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Improving Washable Woolen Fabric by Using Layer-By-Layer Coating

Şule Sultan Uğur[1] 0000-0002-6485-7172
Nazlı Çağlar Cinperi[2] 0000-0001-6858-5760
Ayşe Merih Sarıışık[3] 0000-0003-0402-2955

[1]Süleyman Demirel University, Textile Engineering Department, Isparta, Türkiye
[2]R&D Department of Yunsa, Çerkezköy, Tekirdağ, Türkiye
[3]Dokuz Eylül University, Textile Engineering Department, İzmir, Türkiye

ABSTRACT

There are many different methods used in the industry to upgrade the antifelting and shrinkproof feautures of wool blended fabrics. In the study, Layer-by-Layer technique used to improve the antifelting and shrinkproof properties of wool blended fabrics as an effective nanofabrication method according to the literature. Different polyelectrolytes and nano-polyurethane were applied on ecru and light, medium, dark color dyed suit wool blended fabrics by using Layer-by-Layer method. After the application fabrics, relaxation and felting shrinkage, breaking and tear strength tests and color/strength measurements were performed. Besides, the effect of squeezing roller velocity and pressure on the fabrics were evaluated. It is ensured that the relaxation and felting shrinkage values are within ± 3% and observed soft-handle fabrics. In addition, SEM-EDX and FTIR-ATR analysis were performed to determine the surface properties of the fabrics and bond characterization of the films.

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Washable woven wool blended fabric, layer-by-layer method, felting shrinkage, relaxation shrinkage, nano polyurethane

1. INTRODUCTION

Wool based textiles are sensitive to felting in the wet state and lean to shrink when subjected to mechanical stress under washing conditions. Due to the nature of wool, flake layers on the surface are intertwined and cause felting with mechanical effect, exposure to alkaline or acid solutions. The felting fabric becomes rigid by hardening and thickening. The felting garments lose air permeability, soft and airy grip and the fabric becomes hard and thick in a period that has not changed in size. The woolen fabrics cannot be washed, the cleaning is done with organic solvents. However, washing the wool with water has always been the wish of the user. Anti-felting treatments are aimed to within certain limits subtract the scales or to smooth the edges from the overlapping scales to decrease the felting tendency and make washable woollen fabrics. There are several methods in the industry to increase the washability of woven wool fabrics such as removing, adding and combining methods. Many different methods have been applied in the past and the oxidation of disulfide bonds of wool, called the Hercosett method, has been shown to be the most effective method. Cardamone et al., examined the effectiveness of applying hydrogen peroxide treatment before enzymatic incubation and showed that the shrinkage value of the fabric obtained as a result of the DCCA-Hercosett treatment was approximately 5 %. However, because of such treatment the tensile strength was reduced by approximately 70% [1]. Even though different methods are used to improve the antifelting and shrinkproof properties of woven wool and wool blended in the industry, desired values (<± 3%) cannot be obtained because of felting shrinkage test even if good values are obtained in size change as a result of relaxation shrinkage test using more than one method. Commercial antifelting treatments which are using strong oxidants such as chlorine

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and its derivatives, producing harmful absorbable organic halogens (AOX), causing wastewater pollution and changing of the natural soft handle of wool. Besides resulting a hard handle, additional operations must be applied. This results extra cost by the terms of both energy and chemicals.

For obtaining machine washable standards with avoiding release of AOX, novel and environmentally friendly processes must be developed. Coating with polymer resin is an alternative method to obtain satisfying anti-felting property. But to provide the machine washable standards a large number of resins should be required and thus cause wool fabric a stiff handle. Some researchers used the modified enzyme for the wool fabric treatment which shows improvement of antifelting property. But enzymes modification (immobilization of enzyme) would be too expensive to achieve industrialization. Nowadays, many types of biopolymers such as sericin, collagen and casein are applied for antifelting treatment, where a softer grip can be obtained according to synthetic resins [2-3].

With the studies made, nano polyurethane (Nano PU) is used to achieve a felting shrinkage value of ± 3% in suit and uniform fabrics with multi-layer coating method. It has been found that the nano polyurethane based multilayer coating has soft handle fabrics that do not have a negative effect on the fabric [4,5]. There are many applications in the literature which are made by textile coating with multilayer coating method. Xu et al. applied atmospheric pressure plasma treatment on the wool with a mixture of pure helium and helium/oxygen and investigated the effects of absorbed moisture on antifelting property of wool [6]. Montazer et al. investigated antifelting and antibacterial properties of oxidized and non-oxidized wool samples after application of nano-titanium dioxide on and observed improved shrinkage values [7]. Wang et al. studied on providing bio-antifelting properties to wool by the combination of cutinase, keratinase and protease enzymes. Efficient results were obtained with the combination of cutinase and protease enzymes and it was stated that the shrinkage values could be reduced by 5.2% [8]. Shen et al., have shown that the thermal stability of the enzymes is improved by chemical modification of the proteases with Eudragit, imparting a machine washable fabric felting effect in accordance with Woolmark standards [9]. Kotlińska et al. studied on enzymatic applications in order to develop environmentally friendly processes instead of chlorine treatment with the same level of anti-shrinking and anti-felting properties [10]. In another bio-antifelting study worked by Zhao et al., shrinking rate of the treated wool fabrics was decreased from 5.24% to 0.70% by using waterborne polyurethane and cellulose nanocrystal [11]. Shi et all., used polyurethane/chitosan bio-composite emulsion to treat wool fabric and obtained soft-handled anti-felting effect [12]. Kaur and Chakraborty were used bromelain along with salt in acidic pH for controlled superficial hydrolysis of wool. It has been determined that the addition of salt at pH 6 provides controlled adsorption of bromelain on the outer surface of the wool, providing anti-felting behavior with minimal weight and strength loss [13]. Du et all., obtained a biocomposite from keratin polpeptides and water-based polyurethane and then applied it to wool febrics using the pad-dry-cure method as s bio-anti-felting agent. The results indicated that with 6 wt. % content of keratin polypeptides in the biocomposite, the area-shrinking rate of the treated wool fabrics was obtained 0.47 % [14]. Ugur et al. performed different cationic polyelectrolyte types, different layers on the wool fabrics by electrostatic self-assembly with nano polyurethane [15]. Chen and his colleagues conducted a multi-layered construction on a cotton surface with a self-repairing ability, which was a flammable feature [16]. Ahmed and Emam worked on multi-layer coating of nano silver for high performance cotton fabric [17]. Truong-Phuoc et al. have worked on multilayer photocatalytic devices for textile products that have become self-cleaning with sunlight [18]. Junthip et al. have studied the coating of textile products for extended drug release by multi-layer coating with two oppositely loaded cyclodextrin polyelectrodes [19]. Tian et al. have worked on the ultraviolet protective cotton fabric obtained by self-assembled graphene oxide and chitosan method and electrostatic multi-layer coating method in 2016 [20]. Uğur et al. worked on the multilayer coating system of antibacterial inclusion complexes [21]. Forsman et al. have worked on multi-layered hydrophobic coatings for cellulose nanofibril films and textile products, polylysine and natural-derived particles [22]. Iglesias et all., aimed to assess the potential of proteolytic enzymes in combination with Bacillus subtilis O9 biosurfactant, to reduce felting of Merino wool. The combination of biosurfactant pre-treatment followed by protease treatment rendered the significantly smallest felting density [23]. Li et all., investigated the surface modification of wool by controlled proteinase K treatment with a bioprocess approach to ensure machine washability of wool. While 18% shrinkage reduction decreased to 6,6 and 4,7 % at 8 U/g and 16 U/g enzyme concentrations, respectively, it was found that strength losses increased with increasing enzyme dosages [24]. Cong et al. found that the flake layers of the surface of the wool fibers in knitted wool fabrics for sportswear treated with low oxygen plasma applied severely abraded, and the anti-felting, bursting strength and mouisture absorption properties of knitted wool fabrics were improved [25]. Liu et all., synthesized N-phenylmaleimide (NPMI) and applied it to wool fabrics to obtain antimicrobial properties. After teratment, the composite wool fabric shows excellent bactericidal properties after 10 standard washing tests and improved anti-felting performance compared to the original wool fabric [26].

When the studies carried out in the literature, it is still important to develop more effective and less harmful methods to the environment to improve the anti-felting feature of woolen fabrics. LbL assembly which has been applied to a large variety of polymers and nanomaterials is

a simple and versatile method for material design with nanoscale control over internal architecture. LbL deposition process does not require large investment costs because it is water-based and can be adapted to the impregnation method used in textile finishing. In our previous study, successful results were obtained on 100% wool fabrics with the layer by layer (LBL) method which is one of the most effective and new methods was applied on worsted wool and wool blended fabrics [27,28].

Since the anti-felting process should be applied as a finishing process, it is aimed to investigate the effectiveness of the LbL method using Nano polyurethane, especially on woolen fabrics with different fiber contents and dyed in different colors. In this study, optimum conditions that's we obtained in our previous study were applied to fabrics in the same blends dyed in light, medium and dark colors. In another experiment set, LbL application was veri on the fabric dyed in dark colors at different squeezing roller velocities and pressures.

2. MATERIAL AND METHOD

2.1 Material

In this research, four cationic polyelectrolytes; two cationic dye fixatives (CDF-1, CDF-2), cationic poly (diallyl dimethyl ammonium chloride) (PDDA) and Poly (acrylamide-co-diallyldimethylammonium chloride) (P(AAm-co-DADMAC)) and nano polyurethane were used at the experiments (Table 1). Polyelectrolyte and polyurethane solutions were prepared in determined concentrations and mixed using a magnetic stirrer&heater. The prepared solutions were adjusted to optimum pH values using dilute hydrochloric acid and sodium hydroxide.

One of the selected polyelectrolytes for the experiments is PDDA which is a colorless liquid completely soluble in water, having a density of 1.04 g/cm^3. The other type of polyelectrolyte is P(AAm-co-DADMAC), a viscous, colorless liquid with a pH of 5-8. One of the commercial cationic dye fixatives was selected as CDF-1. The aqueous solutions of this product are used as an enhancer for fastness (especially rubbing and water fastness) for polyester fabrics in the textile industry; at the same time, it increases the washing strength without changing the handle of pigment printed fabrics. It is a clear yellow liquid with a pH of around 3, which can dry at 130-140 °C. Another commercial polyelectrolyte used is CDF-2. It is an anionic, water-soluble yellow liquid with a pH of 6, is a product used for post-staining cleaning of polyester and blends in the textile industry.

Ecru, light, medium and dark colored Wool/Nylon/Elastane (WO/PA/EL) % 86/10/4 blend fabrics were used for coating processes and the encoded given for the samples are given in Table 2.

2.2 Method

LbL method was applied on light, medium and dark color shaded 86/10/4 wool/nylon/elastane blended fabrics by using a horizontal foulard with a Cr-Ni stainless steel body that can be adjusted to a roller speed of 550 mm wide and 70 Shore rigid, adjustable roller pressure of 1-6 bar and roller speed of 0.5-7 m/min was used.

The process was initiated by applying a loaded polyelectrolyte solution in contrast to the fabric surface charge. The excess polymer solution on the fabric surface was removed with the help of the foulard using softened water and then coated with a nano-polyurethane solution containing a counter-charged polyion to reverse the surface charge again. The excess polymer solution was removed by washing with softened water. Each polymer solution applied to the surface was evaluated as a layer and operations were continued until the total number of layers was reached. The nano-layered fabrics obtained after the coatings were dried at 130 ºC and fixed at 180 ºC in the mini-stenter machine at the end of the mill; was subjected to a decatising process. These polyelectrolytes and nano polyurethane solution ratios and application conditions can be seen from Table 2.

Table 1. Properties of the chemicals

Chemicals	Properties	Company
PDDA	Light yellow liquid, pH (25 °C): 5-8 completely soluble in water density (23 °C): 1,04 g/cm^3	Sigma Aldrich
P(AAm-co-DADMAC)	Colorless liquid, pH (25 °C): 5-8	Sigma Aldrich
Akfix PES (CDF-1)	Clear yellow liquid, pH: 3.0 ± 1.0 Purpose: Fastness for PES fabrics	Akkim Chemicals
Zetesal NWM (CDF-2)	Yellow liquid, pH: around 6 Purpose: dye cleaning agent	Tex-Tek Chemical Industries
Nano PU	Yellowish liquid, pH (20 °C): 4,5-5,5 Particle size: <100 nm Ionicity: Amphoteric / anionicDensity (23 °C): 1,10 g/cm^3 Viscosity: about 50 mPa.s	Tanatex Chemicals

Table 2. Application conditions

Sample No	1-19	20-31	32-37
Fabric Blend	86/10/4 wool/nylon/elastane	86/10/4 wool/nylon/elastane	86/10/4 wool/nylon/elastane
Fabric Shade	Ecru	Light, medium, dark	Dark
PU Concentration (g/l)	50	50	50
pH of PU	4.95	4.95	4.95
Polyelectrolyte Concentration (g/l)	10	10	10
pH of polyelectrolyte			
P(AAm-co-DADMAC)	7,77	NU	NU
PDDA	9,5	NU	NU
Akfix PES (CDF-1)	4,5	4.5	NU
Zetesal NWM (CDF-2)	NU	4	4
T of solution (°C)	25, 50, 65	25*, 50**, 65**	50
Layer Number	12, 16	16	16
Squeezing Roller Pressure (bar)	3	3	2, 3
Squeezing Roller Velocity (m/min)	3	3	1, 2, 3
Drying Temperature (°C)	130	130	130
Fixation Temperature (°C)	180	180	180
Fixation Velocity (m/min)	1	1	1
Decatising Pressure (bar)	1	1	1

*25 °C for CDF-1,
**50 & 65 °C for CDF-2 solution
NU: not used in the experiment

To examine the effects of the multilayer coating method on fabric, 5A and 7A wash shrinkage (TS 5720 EN ISO 6330 standard), breaking strength (TS EN ISO 13934 standard) and tear strength (TS EN ISO 13937 standard) tests were performed. Also, the change in fabric color (K/S) was measured. Whiteness indexes were measured in the CIE Lab system with D65-10 measurement in the spectrophotometer. Test results were evaluated comparatively and the optimum conditions for cationic polyelectrolyte type, solution application temperature and number of coating layers, squeezing roller velocity and squeezing pressure were determined. QUANTA 400F Field Emission high-resolution scanning electron microscope (SEM) with Energy Dispersive X-Ray Analysis (EDX) was performed to examine the surface properties and elementary analysis of multi-layer film-coated wool blended fabrics at an acceleration voltage of 10 kV. A Bruker IFS 66/S FTIR spectrometer with an ATR sampler was used to obtain the infrared spectra of surfaces in the range of 400- 4000 cm^{-1} with a resolution of 2 cm^{-1}.

3. RESULTS AND DISCUSSION

In previous studies, four different cationic polyelectrolyte types, 3 different solution application temperatures and 2 different layers were performed on the ecru fabrics in 100% wool (WO) and various conditions were achieved and optimum conditions were obtained [15, 27]. These conditions were applied on ecru, light, medium and dark colored Wool/Nylon/Elastane (WO/PA/EL) blend fabrics [28]. In this study, LBL application was done on the fabric dyed in dark colors at different squeezing roller velocities and pressures.

In the previous study, it was seen that the values of relaxation and felting shrinkage values were improved and the standards of quality test values were provided. It was seen that the multilayer coating applications on 100% ecru wool fabric using CDF-1 solution, a commercial product, gives the best values. It increases the washing resistance without changing the soft handle of the fabrics. It has also been observed that the increase in temperature improves the washing shrinkage values [27]. When relaxation and felting shrinkage test results of ecru wool blended fabrics are examined, it is also seen that the CDF-1 gives lower shrinkage values compared to other polyelectrolytes (Table 3).

Using the commercial cationic dye fixture (CDF-1) on 100% ecru wool fabric increases the tear strength as the temperature and the number of layers increase [16]. On the other hand, the effect of the application on 86/10/4% wool/nylon/elastane fabrics on tensile and strength values can be observed from Table 4 and it is seen that CDF-1 gives lower tensile values than other polyelectrolytes for 86/10/4% wool/PA 6.6/elastane fabrics. The whole tensile strength of the multilayer film coated wool fabrics was slightly reduced compared to the untreated fabric. This is estimated because the wool fabric was slightly damaged during the pH changes of the layers in the cotaing process.

The whiteness indexes were measured and compared for examining the color change on the fabric caused by the application. After application, it was seen the 100% wool fabrics tend to be yellowing in certain amounts [16]. When the test results of wool blend fabrics are evaluated, it was seen that P(AAm-co-DADMAC) polyelectrolyte increased the whiteness change value and the change of whiteness decreased with the other polyelectrolyte (Table 5).

The effects of the application on fabrics dyed in three different colors were also investigated. Dimension changes after washing and fabric quality control tests were performed on fabrics; K/S values were compared. In addition, the color values (L, a, b) were examined and the color changes of the fabric were observed (Table 6, 7, 8). The light, medium, dark shades in the table represent the color tone of the fabric.

Table 3. Relaxation and felting shrinkage test results of ecru 86/10/4 % wool/PA 6.6/elastane fabrics

Sample Number	Polyelectrolyte Name	T of the solution (◦C)	Layer number	pH of PU	pH of poly-electrolyte	Warp (% change)				Weft (% change)			
						7A Fabric	7A Cuff	5A Fabric	5A Cuff	7A Fabric	7A Cuff	5A Fabric	5A Cuff
1	-	25	0	-	-	-2,60	-3,00	-11,00	-12,00	-6,50	-4,75	-8,00	-7,00
2	P(AAm-co-DADMAC)	25	12	4,95	7,77	3,00	-2,00	3,50	-4,50	1,20	1,50	-1,60	1,75
3	P(AAm-co-DADMAC)	25	16	4,95	7,77	-0,50	-2,00	-0,50	-3,00	0,50	1,00	0,75	2,50
4	P(AAm-co-DADMAC)	50	12	4,95	7,77	-1,00	-2,00	-1,00	-4,00	0,80	0,50	1,50	0,50
5	P(AAm-co-DADMAC)	50	16	4,95	7,77	1,30	1,00	1,50	0,25	1,30	1,00	1,75	2,00
6	P(AAm-co-DADMAC)	65	12	4,95	7,77	-1,00	-1,00	-4,60	-6,50	0,80	2,00	-0,50	1,50
7	P(AAm-co-DADMAC)	65	16	4,95	7,77	-2,00	-2,50	-5,50	-7,75	-4,00	-3,00	-1,00	-0,25
8	PDDA	25	12	4,95	9,50	-2,50	-2,50	-4,10	-4,50	-0,25	0,25	-0,60	-0,50
9	PDDA	25	16	4,95	9,50	-3,00	-3,50	-5,30	-6,00	-0,90	0,00	-1,30	-2,00
10	PDDA	50	12	4,95	9,50	-2,60	-2,75	-4,00	-4,50	-1,10	-0,25	-1,10	-0,25
11	PDDA	50	16	4,95	9,50	-2,10	-3,00	-3,30	-5,30	-0,60	-0,25	-1,30	-0,50
12	PDDA	65	12	4,95	9,50	-2,60	-3,25	-4,30	-5,50	-0,50	-0,25	-1,30	-1,50
13	PDDA	65	16	4,95	9,50	-2,25	-2,75	-3,80	-5,00	-0,25	0,00	-0,50	-0,50
14	CDF -1	25	12	4,95	4,50	-1,50	-1,50	-3,10	-2,50	-0,50	-0,30	-0,50	-0,30
15	CDF -1	25	16	4,95	4,50	-2,00	-2,00	-3,10	-3,00	-0,80	-0,50	-0,50	-0,25
16	CDF -1	50	12	4,95	4,50	-0,50	-1,00	-1,80	-2,50	0,50	0,25	0,25	0,50
17	CDF -1	50	16	4,95	4,50	0,30	-0,50	1,30	-1,00	1,50	1,50	1,50	2,50
18	CDF -1	65	12	4,95	4,50	0,30	0,50	1,80	-0,50	1,00	1,50	0,50	2,50
19	CDF -1	65	16	4,95	4,50	-1,50	-2,00	-2,50	-2,75	-0,60	0,25	-0,60	0,75

Table 4. Breaking and tear strength test results of ecru 86/10/4 % wool/PA 6.6/elastane fabrics

Sample Number	Breaking Strength (daN)		Tear Strength (cN)	
	Weft	Warp	Weft	Warp
1	36	35	3014	2555
2	40	25	1652	1604
3	38	22	1769	1334
4	37	23	1384	1231
5	34	23	1746	1231
6	43	33	2639	1971
7	43	30	2622	2014
8	36	29	2601	1736
9	43	32	2201	1992
10	35	26	2140	1699
11	42	27	2057	1699
12	41	31	2201	1927
13	43	32	2035	1949
14	35	25	2120	1792
15	39	25	2181	1883
16	36	26	2120	1792
17	39	23	1949	1631
18	38	25	1883	1629
19	37	24	1860	1792

Table 5. Whiteness indexes of ecru 86/10/4 % wool/PA 6.6/elastane fabrics

Sample Number	CIE Whiteness Index	Whiteness Change (Delta)	CIE Color Value	Color Change (Delta)
1	17,1	-	-1,56	-
2	28,2	11,1	-3,54	1,98
3	49,7	32,6	-6,41	4,86
4	24,3	7,2	-3,73	2,18
5	41,7	24,6	-5,67	4,11
6	0,7	-16,4	-2,40	0,84
7	8,3	-8,8	-2,54	0,99
8	1,6	-15,5	-2,69	1,14
9	0,0	-17,1	-2,41	0,86
10	0,1	-17,0	-2,50	0,96
11	3,3	-13,8	-2,79	1,23
12	0,5	-16,6	-2,37	0,82
13	1,2	-15,9	-2,46	0,90
14	6,7	-10,4	-3,47	1,92
15	4,7	-12,4	-2,98	1,43
16	9,7	-7,4	-2,78	1,23
17	20,7	3,6	-3,48	1,92
18	18,6	1,5	-3,30	1,74
19	10,5	-6,6	-3,07	1,62

Table 6. Application conditions of colored 86/10/4% WO/PA/EL fabrics

Sample Number	Polyelectrolyte Type	T (°C)	Layer number	pH of Polyelectrolyte	pH of PU	Wash Shrinkage								Color Change After 5A (%)
						Warp (Change %)				Weft (Change %)				
						7A Fabric	7A Cuff	5A Fabric	5A Cuff	7A Fabric	7A Cuff	5A Fabric	5A Cuff	
20*	-	-	-	-	-	-1,00	-1,00	-1,10	-1,50	-1,30	-1,00	-2,25	-1,50	4,0
21*	-	-	-	-	-	-0,50	-1,50	-1,00	-1,50	-1,50	-1,00	-1,75	-1,25	4,0
22*	-	-	-	-	-	-1,00	-1,00	-1,30	-0,60	-1,20	-1,25	-1,20	-1,50	4,0
23	CDF -1	25	16	4,5	4,95	1,60	1,00	1,60	1,50	1,50	2,00	2,00	2,00	4,5
24	CDF -1	25	16	4,5	4,95	0,80	0,50	0,60	0,50	1,60	1,00	2,50	2,00	4,0
25	CDF -1	25	16	4,5	4,95	0,80	-0,50	1,10	-1,00	2,00	2,00	2,30	2,50	3,5
26	CDF -2	50	16	4	4,95	1,50	-0,50	1,60	0,50	0,80	0,50	1,10	1,90	4,5
27	CDF -2	50	16	4	4,95	1,50	1,00	1,80	2,00	1,10	1,00	1,90	2,00	3,5
28	CDF -2	50	16	4	4,95	1,10	0,50	2,00	1,50	1,60	1,00	2,50	2,00	4,0
29	CDF -2	65	16	4	4,95	-1,00	-1,00	-1,30	-2,00	0,80	0,50	1,50	2,00	3,5
30	CDF -2	65	16	4	4,95	-1,00	-1,00	-0,60	-1,00	0,25	0,25	0,50	0,60	4,5
31	CDF -2	65	16	4	4,95	-1,10	-1,00	-1,10	-2,00	-0,00	0,50	2,50	2,00	4,0

* Reference without chemical use
Light, medium and dark colors represent the color of dyeing.

Table 7. Strength and K/S test results of colored 86/10/4% WO/PA/EL fabrics

Sample Number	Breaking Strength (daN)		Tear Strength (cN)		K/S
	Weft	Warp	Weft	Warp	
20*	29	30	2042	1219	6,0
21*	31	27	2358	1664	20,6
22*	37	33	1828	2042	21,6
23	27	29	1828	878	5,6
24	28	30	1554	1106	18,9
25	28	29	1719	641	19,2
26	26	30	1719	878	6,8
27	27	32	1664	1280	19,3
28	30	35	1609	1276	19,2
29	28	31	1192	1388	5,7
30	28	33	1664	1609	19,2
31	29	35	1664	1828	19,4

* Reference without chemical use
Light, medium and dark colors represent the color of dyeing.

Table 8. The color values measured on the spectrophotometer after the application of the optimum conditions to the colored 86/10/4% WO/PA/EL fabrics

Sample Number	DL*	Da*	Db*	DC*	CMC dE
23	1,10	-0,23	-0,30	-0,37	0,61
24	0,47	-1,63	1,90	-2,24	1,31
25	1,19	-0,34	0,57	-0,62	1,19
26	0,05	-0,36	0,38	0,21	0,70
27	0,08	-3,49	4,40	-5,11	2,80
28	1,15	-0,56	1,22	-1,30	1,53
29	0,13	0,04	-0,24	-0,21	0,24
30	0,31	-0,37	0,60	-0,67	0,39
31	1,05	-0,17	0,33	-0,36	0,96

CDF: Cationic Dye Fixator

	DL*	Da*	Db*	DC*
+	lighter	more red	more yellow	more saturated
-	darker	more green	more blue	less saturated

At 100% WO fabrics, light color dyed fabric using CDF-2, yielded the lowest tensile values as a result of 16 layers of coating at 65 ˚C. Fabric dyed in medium color showed the lowest shrinkage and strength change values as a result of 16 layer coating at 50 ˚C using CDF-2. The darkest dyed fabric using CDF-2 gave the lowest shrinkage change values at 50 ˚C. When the changes in light, medium and dark fabrics with the same recipe were compared, it was seen that the darkness of the color had not cause a big difference in the shrinkage values [28]. At light-colored 86/10/4% WO/PA/EL fabrics, the lowest tensile values were obtained by applying 16 layers at 65 ˚C. At medium-colored fabric, the lowest shrinkage and strength change values were obtained as a result of 16-layer coating at 65 ˚C using CDF-2 polyelectrolyte. Also, 16 layer coating at 65 ˚C by using CDF-2 polyelectrolyte gave the lowest shrinkage values at dark colored fabric. When the changes in light, medium and dark fabrics with the same recipe were compared, it was seen that the darkness of the color had not cause a big difference in the shrinkage values (Table 6, Table 7). It was concluded that nanopolyurethane multilayer coated films importantly reduce both felting and shrinkage, as they significantly reduce the friction between the flakes on the surface of the fibers. But with the LBL depoisiton process pH changes in the multilayer coating steps can affected tensile strength values, but this is not as big as commercial methods [1].

When the Table 8 was examined, it was seen that the applications usually lead the fabric to green, blue and lighter shade in every color. The application of dark colors in 100% wool fabrics leaded to less delta E change [28], while the effect on 86/10/4% wool/nylon/elastane fabrics was the opposite.

In another experiment set, the effect of squeezing roller velocity and pressure on the fabrics were tested on the dark colored fabric. The combination of "3 bar squeezing roller pressure-2 m/min squeezing velocity" and "2 bar squeezing roller pressure-2 m/min squeezing velocity" in the fabric yielded the best 7A and 5A wash shrinkage results. However, the application in these samples affected the color changes after washing more than the other samples. When the wash shrinkage and strength values were evaluated together, it was determined that these two combinations were the most suitable conditions. It was observed that 86/10/4% wool/nylon/elastane blends had less color changes than 100% wool fabrics (Table 9, Table 10, Table 11) [28].

Table 9. Wash shrinkage and color change test results after squeezing roller velocity and pressure trials of colored 86/10/4% WO/PA/EL fabrics

Sample Number	Squeezing Pressure (bar)	Squeezing Roller Velocity (m/min)	Wash Shrinkage								Color Change After 5A (%)
			Weft (Change %)				Warp (Change %)				
			7A Fabric	7A Cuff	5A Fabric	5A Cuff	7A Fabric	7A Cuff	5A Fabric	5A Cuff	
32	-	-	-1,20	-1,25	-1,20	-1,50	-1,00	-1,00	-1,30	-0,60	4,0
33	3	1	0,25	0,75	0,50	0,75	-0,90	-1,25	-1,10	-1,75	4,0
34	3	2	-0,50	0,25	0,25	0,50	-1,10	-2,00	-0,90	-1,75	4,0
35	2	2	-0,90	0,75	1,80	1,00	0,80	-0,50	2,00	-0,50	3,5
36	2	3	-0,75	-0,25	-0,33	-0,25	-2,00	-1,50	-2,41	-2,25	4,0
37	3	3	1,60	1,00	2,50	2,00	1,10	0,50	2,00	1,50	4,0

Table 10. Strength test results after squeezing roller velocity and pressure trials of colored 86/10/4% WO/PA/EL fabrics

Sample Number	Breaking Strength (daN)		Tear Strength (cN)		K/S Change (%)
	Weft	Warp	Weft	Warp	
32	37	33	1828	2042	-
33	28	38	2254	1609	-6,9
34	32	31	2307	1664	-5,1
35	29	35	2149	1664	-1,4
36	29	33	2307	1498	-18,5
37	30	35	1609	1276	-11,1

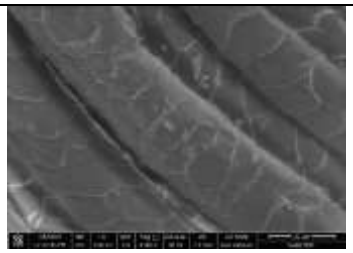
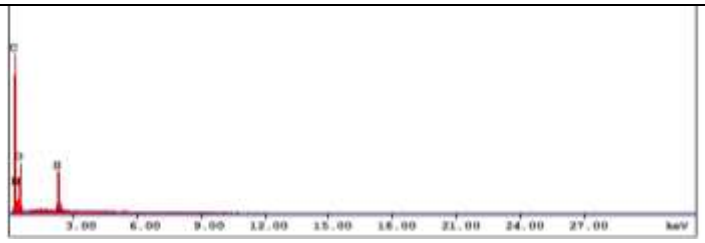
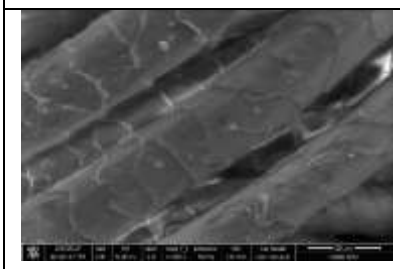
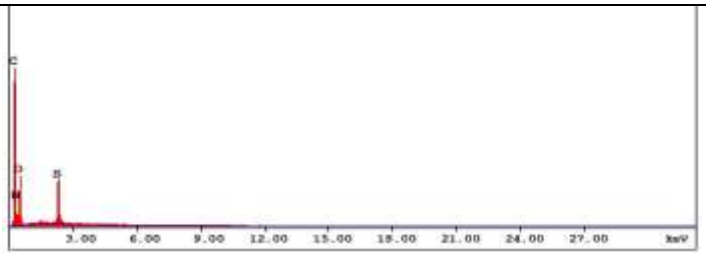
Table 11. The color values measured on the spectrophotometer after squeezing roller velocity and pressure trials on colored of 86/10/4% WO/PA/EL fabrics

Sample Number	Squeezing Pressure (bar)	Squeezing Roller Velocity (m/min)	DL*	Da*	Db*	DC*	CMC dE
32	-	-	-	-	-	-	-
33	3	1	0,29	-0,15	0,69	-0,71	0,64
34	3	2	0,11	-0,17	0,66	-0,68	0,58
35	2	2	-0,26	-0,10	0,51	-0,52	0,49
36	2	3	1,46	-0,30	1,45	-1,48	1,74
37	3	3	1,15	-0,56	1,22	-1,30	1,53

SEM-EDX and FTIR-ATR analyzes of the fabrics covered with the parameters of "2 m/min squeezing roller velocity and 2 bar squeezing roller pressure" under optimum conditions were performed (Figure 1-2). The cuticle surface in the outermost layer of the wool fibers is composed of flakes shaped by the cuticular cells. Cuticle surface with this shape can be likened to the shape of the fish scales. Fish scale appearance, under the microscope can be easily examined by showing a characteristic feature of wool fiber identification. SEM images of 100 % wool and 86/10/4% wool/nylon/elastane fabrics clearly show that the fibers have flakes to protrude outwards. In the SEM images of multi-layer film coated wool fibers with Nano PU, it is seen that the edges of the flakes on the surfaces of the fibers are completely covered and the sharp lines disappear. It is not possible to make a clear comment in the EDX analysis results. Because of the NH bonds present in both wool and polyurethane, small changes were observed in the results of elemental analysis.

The characteristic FTIR spectrum of raw wool fibers was observed in the FTIR spectra obtained from 86/10/4% wool/nylon/elastane fabrics as a result of the multilayer coating process. FTIR and SEM analysis results of coated 86/10/4 wool/nylon/elastane fabric (dark colored) 16 layers at 25 ^{0}C using CDF-1, 16 layers at 50 ^{0}C using CDF-2 and 12 layers at 65 ^{0}C using CDF-2 applications obtained and given together. For LbL coated samples, between 3200 cm^{-1} to 3400 cm^{-1}, centered broadband at 3380 cm^{-1} resulted from the properties of N-H functional groups in the product and shows an increase in the intensity of the band. The same density increases can be seen between 2800-3400 cm^{-1} depending on NH bonds of wool fiber and NH bond of polyurethane. A strong adsorption band with a maximum of 1535 and 1614 cm^{-1} were the bands attributed to the functional groups of the carbonyl groups of urethanes. Absorption peaks at 2972 cm^{-1} and 2930 cm^{-1} are respectively the asymmetric stretching vibrations of $–CH_3$ and $–CH_2$ and the intensity increases can be seen after coating applications. As a result of the coating process, it was clearly determined from the FTIR-ATR results that the intensity increased in all these bands and the% Transmission (permeability value) values decreased. SEM images show the edges of the flakes on the surfaces of the fibers covered.

Figure 1. SEM-EDX test results of (a) uncoated 100% wool, (b) coated 100% wool, (c) uncoated 86/10/4% wool/nylon/elastane fabric (dark colored), (d) coated 86/10/4% wool/nylon/elastane fabric (dark colored)

SEM images	EDX analysis
	
(a)	
	
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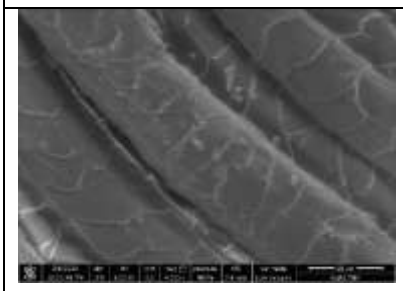
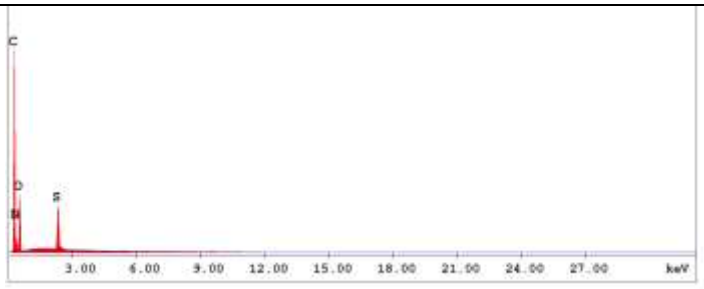
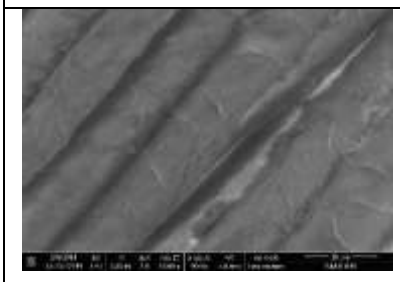
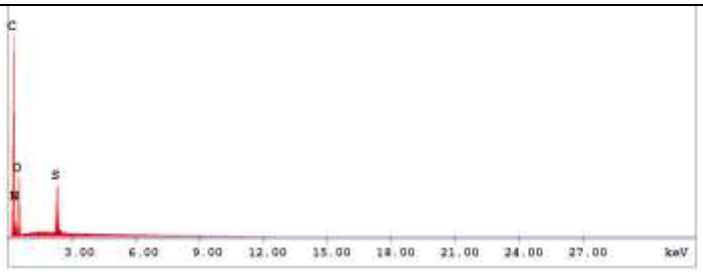
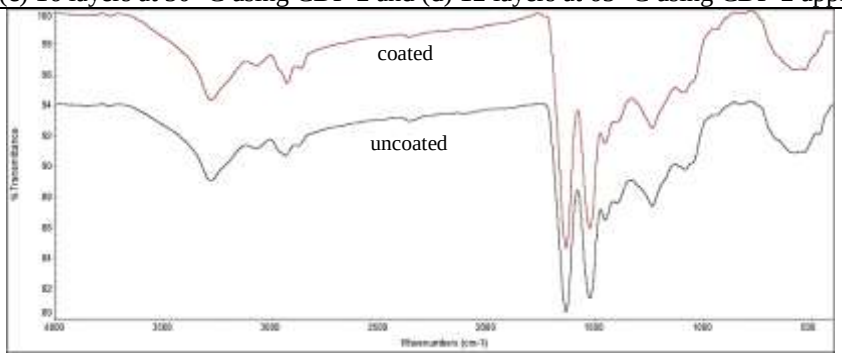
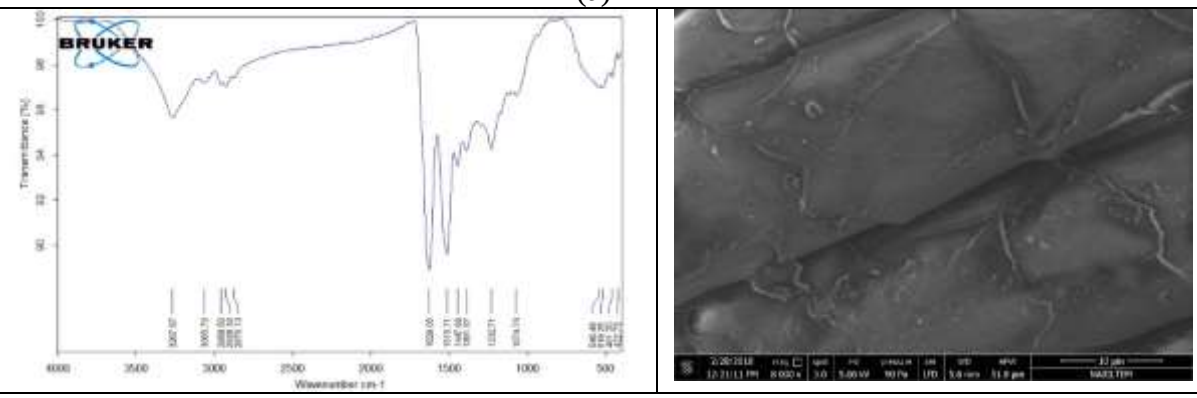
	
(c)	
	
(d)	

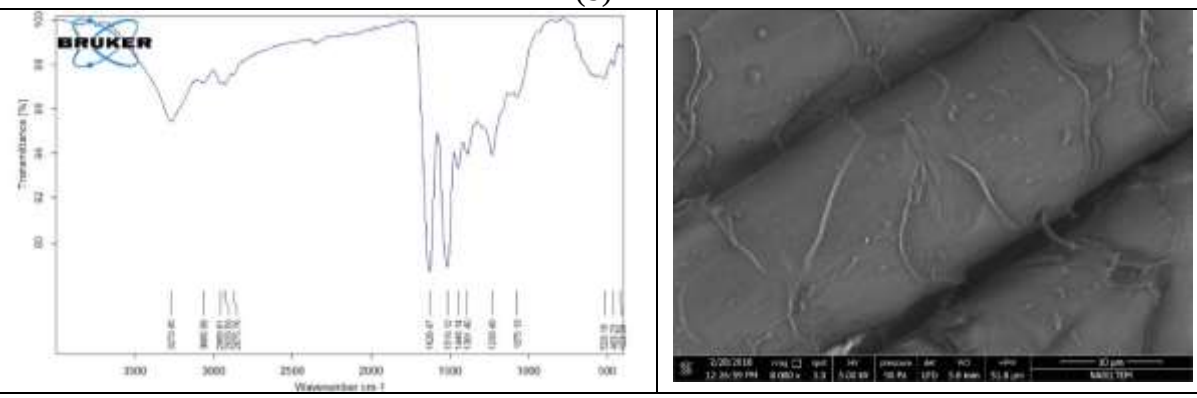
Figure 2. FTIR results of uncoated (black line) and coated 86/10/4 wool/nylon/elastane (red line) fabrics (dark colored) (a), FTIR and SEM analysis results of coated 86/10/4 wool/nylon/elastane fabric (dark colored): (b) 16 layers at 25 ^{0}C using CDF-1, (c) 16 layers at 50 ^{0}C using CDF-2 and (d) 12 layers at 65 ^{0}C using CDF-2 applications



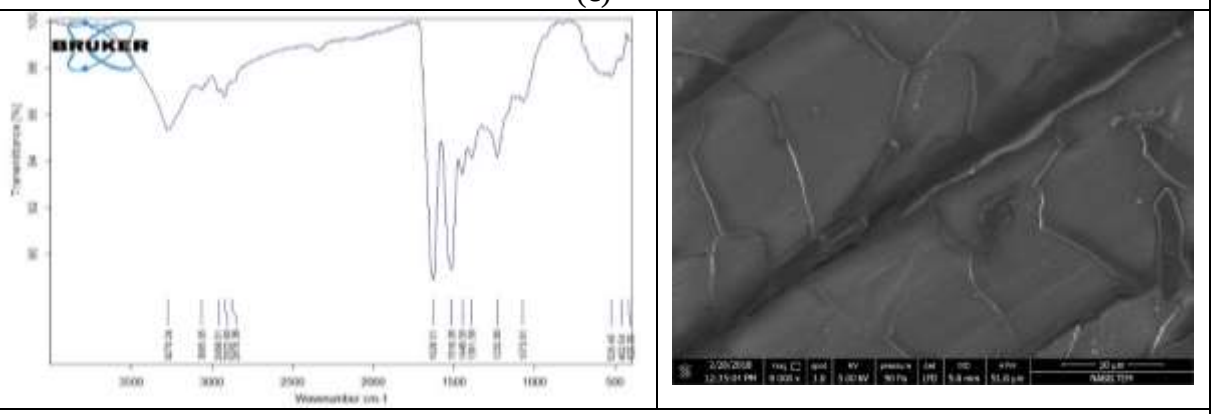
(a)



(b)



(c)



(d)

4. CONCLUSION

The main purpose of this study was to evaluate antifelting properties of wool fabric treated with nano polyurethane by LbL method.

In shrinkage tests, the best results for 86/10/4% wool/nylon/elastane blended ecru fabrics were achieved with one of commercial dye fixator (CDF-1) as with 100% wool ecru fabrics. When the obtained values are compared with untreated fabric, it demonstrates that the LbL treatment could impose significant shrink-resistant and anti-felting effects to the dyed wool fabric as a finishing process. And lower tensile values were seen with CDF-1 compared to other polyelectrolytes. It was seen that P(AAm-co-DADMAC) polyelectrolyte increased the whiteness change value and the change of whiteness decreased with the other polyelectrolyte.

± 3% shrinkage values were obtained at 86/10/4% wool/nylon/elastane blended three different tones dyed fabrics without loss of strength values by the optimization of factors such as the type of polyelectrolyte, temperature of the solution, number of layers, squeezing roller velocity, squeezing roller pressure. It has been observed that multilayer coating application had a slight change in strength values in 86/10/4% wool/nylon/elastane fabrics and it has been observed that it did not have a negative effect on other finished fabric tests. Strength values changes can be attributed to the LbL deposition process pH changes in the different layers. Also, it was seen that the application caused some darkening of the color and thickening in the fabrics. It was prevented that wool fibers becoming a grift with each other by the help of nano-size chemicals applied on. In this way, it has maintained its soft and bulky appearance. SEM analysis revealed that the end portions of the wool flakes became more rounded after coating application. Surrounding wool fibers in form of multilayer films, nano polyurethane can in fact significantly decrease the friction between the surface scales, reducing both felting and shrinkage. LbL treatment with nano polyurethane offer chlorine-free alternative to obtain anti-felting effects on woolen fabrics. This novel LbL process, based on nano polyurethane, showed an anti-felting result similar to traditional methods, but without using chemicals that could be harmful to the environment.

A sustainable method has been developed for the first time in the world by using multi-layer coating method using nano-polyurethane, ensuring that suits, uniforms and upholstery wool blended fabrics are washable in the washing machine. In this way, the need for dry cleaning will be removed, so energy resources will be used more efficiently.

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