtewax 4012 N (Farben b.v.) as wax, Supronil Dark Brown (Clariant b.v.) as anilin dye, Melio EW 348B (Clariant b.v.) as hydrolacque, Melio WF 5226 (Clariant b.v.) as feeling agent.

2.2. Method

2.2.1. Retanning Process

The retanning proces of leather samples was made according to upholstery leather manufacture recipe given in Table 1.

2.2.2. Plasma Treatment

Surface modification of leather samples was achieved by atmospheric pressure plasma device of laboratory scale (Technoplasma, Turkey) that produces plasma at radio frequency for improvement of wetting characteristics of all leather samples before borax flame retardant chemical applications. After placing the samples below the nozzle of the plasma device, argon ions were discharged to the leathers. The physical parameters such as power supply, nozzle's diameter, and distance of electrodes were optimized for leathers. The optimized plasma parameters were at a frequency of 50 kHz and 200 Watts power. Argon gas pressure was set as 150 bar pressure and gas flow rate as 18 min/L. (Figure 2.) A copper electrode of length 15 cm and diameter 2 mm was placed in the center of the nozzle and the distance from the tip of the nozzle to the leather was set to 10 mm. The nozzle had an internal diameter of 8 mm, a thickness of 1 mm and the internal diameter of the glass at the mouth of the nozzle was 5,5 mm.

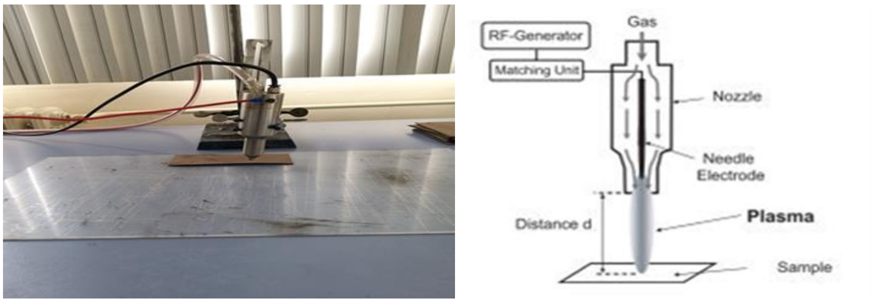

Figure 2. Experimental set-up of Atmospheric Plasma Machine

Table 1. Retanning Process Recipe of Leathers

Process	Chemical	Rate (%)	Time (min)	Temperature (ºC)	Remarks
Weight					
Bleaching	Water	300		40	
	Oxalic Acid	0,2			
	Nonionic Tencid	0.3			
	Formic Acid	0,2	60		Drain
Washing	Water	200	10	30	Drain
Chrome Retanning	Water	200		30	
	Chrome	3	60		
	Sodium Formate	0,5	30		pH:3.8-4.0
Neutralization	Water	150		35	
	Sodium Formate	2	20		
	Sodium Bicarbonate	1,2	60		
					pH:5,5
Washing	Water	200	10	30	
					Drain
Retanning	Water	150		25	
	Resin Tannin	2	10		
	Phenolic Syntan	3	10		
	Vegetal Tannin	2	10		
Dyeing	Ammonia	0,5	5		
	Acid Dye	4	60		
	Formic Acid	2	30		pH:4
Fatliquoring	Water	150		70	
	Synthetic Oil	5			
	Phosphoric Ester Oil	5			
	Fish Oil	3	60		
	Formic Acid	0,5	30		pH:4 Drain
Washing	Water	200	10	30	Drain

2.2.3. Flame Retardant Application

The rates of borax flame retardant solution were prepared from borax (0, 30 g/L, 40 g/L, 50 g/L) and boric acid (10 g/L). They were dissolved in distilled water and the solutions were stirred for 30 minutes at 90ºC to obtain homogeneous mixture. Leather padding technique, which is a kind of finishing technique made by hand, is used for the intense or decorative pattern finishing applications. Borax solutions were applied to leathers at different concentrations by this technique (Acikel etc., 2018). All leathers were dried at the room temperature for 24 h and then same application was repeated once again.

2.2.4. Finishing Process

After application of the proposed flame retardant mixture, the leather samples were finished with the standard finishing recipe given in Table 2.

Table 2. Finishing Recipe of Leathers

Chemical	Rate	Application
1) Polyurethane Binder (g)	100	1) 2x Spray Press (85 atm, 80 oC,1sn) 2 x Spray Press (85 atm, 80 oC,1sn)
Acrylic Binder (g)	100	
Protein Binder (g)	50	
Filler (g)	50	
Casein Binder (g)	25	
Waks (g)	75	
Pigment Dye (g)	80	
Anilin Dye (g)	20	2) 1 x Spray Press (100 atm, 90oC, 1 sn)
Water (g)	500	
2) Hydrolacque (g)	100	

2.3. Measurements

Limit oxygen index (LOI) tests were performed in a limiting oxygen index chamber with strips of leathers according to ASTM D 2863-77 in the Textile Department Test Laboratory of Dokuz Eylül University. 15 pieces of leather samples for each group (140 mm x 60 mm) were taken from flame-retardant leathers and were used for parallel tests.

2.3.1. Thermogravimetric (TGA) Analysis

Thermogravimetric analysis (TGA) of the flame retardant leathers (0, 30 g/L, 40 g/L and 50 g/L) were conducted at heating rates of 20ºC min^{-1} under air atmosphere (flow 60 mL min^{-1}) between 35ºC and 800ºC temperatures using TGA (Mettler Toledo). Sample mass was approximately 5 mg. TGA curves were mapped by computer automatically.

2.3.2. Scanning electron microscope (SEM) Analysis

For SEM analysis, the samples were placed on a scanning electron microscope (Fei-Quanta Feg 250) and their images were taken at 400 µm magnification.

2.3.3. FTIR Analysis

FTIR analysis was conducted in order to determine the differences in the chemical properties of leather treated with Borax and control group. FTIR studies were conducted on JASCO FT/IR-6700. For this purpose, the leather samples were scanned with IR spectrums at a wavelength of 4000-600 cm^{-1} and the results were evaluated in the FTIR Spectrum Software and compared with the spectrums in the literature.

2.3.4. Hydrophilicity Measurements

Plasma treated leathers were conditioned under standard atmospheric conditions as recommended in IUP 1 and IUP 3 at a temperature of 23°C ± 2°C and 50% ± 5% relative humidity, and the sampling location was determined according to IUP 2. Wettability of the leather samples was characterized by the water droplet test (IUP/420). Five readings were taken from different parts of the treated and untreated leather samples.

3. Results and Discussion

3.1. Limit Oxygen Index (LOI) Tests

LOI results of plasma applied and borax treated upholstery leathers were given in Table 3. According to the obtained results, 30 g/L, 40 g/L, 50 g/L borax applied leather groups had 29.2%, 30.5% and 31.2% LOI values respectively, while control sample had 19.0%. When these results were examined, it was found that there were quite high LOI values compared to other flameretardant chemicals used for leather in the literature.

Açıkel used in a research the boron derivatives to increase the effect of commercial flame retardant and in this research the chemical mixture ratios of 10 g/L zinc borate + 60 g/L boric acid + 200 g/L commercial flame retardant were found to have maximum 29.9% of LOI results. In another research Açıkel (2018) was reached maximum 30.5% LOI value with tributyl phosphate (TBP) applied upholstery leathers. Lyu etc. (2019) prepared Zanthoxylum bungeanum Maxim Seed Oil nanocomposites to enhance thermal stability of leather by the oil barrier on the collagen fibers and they reached maximum 28.0% limiting oxygen index (LOI). So in our study, these high LOI values were thought to be due to a synergistic effect between atmospheric pressure plasma treatment and borax.

Table 3. LOI Results of Borax Treated Leathers

Group (g/L)	LOI (%)
0	19.0
30	29.2
40	30.5
50	31.2

3.2. Thermogravimetry Thermal (TGA) Analysis

TGA results of the upholstery leathers treated with borax chemical and then plasma modified are given in Figure 3. According to TGA results, TGA curve by graphical illustration is seen that 0 g/L group is at the bottom of the graph because it burns much faster than other groups. The completely burned temperature of 0 g/L group which is mean the temperature of maximum weight loss, is much lower than that for the others groups. While the temperature of maximum weight loss is reached 290ºC in 0 group, the temperatures of 30 g/L, 40 g/L, 50 g/L groups are increased respectively to 310ºC, 330ºC and 360ºC because of flame reterdant effect of Borax chemical (Table 4).

Açıkel (2018) used phosphorous-based TBP chemical for flame retardancy effect in upholstery leather. In this study, while the maximum mass loss in the untreated leathers TGA analysis was 317 ºC, the temperatures in the TBP applied leathers were reached between 322 ºC and 328 ºC. So plasma treated and borax applied uphosltery leathers gave better TGA results than TBP chemicals (Table 4).

Table 4. The Temperature of Maximum Weight Loss in TGA Analysis of Borax Treated Leathers

Group	0 g/L	30 g/L	40 g/L	50 g/L
Tmax (ºC)	290 ºC	310 ºC	330 ºC	360 ºC

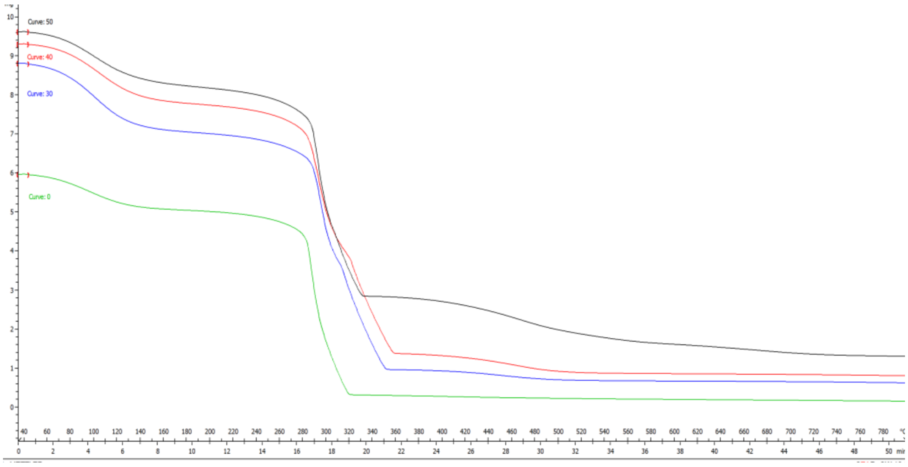

Figure 3. TGA Results of Borax Treteated and Plasma Applied Leathers

3.3. FTIR Analysis

FTIR results of borax applied leathers are shown in Figure 4. According to results, FTIR curves gave in all gorups, which have some characteristic peaks of collagen structure. However some bands were occurred or increased after borax applications and these are 798 cm^{-1}, 1080 cm^{-1}, 2306 cm^{-1}, 3411 cm^{-1}, 3728 cm^{-1}. The band at 798 cm^{-1} was related to O-H and symmetric stretching band of B-O (Acikel, 2018b). The peak at 1080 cm^{-1} observed in the leather sample with 50 g/L borax solution indicated the stretching of B-O vibrations (Yılmaz and Pişkin, 2017).

The 3400 cm^{-1} and 3500 cm^{-1} bands interval represent intermolecular bonded of O-H stretching. 3411 cm^{-1} and 3728 cm^{-1} peaks were correspounding to the bounding B-O and O-H groups in leather samples. Another proof of this was shown in 2306 cm^{-1} peak which is C-O-C strong stretching occurred because of chemical bounding of borax. These new peaks are indicated the presence of borax and boric acid in the treated leather samples (Bozacı, 2018).

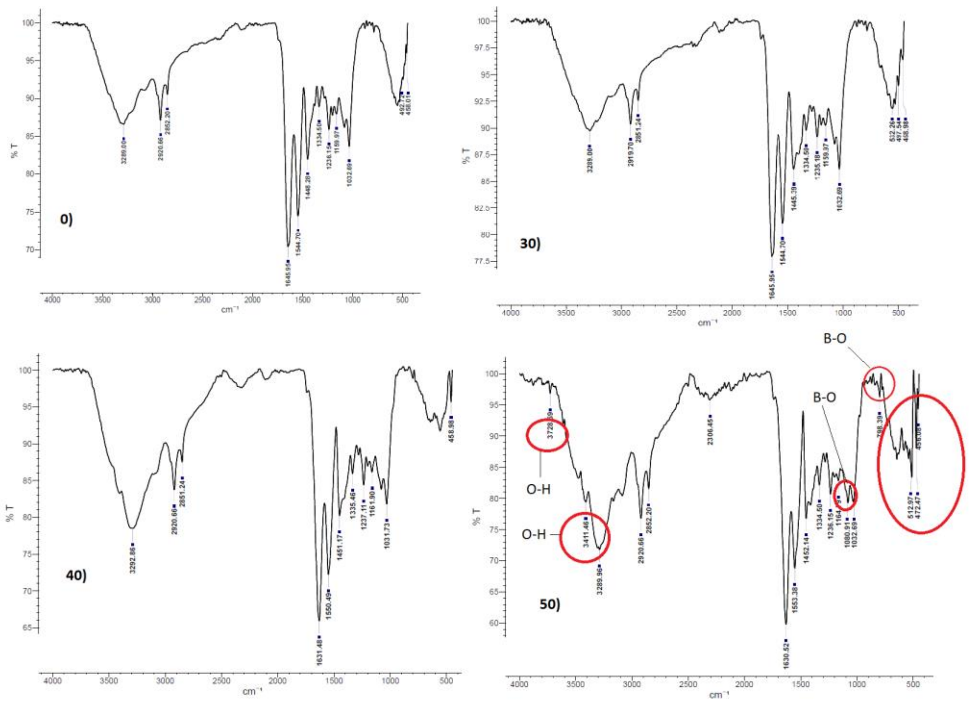

Figure 4. FTIR Results of 0 g/L, 30 g/L, 40 g/L and 50 g/L Leathers

3.4. Hydrophilicity Results

Plasma treatment causes changes in the hydrophilicity of the surface of the material by the effect of the gas used (Acikel etc., 2013). Particularly, the increase in hydrophilicity will provide better penetration of the chemical to the surface. In this study; 30 g/L, 40 g/L and 50 g/L group leathers were treated by same plasma parameters in order to see increasing hydrophilicity on the leathers by synergic effect of borax and plasma. Hydrophilicity results of plasma treated and borax applied leathers are given in Table 5.

Table 5. Hydrophilicity Results of Leather Samples

Samples	Hydrophilicity (Second)	Samples	Hydrophilicity (Second)
0-1	300	40-1	59
0-2	362	40-2	54
0-3	358	40-3	55
0-4	374	40-4	58
0-5	360	40-5	60
Total	**350,8**	**Total**	**57,2**
30-1	61	50-1	55
30-2	69	50-2	51
30-3	58	50-3	52
30-4	60	50-4	59
30-5	65	50-5	50
Total	**62,6**	**Total**	**53,4**

According to results; it is seen that 0 group leathers which were not treated with atmospheric pressure plasma, have very high hydrophobic properties. However, the hydrophilicity of the leathers was significantly increased after argon gas-containing atmospheric pressure plasma treatment and application of borax at different concentrations. The fact that the absorption forces of the leathers had approximately the same values was not related to the amount of borax used, but this result was associated with the same plasma duration. In other words, the application of atmospheric pressure plasma has changed the surface hydrophilicity properties of the material.

3.5. SEM Results

SEM images of the leather samples are shown in Figure 5. SEM photographs showed that the pores of leathers activated with argon had widened in all borax applied samples. It also caused some roughness on the leather surface due to plasma application (Koizhaiganova etc., 2017).

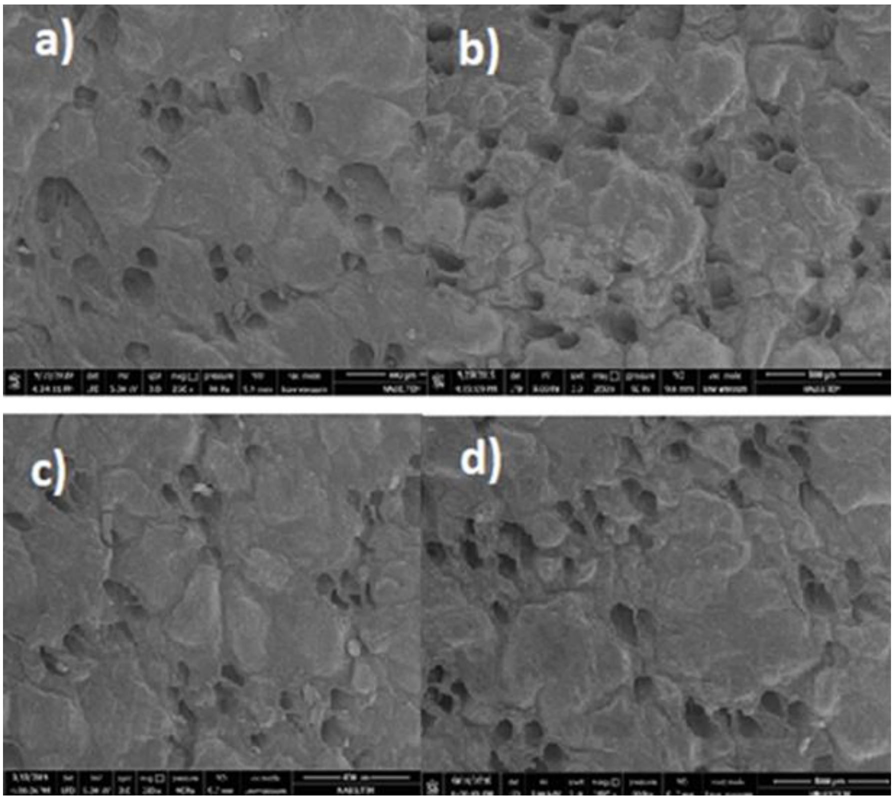

Figure 5. SEM Results of Treated Leathers

4. Conclusions

In this study, in order to improve the flame reterdancy property of upholstery leathers; borax solution with different concenrtrations (0 g/L, 30 g/L, 40 g/L and 50 g/L) were used after argon atmospheric pressure plasma application. In the results, the maximum LOI value was obtained as 31.2% in 50 g/L borax applied leathers. Borax chemical, which is more ecological and cheaper than phosphorus or halogen-based chemicals, show much better flame retardant effect in the upholstery leathers. When TGA thermograms are examined, it was determined that flame temperature of leathers was increased after treatment with borax compound. Finally it was conluded that the flame retardancy property of the leathers has been improved when boron compound and plasma applied together to the leathers.

References

Açikel S.M., Aslan A., Oksuz L., Aktan T. 2013. Effects of Atmospheric Pressure Plasma Treatments on Various Properties of Leathers, Journal of the Amerıcan Leather Chemısts Assocıatıon, 108(7):266-276.

Açikel S.M., Çelik C., Gültek A.S., Aslan A. 2017. The Flame Retardant Effect of Tributyl Phosphate on The Leathers, International Journal of Scientific and Technology Research, 6:44-48.

Açıkel S.M. 2018a. Researching of Properties of Gained Flame Retardancy on the Upholstery Leathers by Tributyl Phosphate Chemical, Sakarya University Journal of Science, 22 (5):1-7.

Açikel S.M., 2018b. Development of Commercial Flame Retardant in Upholstery Leathers by Boron Derivatives, Tekstil ve Konfeksiyon, 28:319-323.

Açikel S.M., Çelik C., Gürbüz D., Çinarli A. 2018. Flame Retardant Effect of Trı Butyl Phosphate (TBP) İn Vegetable Tanned Leathers, Tekstıl ve Konfeksıyon, 28:135-140.

Akarslan F. 2015, Investigation on Fire Retardancy Properties of Boric Acid Doped Textile Material", Acta Physica Polonica Series a, 128:403-405.

Aslan A., Oztarhan A., Acikel S.M., Oks E., Nikolaev A.G. 2015. Properties of Metal and Metal-Gas Hybrid Ion Implanted Chrome-tanned Leather Surfaces, Journal of The Socıety of Leather Technologısts and Chemısts, 99(5):209-215.

Aydın D.Y., Gürü M., Ayar B., Çakanyıldırım Ç. 2016, Bor Bileşiklerinin Alev Geciktirici ve Yüksek Sıcaklığa Dayanıklı Pigment Olarak Uygulanabilirliği, Boron Dergisi, 1 (1):33 – 39.

Bozacı E. 2018, Borlu bileşiklerin çevre dostu yöntemlerle poliakrilnitril kumaşlara uygulanması, Boron Dergisi, 3 (1):17-23.

Çakal G.Ö., Göğebakan Z., Coşkun S. 2012, Investigation of Synergistic Effect of Boron on Fire Retardancy of Cotton Fabrics, Textile and Apparel, 18 (4):547−553.

Gelgeç E., Yıldırım F.F., Yumru Ş., Çörekoğlu M. 2018. Bor Bileşikleri Pamuklu Kumaşların Güç Tutuşurluk Özelliklerinin Geliştirilmesi, Soma Meslek Yüksekokulu Teknik Bilimler Dergisi, 2 (26): 27-44.

IULTCS, 1998, Water Droplet Test, IUP/420 EN ISO 15700.

IULTCS, 2002, Sampling, UP/2 EN ISO 2418.

IULTCS, 2012a, General Remarks, IUP/1 EN ISO 2419.
IULTCS, 2012b, Conditioning in Standard Atmosphere, IUP/3 EN ISO 2419.
Kaya M., 1998, Alev Geciktirici Ve Duman Bastırıcı Katkı Maddeleri, Eskişehir Osmangazi Üniversitesi Mühendislik ve Mimarlık Fakültesi, 11(2):77-88.
Kaygusuz M., Meyer M., Junghans F., Aslan A. 2018. Modification of Leather Surface with Atmospheric Pressure Plasma and Nanofinishing, Polymer-Plastıcs Technology and Engıneerıng, 57(4):260-268.
Koizhaiganova M., Meyer M., Junghans F., Aslan A. 2017. Surface Activation and Coating on Leather by Dielectric Barrier Discharge (DBD) Plasma at Atmospheric Pressure, 101(2):86-93.
Lyu B., Wang Y.F., Gao D.G., Ma J.Z., Li Y., 2019, Intercalation of modified zanthoxylum bungeanum maxin seed oil/ stearate in layered double hydroxide: Toward flame retardant nanocomposites, Journal of Environmental Management, 238:235-242.
Yılmaz M.S and Pişkin S., 2017, Comparative Study on Two Different Methods for the Synthesis of Hydrated Sodium Metaborates Karaelmas Fen ve Mühendislik Dergisi, 7(2):563-567.