(REFEREED RESEARCH)

INVESTIGATION OF SYNERGISTIC EFFECT OF BORON ON FIRE RETARDANCY OF COTTON FABRICS

BORUN PAMUKLU KUMAŞLARIN GÜÇ TUTUŞURLUĞU ÜZERİNDEKİ SİNERJİK ETKİSİNİN ARAŞTIRILMASI

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ABSTRACT

This study investigates synergistic fire retardancy effect of boron on cotton fabrics. Three types of boron compounds were added to fire retardant solution composed of an organic phosphorus compound and urea based cross-linking agent. Fabrics were treated with fire retardant solution, washed and analyzed by SEM/EDX, TGA and LOI methods. Durability of boron on fabrics was also investigated by boron analysis in washing water. The results revealed that treated fabrics turn out to be nonflammable; LOI>45. The highest LOI for fabrics treated and 5 times washed was achieved when the fire retardant solution composed of 15 % phousporous compound, 12 % cross-linking agent and 1 % borax pentahydrate was used. Above 98 % of boron remained within fabric structure after washing. This is an indicator for boron to be used as fire retardant material in industrial applications of cotton fabrics.

Key Words: Fire retardancy, Boron, Phosphorous, Urea, Cotton fabric.

ÖZET

Bu çalışmanın amacı borun pamuklu kumaşlar üzerindeki sinerjistik güç tutuşurluk özelliğinin araştırılmasıdır. Güç tutuşurluk çözeltisi hazırlanırken üç farklı bor bileşiği ile fosfor bileşiği ve üre bazlı bir bağlayıcı kullanılmıştır. Kumaşlar öncelikle güç tutuşurluk çözeltisi ile muamele edilmiş ve daha sonra yıkanmıştır. Yıkama öncesi ve sonrası elde edilen kumaşlara SEM/EDX, TGA ve LOI analizleri yapılmıştır. Borun pamuklu kumaş üzerindeki kalıcılığı yıkama suyunda bor analizi yapılarak incelenmiştir. Bu çalışmanın sonuçları güç tutuşurluk çözeltisi uygulanan kumaşların alev almadığını göstermiştir; LOI>45. Güç tutuşurluk çözeltisi uygulanmış ve 5 kez yıkanmış kumaşların arasında en yüksek LOI, güç tutuşurluk çözeltisi olarak % 15 fosfor bileşiği, % 12 bağlayıcı ve % 1 boraks pentahidrat uygulandığında elde edilmiştir. Yıkama sonrası %98'in üzerinde borun kumaşın yapısında kaldığı tespit edilmiştir. Bu sonuç endüstriyel uygulamalarda borun pamuklu kumaşlarda güç tutuşturucu madde olarak kullanılabilirliği hakkında bir gösterge niteliğindedir.

Anahtar Kelimeler: Güç tutuşurluk, Bor, Fosfor, Üre, Pamuklu kumaş.

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1. INTRODUCTION

Textiles are used in many fields such as housing materials, underwear and outwear clothes, work clothes, bedding, military garments and transportation (aircraft blankets and seat coverings). Cotton is one of the most commonly used of textile fibers. Cotton fibers are one of the most easily flammable textiles due to their chemical nature and hence it is important to use flame-retardant systems to modify flaming properties of these fibers. One way to achieve fire retardancy in textile products is incorporation of additives. The function of additives are retarding ignition, controlling burning and reducing smoke formation. Fire retardant chemicals are classified as halogen, phosphorus, nitrogen and inorganic compounds. Halogen and halogen-antimony systems tend to be flame inhibitors, phosphorus and boron tend to enhance charring and formation of surface barrier layers, and metal hydroxides tend to be endothermic water-releasing systems (1). Halogen compounds are shown to have disadvantage of emitting toxic and corrosive gases during thermal degradation (2). Phosphorus containing coatings perform as intumescent which form a barrier of foamed char when exposed to a flame. The effectiveness of phosphorus based coatings has been shown to be favored by the melting and penetrating of the intumescent material through the surface of the fabric (3,4). The effect of phosphorous based flame retardants can be improved by nitrogen containing compounds (5-8). Boron containing flame retardants are developed as cheaper, yet less toxic alternatives to such traditional flame retardants as antimony oxide (9). Boric acid and borates are effective flame retardants as impenetrable glass coatings form during thermal degradation which contribute the intumescent effect and prevent further propagation of combustion. The hydrated water from boron compounds also absorbs the thermal energy of the flame (2). Boron derivatives are non-durable flame retardants for cellulosics that they are easily leachable with water. This makes necessary for them to be applied together with a fire retardant solution and a binder to show a synergy and increase its durability.

There are many studies carried out on application of several combinations of fire retardant chemicals for polymeric materials (10-14) and cotton fabrics (15-21); however, there exist no such investigations on inflammability of cotton fabrics provided by phosphorus-nitrogen based flame retardants together with boron compounds. Therefore, the aim of this study is treatment of cotton fabrics with a phosphorus based fire retardant chemical and a urea based cross-linking agent incorporated with different types of boron compounds on one hand, and investigation of the synergic role of boron in enhancing flame resistance of cotton fabrics, on the other.

2. MATERIALS AND METHODS

2.1. Materials

Boric acid (H_3BO_3, with a purity of 99.9% by weight), borax pentahydrate ($Na_2B_4O_7{\cdot}5H_2O$, with a purity of 99.9% by weight), disodium pentaborate decahydrate ($Na_2O{\cdot}5B_2O_3{\cdot}10\ H_2O$) together with the phosphorus based fire retardant chemical (ammonium phosphate with a purity of 99 % by weight, JT Baker) and its cross-linking agent (dimethylol dihydroxyethylene urea with purity of 99 % by weight) are used to produce a fire retardant solution. Boric acid and borax pentahydrate were provided from Eti Mine Works, Ankara, Turkey. Disodium pentaborate decahydrate was produced according to the previous study (22). Ammonium phosphate and dimethylol dihydroxyethylene urea and cotton fabrics are supplied from Hursan Textile Inc., Denizli, Turkey. The weight of the cotton fabrics were 200 g/m^2 with plain weave texture.

2.2. Experimental Procedure

Phosphorus compound (PC) was dissolved in distilled water and the solution was stirred for 15 minutes at 40 ºC. Dimethylol dihydroxyethylene urea which was used as cross-linking agent, and boron compound (boric acid, BA; borax pentahydrate, BX; disodium pentaborate decahydrate, NB) were added to the solution simultaneously. The resulting solution was stirred again for 15 minutes at 40 ºC for obtaining a homogeneous solution. The fabric having 10×10 cm dimensions was dipped into the prepared fire retardant solution for 5 minutes. It was then squeezed by hand and put into the 150 ºC oven for 5 minutes in order to produce cellulose phosphate by evolving its water content. The fabric was air dried and then analyzed. The samples were subjected to a leaching test by applying BS 5852 standard which is a typical test for treatment of durability of cotton fabrics where the fabric is soaked for 30 minutes in water at 40 ºC (1). The experimental parameters are given in Table 1.

2.3. Analyses

Scanning Electron Microscope, Thermogravimetric analyses and Limiting Oxygen Index were performed to the untreated, treated and washed fabrics. Boron analysis in washing water was also performed.

Scanning Electron Microscope/ Energy Dispersive X-Ray (SEM/EDX) Analysis: Images and elemental composition of the cotton fibers were obtained by a scanning electron microscope using Carl Zeiss Evo 50 EP SEM equipped with Bruker-AXS XFlash 3001 SDD (Silicon Drift Detector).

Limiting Oxygen Index (LOI) Analysis: LOI test was performed according to the ASTM D 2863 standard by Dynisco Limiting Oxygen Index equipment. Materials with an LOI below 25 are classified as combustible whereas those with an LOI above 25 can be classified as self-extinguishing, because their combustion can not be sustained at ambient temperature without an external energy contribution. The higher the LOI gives the better the flame retardant property (23).

Boron Analysis Boron percentage in washing water was determined by titration with standard sodium hydroxide solution in the presence of mannitol. (24,25).

Thermogravimetric (TGA) Analysis: TGA analyses of the treated and washed samples were performed by Shimadzu DTG 60H. The measurements were performed under air flow of 100 ml/min. Uniform heating rate of 20 °C/min was applied during the measurements.

Table 1. Experimental parameters

RUN	PC, %	Cross-linking Agent, %	BA, B %	BX, B %	NB, B %
R1	7.50	2.00	-	-	-
R2	7.50	2.00	1.14	-	-
R3	7.50	2.00	-	1.24	-
R4	7.50	2.00	-	-	1.23
R5	7.50	2.00	1.98	-	-
R6	7.50	2.00	-	2.20	-
R7	7.50	2.00	-	-	1.98
R8	15.00	2.00	-	-	-
R9	15.00	6.00	-	-	-
R10	15.00	12.00	-	-	-
R11	15.00	2.00	1.44	-	-
R12	15.00	2.00	-	1.53	-
R13	15.00	2.00	-	-	1.35
R14	15.00	2.00	2.03	-	-
R15	15.00	2.00	-	2.06	-
R16	15.00	2.00	-	-	2.12
R17	20.00	3.00	-	-	-
R18	20.00	3.00	-	1.00	-
R19	15.00	12.00	-	1.00	-

3. RESULTS AND DISCUSSION

3.1. SEM/EDX Analysis

SEM/EDX analyses of the untreated, treated and treated-washed fabrics were carried out in order to investigate the effect of fire retardant treatment on composition and crystal structure formed on the fabrics. SEM micrographs of the representative fabric samples are shown in Figure 1. For the untreated sample, small amount of particles were observed on the fibers of the fabrics due to the treatments in the production stage (Figure 1 (a)). When fabric was treated with fire retardant solution with/out borax pentahydrate (Figures 1 (b), (d)), the fabric was observed to be covered with particles having size less than 20 µm. After washing, treated fabric returned to its original image (Figures 1 (c), (e)). The compositions of the fabrics analyzed by EDX method showed that application of fire retardant solution resulted in an increase in phosphorus amount on fabric surface which was then reduced after washing of the fabric. Presence of boron on fabric structure could not be detected by SEM/EDX method due to its small contribution to the fire retardant chemical.

3.2. LOI Analysis

Each sample treated with the fire retardant solution with/out boron addition was analyzed with LOI analyzer to obtain the amount of oxygen required to burn the fabric. LOI values of the treated samples were displayed in Figure 2 in terms of percent oxygen. As can be seen from the figure, all the measured LOI values were greater than 45. Therefore, the samples treated with prepared fire retardant solution with/out boron addition turn out to be nonflammable. Synergy provided by boron addition is clearly seen from the figure. The highest LOI value was achieved when 15 % phosphorus compound, 12 % cross linking agent and 1 % borax pentahydrate were used as fire retardant mixture.

Durability of flame retardancy of the treated fabrics was investigated by performing washing tests at 40 ºC for 30 minutes. LOI results of the treated and 5 times washed fabrics are displayed in Figures 3 and 4 in terms of percent oxygen.

LOI results revealed that the prepared fire retardant solution was semi-durable as LOI values of the fabrics decrease after washing due to the cleavage of the phosphate to cellulose bonds which partly destroyed the flame retardancy (1).

As seen from Figure 3, increase of phosphorus compound in the fire retardant solution from 7.5 to 20 % resulted in an increase in LOI of the washed samples from 19 to 21 %. Besides, increase of cross-linking agent in the fire retardant solution from 2 to 12 % increased LOI of the washed samples from 20 to 22.5 %. Figure 4 shows the effect of boron addition to the fire retardant solution. Addition of ~1 % boron to fire retardant solution resulted in an increase of LOI to 22. Further increase of boron to 2 % was found to have no significant change in the LOI values. Among the boron compounds used in the experiments borax pentahydrate was the most effective one which results in an increase in LOI about 10 % with respect to the washed samples treated with fire retardant solution only. The highest LOI for the boron added fire retardant solution was achieved when 15 % phosphorus compound, 12 % cross linking agent and 1 % borax pentahydrate (Run R19) were used.

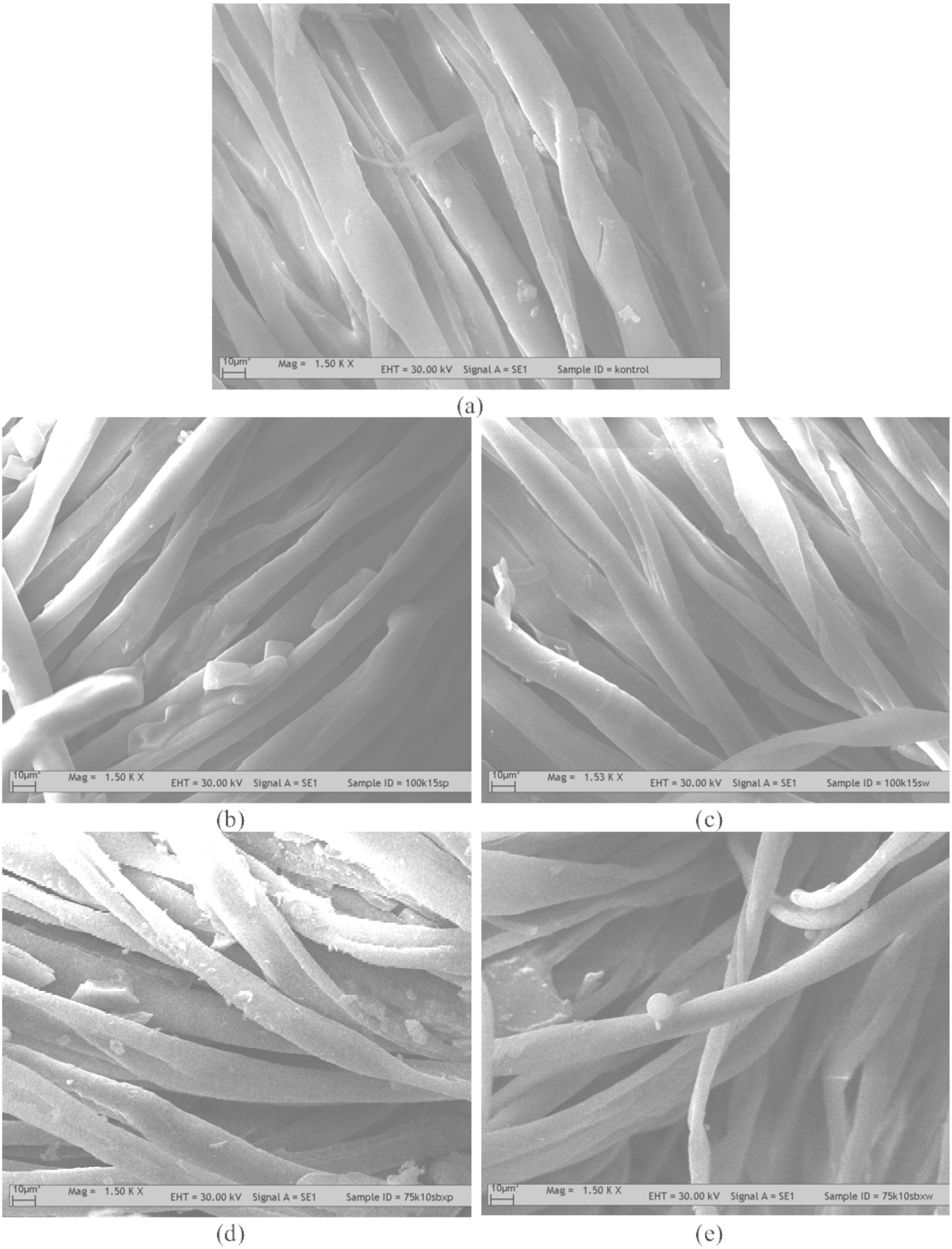

Figure 1. SEM micrographs of (a) untreated fabric, (b) fabric treated with fire retardant solution R17, (c) fabric treated with fire retardant solution R17 and 5 times washed, (d) fabric treated with fire retardant solution R12, (e) fabric treated with fire retardant solution R12 and 5 times washed.

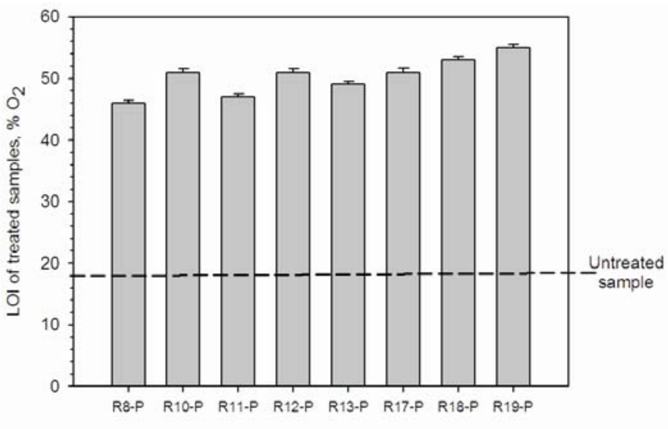

Figure 2. LOI of samples treated with fire retardant solution with/out boron addition (P denotes pre- washed samples).

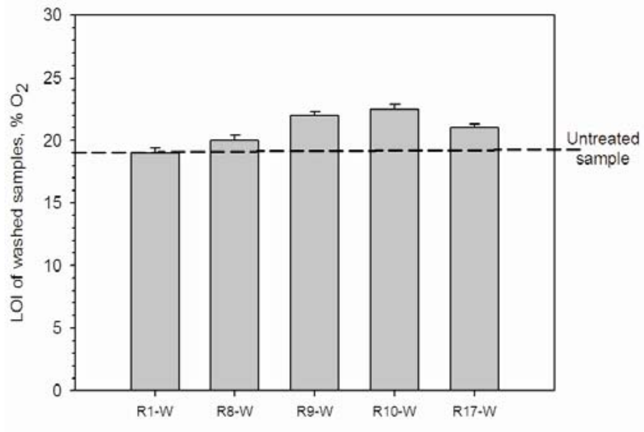

Figure 3. LOI of samples treated with fire retardant solution without boron addition and 5 times washed (W denotes washed samples).

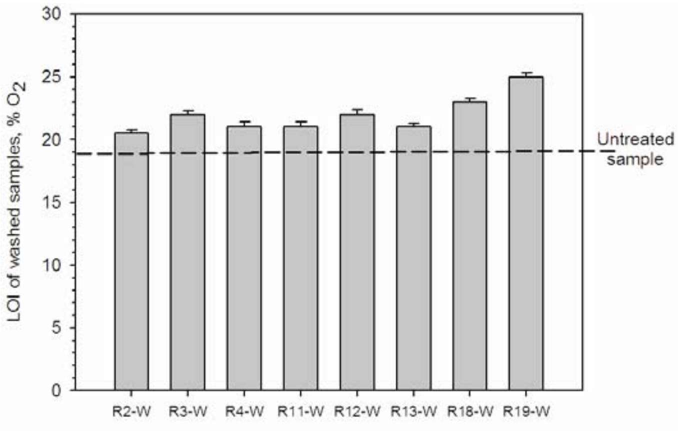

Figure 4. LOI of samples treated with fire retardant solution with boron addition and 5 times washed (W denotes washed samples).

A synergistic effect occurs when the combined effects of two chemicals are greater than the sum of effects of each agent give alone (26). The synergistic effect of phosphorus and nitrogen has been proven to be an effective method for flame retarding cellulose materials (27). Nitrogen is known to demonstrate significant synergistic effect with phosphorous by reinforcing their function. Nitrogen decomposes in the vapor phase to form non-flammable gases such as HNO_2 and HNO_3 and also prevents the phosphorous compounds from being pyrolized in the vapor phase. Phosphorous acts to dehydrate the cellulose to form a layer of non-flammable phosphoric acid which forms char that insulates the condensed phase (28). Boric acid is effective in both flaming and smoldering combustion, whereas sodium borates are effective against flaming combustion but can promote smoldering combustion. When fabrics treated with flame retardants containing phosphorous, nitrogen and boron, combination of different flame retardancy mechanisms increase the overall flame retardancy of the product. Borates are synergistic with N/P compounds in the field of fire retardancy however, solution for problems concerning leachibility is still continuing (26).

Smoke density is another important factor that should be considered during fire. It indicates relative hazard from inhalation of smoke and toxic fumes. The control of smoke is becoming the decisive factor in assessing the fire retardant additives. Smoke density of the samples was also measured during LOI analysis. Smoke formation was not observed even on the untreated fabric. Therefore, smoke formation was not an issue in burning of cotton fabrics.

3.3. TGA Analysis

TGA can be used as an indicator for flammability. TGA of the treated samples and treated-washed samples carried out in air atmosphere are displayed in Figures 5 and 6, respectively, in comparison with the untreated sample. As can be seen from Figure 5, application of fire retardant solution provided a decrease in thermal degradation rate (slopes of the curves) of the fabric that the weight loss of the fabric treated with fire retardant solution reduced about 20 % compared to untreated fabric below 400 °C. Addition of boron to the fire retardant solution resulted in further decrease in weight loss (~35 %) of the fabric at the same temperature. It can be noted that thermal degradation of the untreated fabric was almost finished at about 500 °C whereas treated samples were found to complete above 800 °C which showed the positive effect of fire retardant solution. The same was also valid for the fabrics treated with boron added fire retardant solution that temperature required for complete burning of the fabric was increased. Boron inclusion increased the residual amount from 8 % to 17 %. The weight loss of the treated fabrics was found to remain constant even at 1000 °C.

The effect of washing on TGA of the treated fabrics is displayed from Figure 6. Reduction in thermal degradation rate of the fabrics was observed to reduce after 5 times of washing. However, the positive effect of applying fire retardant solution together with boron was still observed. Weight loss of the fabric treated with fire retardant solution was reduced about 5 % compared to untreated fabric below 400 °C. Addition of boron to the fire retardant solution resulted in further decrease in weight loss (10-15 %) of the fabric at the same temperature. Among the boron types used in the experiments borax pentahydrate was found to be more effective than boric acid and disodium pentaborate decahydrate.

3.4. Boron Analysis

The amount of boron remained on the treated fabrics after washing procedure was determined by boron analysis in washing water. It was obtained that the amount of boron in the washing bath was about 1960 g/l, which refers to the amount of boron (g) bounded to the fabric per 100 g boron loaded to the fabric is greater than 98 % for all the boron treated samples. The amount of the boron bound to the fabric was found to be ~3.3 g /m^2 dry fabric when fabrics were treated with 1 % boron added fire retardant solutions. It can also be noted that boron leaching was almost completed within the first washing period (30 minutes).

4. CONCLUSIONS

Application of a phosphorus based fire retardant chemical and a urea based cross-linking agent incorporated with different types of boron compounds were carried out in this study to investigate the synergic effect of boron on fire retardancy of the cotton fabrics.

The following conclusions were reached under the observations of this study:

1. SEM analysis of the treated and washed fabrics revealed that application of fire retardant chemicals incorporated with boron does not retain any impurities on fabric structure.
2. LOI value jumps from 19 (untreated fabric) to 45-55 for the treated fabrics.
3. Boron addition to the phosphorus based fire retardant chemical and urea based cross-linking agent shows a positive synergy to increase the LOI even after 5 times of washing.
4. TGA analysis show that burning of the untreated fabric was almost finished at about 500 °C whereas treated samples were found to complete above 800 °C.
5. Borax pentahydrate was found to be more effective than boric acid and disodium pentaborate decahydrate to be used in the fire retardancy applications.
6. Boron was almost completely bonded to the fabric that > 98 % of boron remained on the fabrics after 5 times washing for all samples treated with boron added fire retardant solution.

In conclusion, the synergic interaction between phosphorous-nitrogen based flame retardants and boron inhibit thermal decomposition of cellulose, contributes the dehydration process, increasing the amount of solid char and substantially enhance the flame resistance of the treated cotton fabric.

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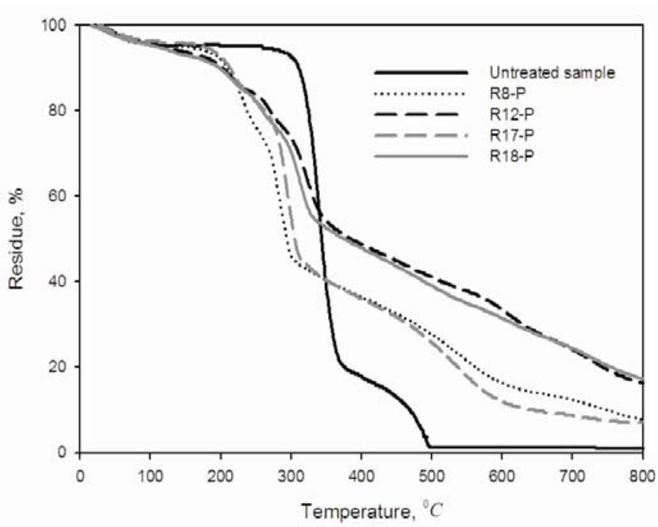

Figure 5. TGA curves for fabrics treated with fire retardant solution (Heating rate: 20 °C min^1, under air atmosphere).

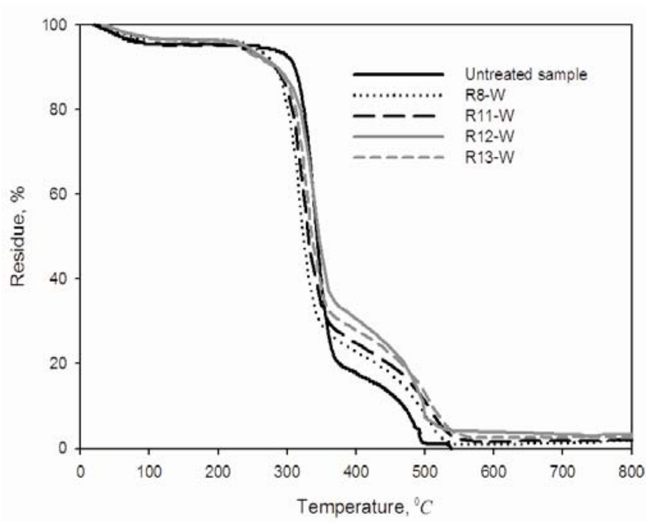

Figure 6. TGA curves for fabrics treated with fire retardant solution and 5 times washed (Heating rate: 20 °C min^{-1}, under air atmosphere).

REFERENCES

1. Weil E. D. and Levchik S. V., 2008, Flame Retardants in Commercial Use or Development for Textiles, Journal of Fire Sciences, Vol 26, pp: 243-276.
2. Martin C., Ronda J.C. and Cadiz V., 2006, Boron-containing Novalac Resins as Flame Retardant Materials, Polymer Degradation and Stability, Vol: 91, pp: 747-754.
3. Horrocks, A.R., Wang, M.Y., Hall, M.E., Sunmonu, F. and Pearson, J.S., 2000, Flame Retardant Textile Back-Coatings. Part 2. Effectiveness of Phosphorus-containing Flame Retardants in Textile Back-coating Formulations, Polymer International, Vol: 49, pp: 1079–1091.
4. Chivas C., Guillaume E., Sainrat A. and Barbosa V., 2009, Assessment of risks and benefits in the use of flame retardants in upholstered furniture incontinental Europe", Fire Safety Journal, Vol: 44 (5), pp: 801-807.
5. Wu W., 2004, Flame Retardant Finishing for Cotton using a Hydroxy-functional Organophosphorous Oligomer, Ph. D. Dissertation, University of Georgia.
6. Willard J. J., and Wondra R. E., 1970, Quantitative Evaluation of Flame-retardant Cotton Finishes by the Limiting Oxygen Index (LOI) Technique, Textile Research Journal, Vol: 40 (3) pp: 203-210.
7. Reeves W. A., Perkins R. M., Piccolo B. and Drake G. I., 1970, Some Chemical and Physical Factors Influencing Flame Retardancy. Textile Research Journal, 40 (3), pp: 223-231.
8. Tesoro G. C. and Meiser C. H., Some Effects of Chemical Composition on the Flammability Behavior of Textiles, Textile Research Journal, 40 (5), pp: 430-436.
9. Lu S.Y. and Hamerton I., 2002, Recent Developments in the Chemistry of Halogen-free Flame Retardant Polymers, Progress in Polymer Science, Vol: 27, pp: 1661–1712.
10. Fontaine G., Bourbigot S. and Duquesne S., 2008, Neutralized Flame Retardant Phosphorus Agent: Facile Synthesis, Reaction to Fire in PP and Synergy with Zinc Borate, Polymer Degradation and Stability, Vol: 93, pp: 68-76.
11. Jimenez M., Duquesne S. and Bourbigot S., 2006, Intumescent Fire Protective Coating: Toward a Better Understanding of Their Mechanism of Action, Thermochimica Acta, Vol: 449, pp: 16-26.
12. Martin C., Hunt B.J., Ebdon J.R., Ronda J.C. and Cadiz V., 2006, Synthesis, Crosslinking and Flame Retardancy Polymers of Boron Containing Difunctional Styrenic Monomers, Reactive and Functional Polymers, Vol: 66, pp: 1047-1054.
13. Yıldız B., Seydibeyoglu M.Ö. and Guner F.S., 2009, Polyurethane-Zinc Borate Composites with High Oxidative Stability and Fire Retardancy, Polymer Degradation and Stability, Vol: 94, pp: 1072-1075.
14. Chattopadhyay D.K., and Webster D.C., 2009, Thermal Stability and Flame Retardancy of Polyurethanes, Progress in Polymer Science, Vol: 34 (10), pp: 1068-1133.
15. Horrocs A. R., 1986, Flame-Retardant Finishing of Textiles, Review in Progress Coloration, Vol: 16, pp: 62-101.
16. Smith J. K., Rawls H. R., Felder M. S. and Klein E., 1970, A Thermochemical Investigation of Cotton Flame Retardancy, Textile Research Journal, Vol: 40 (3), pp: 211-216.
17. Pandya H. B. and Bhagwat M. M., 1981, Mechanistic Aspects of Phosphorus-Nitrogen Synergism in Cotton Flame Retardancy, Textile Research Journal, Vol: 51 (1), pp: 5-8.
18. Momoh M., Eboatu A. N., Kaliel M., and Abdulrahman F. W., 1990, Effect of Flame-Retardant Treatment on the Thermal Behavior of Cotton Fabric, Textile Research Journal, Vol: 60 (10), pp: 557-560.
19. Nakanishi S., Masuko F., Hori K., and Hashimoto T., 2000, Pyrolytic Gas Generation of Cotton Cellulose with and without Flame Retardants at Different Stages of Thermal Degradation: Effects of Nitrogen, Phosphorus, and Halogens, Textile Research Journal, Vol. 70 (7), pp: 574-583.
20. Ozcan G., Dayioglu H. and Candan C., 2004, Impact of Finishing Processes on Flame Resistance of Knitted Fabric, Textile Research Journal, Vol: 74 (6), pp: 490-496.
21. Mettananda C. V. R. and Crown E. M., 2010, Quantity and Distribution of Oily Contaminants Present in Flame-resistant Thermal-protective Textiles, Textile Research Journal, Vol: 80 (9), pp. 803-813.
22. Çakal G., Soylu F. and Çelen E., 2006, Sodium Pentaborate And Its Production Process, Patent No: TR2006 04991 B.
23. Laoutid F., Bonn aud L., Alexandre M., Lopez-Cuesta J.-M. and Dubois Ph., 2009, New Prospects in Flame Retardant Polymer Materials: From Fundamentals to Nanocomposites, Materials Science and Engineering R, Vol: 63, pp: 100–125.
24. Easton A. J., 1972, Chemical Analysis of Silicate Rocks, Elsevier Publishing Company, London.
25. Çakal G., 2004, Dynamic Behavior of Continuous Flow Stirred Slurry Reactors in Boric acid Production, Ph. D. Dissertation, Middle East Technical University.
26. Wilkie C. A., Morgan A. B., 2010, Fire Retardancy of Polymeric Materials, 2 nd Ed.,
27. CRC Press, Taylor & Francis, USA.
28. Lyons J.W., The Chemistry and Uses of Fire Retardants, 1986, John Wiley and Sons Inc., New York.
29. Troitzsch J., International Plastics Flammability Handbook, 1990, 2nd Ed, Hanser Publishing, New York.

Bu araştırma, Bilim Kurulumuz tarafından incelendikten sonra, oylama ile saptanan iki hakemin görüşüne sunulmuştur. Her iki hakem yaptıkları incelemeler sonucunda araştırmanın bilimselliği ve sunumu olarak ***"Hakem Onaylı Araştırma"*** *vasfıyla yayımlanabileceğine karar vermişlerdir.*