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The Combination of Atmospheric Plasma and Chemical Treatments for Antibacterial Finish on Cotton

Pamuklu Kumaşlarda Antibakteriyel Bitim İşlemi için Atmosferik Plazma ve Kimyasal İşlemlerin Kombinasyonu

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THE COMBINATION OF ATMOSPHERIC PLASMA AND CHEMICAL TREATMENTS FOR ANTIBACTERIAL FINISH ON COTTON

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ABSTRACT: The aim of this study was to investigate the incorporation of triclosan based chemical into cyclodextrin based commercial product, bonded onto cotton fabric with and without plasma modification. The treated samples were characterized by SEM analysis. The antibacterial activities of the washed and unwashed samples were evaluated according to the AATCC Test Method 147-1998 and some physical properties were also investigated. It was observed that after the combination process of triclosan, cyclodextrin and atmospheric plasma modification, cotton fabric was able to retain its antibacterial activity up to the 5 washing cycles at 60°C.

Keywords: Cotton, Triclosan, Cyclodextrin, Plasma Modification, Antibacterial Textile

PAMUKLU KUMAŞLARDA ANTİBAKTERİYEL BİTİM İŞLEMİ İÇİN ATMOSFERİK PLAZMA VE KİMYASAL İŞLEMLERİN KOMBİNASYONU

ÖZET: Bu çalışmanın amacı, triklosan esaslı kimyasal ile siklodekstrin esaslı ticari ürün birleşimin plazma modifikasyonu yapılarak ve yapılmayarak pamuklu kumaşlara bağlanmasının incelenmesidir. İşlem gören numuneler SEM analizi ile karakterize edilmiştir. Yıkanmış ve yıkanmamış kumaşların antibakteriyel aktiviteleri AATCC Test Metot 147-1998'e göre değerlendirilmiş ve numunelerin bazı fiziksel özellikleri de incelenmiştir. Triklosan, siklodekstrin ve atmosferik plazma kombinasyonu ile pamuklu kumaşların antibakteriyel aktivitesini 60°C'de 5 yıkamaya kadar koruduğu gözlenmiştir.

Anahtar Kelimeler: Pamuk, Triklosan, Siklodekstrin, Plazma Modifikasyonu, Antibakteriyel Tekstil

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1. INTRODUCTION

Natural fibers such as cotton, wool, and flax are generally more susceptible to bacterial attacks than synthetics because of their porous hydrophilic structure. Therefore, the antibacterial activity is an important property for cellulosic functional fabrics. The durability of the antibacterial action of textile materials is essential and a number of approaches have been used for this aim [1, 2]. Triclosan [5-chloro-2-(2.4-dichlorophenoxy) phenol] is known as an effective finishing agent for textile applications [1]. At bactericidal concentration, triclosan is very effective against a broad range of microorganisms, including antibiotic-resistant bacteria [3]. Triclosan inhibits the growth of microorganisms by inhibiting fatty acid biosynthesis through blocking the active site of the protein reductase enzyme (ENR), which is fundamental for fatty acid synthesis in bacteria. By blocking this enzyme, the bacteria can't synthesize fatty acid, which is necessary for building cell membranes and reproducing [1, 4]. Cyclodextrins, which are obtained from degradation of starch by the cyclodextrin transglycosylase enzyme, belong to the family of oligosaccharides. Polar and hydrophilic outer surface and hydrophobic cavitation of cyclodextrins enable them to retain hydrophobic compounds in a hydrophilic medium. As a result of this retention, they can form inclusion complexes (host–guest complexes) with many other organic compounds. Inclusion complexes are used widely in the food, pharmaceutical, medical, chemical, and textile industries. Since cyclodextrins do not cause any problems in waste water and are biodegradable, they are suitable for using as auxiliary agents in textile finishing [4-9]. In order to make a treatment durable, β-cyclodexrins are modified by adding reactive groups that are able to graft on textiles. In general, reactive cyclodextrins are grafted on the fabric and the active agent is complexed into cyclodextrin cavity [21]. Fabrics have been finished with cyclodextrin complexes to attain wash resistant, odor absorbing, antimicrobial, and insect resistant properties [4].

Plasma is a dry process providing modification of the top nanometric surface without using solvents or generating chemical waste. The type of functionalisation imparted can be varied by the type of plasma gas (e.g. Ar, He, N_2, O_2, H_2O, CO_2 and NH_3) and operating parameters (e.g. power, time and gas flow rate) [10, 11]. Despite the fact that more studies have been done concerning the antibacterial activity of triclosan, the combination of triclosan application with plasma technology and cyclodextrin compound has not been studied in details yet.

The aim of this study was to investigate the incorporation of triclosan based chemical into cyclodextrin based commercial product, bonded onto cotton fabric with and without plasma modification. The plasma+ cyclodextrin+ antibacterial agent treated samples were characterized by SEM analysis. To evaluate the washing durability the treated samples were washed up to five cycles. The antibacterial activities of the washed and unwashed samples were evaluated according to the AATCC Test Method 147-1998 and some physical properties were also investigated.

2. MATERIALS AND METHOD

2.1. Materials

100% scoured and bleached plain woven cotton fabric with a weight of 153 g/m^2 was used in the experiments. Yarn count of the fabric was Ne 30 and Ne 20 for weft and warp respectively. Weft yarn per unit length was 28 yarns/cm, warp yarns per unit length was 20 yarns/cm. The cotton fabrics were cut in the size of 10 cm x 50 cm. For the finishing process, triclosan based chemical and β-cyclodextrin based commercial product in recommended concentrations were applied to the cotton fabrics with and without plasma modification. Triclosan based chemical and β-cyclodextrin based commercial product were supplied from Setas and Huntsmann respectively.

2.2. Methods

A hand-made dielectric barrier discharge (DBD) atmospheric plasma device was used. The distance between the electrodes was 0.2 cm. The samples were placed between the electrodes and passed continuously with the speed of 0.45 m/min. In all treatments, argon gas was used under a constant power of 130 W with 0,5 l/min gas flow. Argon gas was selected due to its effects on surface activation of cotton fabrics as observed from the previous studies [11,18,19,20]. The samples were treated for 20 secs in the plasma. After plasma treatments, there are two different chemical applications. Two chemicals (Triclosan based antibacterial chemical and β-cyclodextrin based chemical) were used. The first treatment is with only antibacterial agent; second one is with cyclodextrin and antibacterial agent. Cotton samples were dipped in the triclosan based antibacterial agent of 30 g/l at pH 7 and then padded with a wet-pick-up of 80±1% at room temperature. The padded materials were then dried at 100^{0}C for 2 min and cured at 130^{0}C for 3 min [21]. For the combination of triclosan based antibacterial agent and β-cyclodextrin based chemical, the samples were firstly treated according to the Figure 1 (the fabric was added immediately after dissolution of cyclodextrin and Glauber's salt.) and then treated with antibacterial agent as mentioned before.

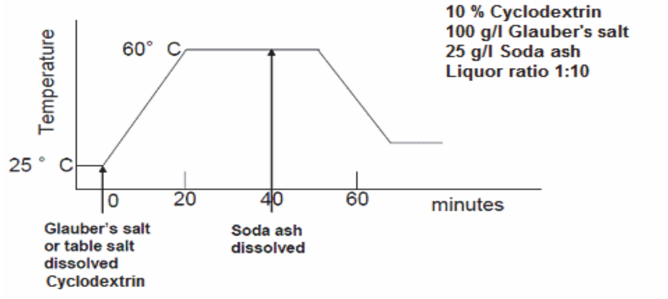


Figure 1. The graph of cyclodextrin treatment

To evaluate the washing durability, the treated samples were washed in Linitest Plus (Atlas), with a liquor ratio of 50:1. Washing process was carried out at 60^0C for 30 min. In order to prevent any antibacterial effects of detergent, washings were carried out in an additive free soap solution with a concentration of 5 g/l. After washing, the samples were rinsed in cold pure water, squeezed and dried at room temperature.

The structures of the Plasma+ Cyclodextrin+ Antibacterial agent combination process treated cotton fabrics before and after, first and fifth washing cycle and untreated cotton fabric were determined by scanning electron microscopy (SEM) using Phillips XL-30S FEG device. The finishing process should not affect the physical properties of textile material negatively. To investigate this fact, some physical properties like whiteness index, tensile strength and bending length were also tested as well as antibacterial activity and washing durability.

Tensile strength tests were carried out according to ISO 13934-1 on a Lloyd Tensile Tester. Five samples for each sample were tested and averages of the test results were calculated.

Bending length measurements were performed on a Shirley stiffness tester according to TS 1409. The whiteness index (CIELAB) (WI CIE) of the fabrics was determined by using a reflectance measuring HunterLab ColorQuest II spectrophotometer (HunterLab, USA) at standard illuminant D_{65}.

The antibacterial activity was also assessed after the first and fifth washing cycles. AATCC Test Method 147-1998 was used to test the antibacterial activity of the untreated and all treated fabrics. Two different kinds of bacteria, *Staphylococcus aureus* (ATCC 6538) as Gram positive bacteria and *Klebsiella pneumoniae* (ATCC 4352) as Gram negative bacteria were studied. All tests were performed in duplicate.

3. RESULTS AND DISCUSSION

3.1. Antibacterial Test Results

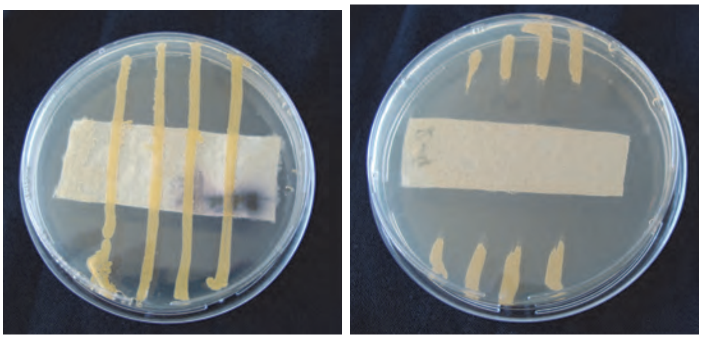
The antibacterial activity results of the treated cotton samples are given in Table 1.

It was observed that the combination process of plasma, antibacterial agent and cyclodextrin had better antibacterial activity than other processes. The order of the clear zones was plasma+cyclodextrin+antibacterial agent treatment > cyclodextrin+antibacterial agent treatment > plasma+antibacterial agent treatment > only antibacterial agent treatment. So, it was concluded that the combined processes were more effective than only one process. It can be also concluded that cyclodextrin treatment is more efficient than plasma treatment in terms of antibacterial activity.

According to the clear zone diameters, it was also observed that the antibacterial activity was better against *S.aureus* (gram positive bacteria) than *K.pneumoniae* (gram negative bacteria). This result confirmed the previous study of Orhan et al [12].

After washing process, the antibacterial activity slightly decreased. It was found that the effects of the treatments depended on the bacteria species. However, the best antibacterial results were obtained by the combination process of plasma, antibacterial agent and cyclodextrin. After fifth washing cycle, the clear zone was considerably changed and there was only slight activity under the samples. Figure 2 shows the antibacterial activity of the untreated and combination treated samples against *S.aureus*.

As seen in the Figure 2, heavy growth of bacteria was observed both under and around the untreated sample. Otherwise, clear inhibition zones were seen around all treated samples.



(a) (b)

Figure 2. The inhibition zones of the samples (a) untreated cotton (b) Plasma+Cyclodextrin+ Antibacterial agent treated cotton

Table 1. The clear zone diameters of the treated cotton samples

Treatment	Clear zones in mm					
	S.aureus			***K.pneumoniae***		
	Before Washing	***After first Washing***	***After fifth Washing***	***Before Washing***	***After first Washing***	***After fifth Washing***
1. Untreated cotton	Growth	Growth	Growth	Growth	Growth	Growth
2. Only Antibacterial Agent	12	9	1	7	1	Light growth
3. Cyclodextrin + Antibacterial Agent	15	14,5	6	9	3	Light growth
4. Plasma + Antibacterial Agent	13,5	10	4	8	1	Light growth
5.Plasma+Cyclodextrin+ Antibacterial agent	17	15	8,5	11	3,6	Contact zone

The increase in the activity and the stability of the samples after plasma based treatment was thought to be due to the chemical modifications on the fiber surface. This fact probably influences the adsorption of the particles, and other sorptive properties of the fiber [13].

3.2. SEM Analysis

In Figure 3, the SEM images of the untreated and the combination process treated cotton are shown.

As seen from the images, the untreated cotton surface is quite smooth and clean whereas the combined process treated cotton surface is rougher and full of microcracks, which occurred because of the etching effect of plasma treatment [11,18,19,20]. Also the particles of cyclodextrin and antibacterial agent can be observed on both washed and unwashed samples. As expected, after washing there was a decrease in the amount of the adsorbed particles. From the previous studies, it was also reported that plasma treatment was a useful technique to modify polymer surfaces and leaded to polymerization, grafting and crosslinking of chemical inclusion [4, 14]. Our antibacterial test results and SEM images verified this fact.

3.3. Physical Properties

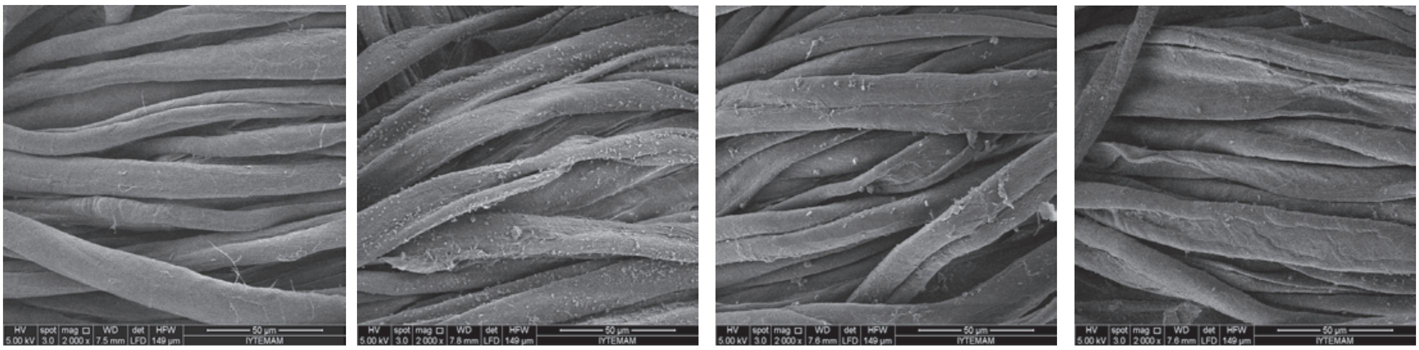
The whiteness color index values of the samples are shown in Table 2.

Since the process conditions were mild, any significant difference in whiteness of the samples was not observed when compared to untreated one. This fact verified that there was no negative effect like yellowness arised from antibacterial finishing. In addition to this, after washing, the whiteness index increased in all samples.

The bending length values of the samples are given in Table 3.

According to the standard, the higher the bending length values, the higher the stiffness. From the results, it can be concluded that there was no deterioration in the handle of the samples, but there was a little improvement in terms of all treatments. However, after washing, it was observed a slight increase in stiffness.

The tensile properties of a fabric depend on various factors and the applications like washing, coating etc., and changes in fabric structure would extremely affect the tensile strength [15, 16]. According to the Table 4, the reduction in tensile strength can be seen clearly. But the values are still in acceptable limits. As seen in the Table 4, only antibacterial agent treatment and cyclodextrin + antibacterial agent treatment did less reduction than the plasma based treatments. This fact was attributed to the formation of plasma induced micro-cracks as shown in SEM and degradation of the fibers to some extent after plasma subjection [16, 17].



(a) (b) (c) (d)

Figure 3. SEM images of the samples (a) untreated cotton (b) Plasma+ Cyclodextrin+ Antibacterial agent treated cotton (c) Plasma+ Cyclodextrin+ Antibacterial agent treated cotton after first washing (d) Plasma+ Cyclodextrin+ Antibacterial agent treated cotton after fifth washing

Table 2. Whiteness color index values of the samples

Treatment	***Whiteness Color Index***		
	Before Washing	***After first Washing***	***After fifth Washing***
Untreated	76,51	79,58	82,47
Only Antibacterial Agent	77,21	83,47	94,15
Cyclodextrin + Antibacterial Agent	74,08	79,13	89,95
Plasma + Antibacterial Agent	75,46	82,28	91,18
Plasma+Cyclodextrin+ Antibacterial agent	74,08	76,22	83,24

Table 3. Bending length values of the samples

Treatment	*Bending length values (cm)*		
	Before Washing	*After first Washing*	*After fifth Washing*
Untreated	2,45	2,46	2,49
Only Antibacterial Agent	2,45	2,48	2,48
Cyclodextrin + Antibacterial Agent	2,23	2,33	2,33
Plasma + Antibacterial Agent	2,33	2,38	2,38
Plasma+Cyclodextrin+ Antibacterial agent	2,20	2,25	2,30

Table 4. Tensile strength properties of the samples

Treatment	Tensile strength (N)			Tensile strength reduction (%)		
	Before Washing	*After first Washing*	*After fifth Washing*	*Before Washing*	*After first Washing*	*After fifth Washing*
Untreated	678,2	671,4	667,5	-	1,00	1,57
Only Antibacterial Agent	660,3	647,5	625,3	2,64	4,52	7,80
Cyclodextrin + Antibacterial Agent	656,1	641,3	622,5	3,26	5,44	8,21
Plasma + Antibacterial Agent	619,6	608,6	591,7	8,64	10,26	12,75
Plasma+Cyclodextrin+ Antibacterial agent	611,0	603,9	601,7	9,91	10,95	11,27

4. CONCLUSION

This work suggested an alternative process for antibacterial finish on cotton treatment with triclosan based chemical, cyclodextrin based commercial product, plasma modification and their different combinations. It was observed that after the combination process of triclosan based chemical, cyclodextrin and atmospheric plasma modification, cotton fabric was able to retain its antibacterial activity up to the 5 washing cycles at 60°C. Plasma modification promoted the stability but the effect of β-cyclodextrin was found to be more significant than plasma application. Antibacterial test results showed that five washing cycles caused decreases in the values of clear zone diameters but the antibacterial activity was still observed in all treated samples. In addition, in terms of washing durability, the most effective one was found to be the triple combination. SEM analysis also indicated the cyclodextrin and antibacterial agent particles were grafted onto the cotton surface and plasma modification promoted the stability. It was also found that the physical properties of the samples were not severely affected by these alternative processes.

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