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Wool Fabrics Coated with an Anionic Bunte Salt-Terminated Polyether: Physicomechanical Properties, Stain Resistance, and Dyeability

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ABSTRACT: The Bunte salt-terminated polyether (BSTP)-based treatment has been developed for the chlorine-free shrink-resist treatment of wool fibers and fabrics. However, the effect of BSTP treatment on the physicomechanical and chemical properties of wool fabrics has not been thoroughly investigated. In this work, wool fabrics were treated with a commercially available BSTP at various concentrations by the pad-dry-cure process. The effect of BSTP coatings on the dyeability, shrink resistance, mechanical properties, wettability, hydrophilicity, and yellowness of the treated wool fabrics was systematically evaluated. It was found that the shrinkage of the treated wool fabrics considerably decreased with an increase in the BSTP concentration. On the other hand, the tensile strength, elongation at break, and surface hydrophilicity highly increased with an increase in the BSTP concentration. The tensile strength of the treated fabric was better than the tensile strength shown by the blank-treated fabric even at the lowest investigated concentration of BSTP (60 g/L). The bending rigidity as well as the bending modulus of wool fabric also decreased with an increase in the applied concentration of BSTP. The treatment showed very little effect on the yellowness and whiteness indices of wool fabric. The stain resistance against C.I. Acid Red 40 of the treated wool fabrics increased with an increase in the applied concentrations of BSTP. However, against red wine, the stain resistance decreased at lower concentrations of BSTP but showed a little effect for the higher concentrations. The coating of wool fabrics with the BSTP not only reduced the shrinkage of the fabrics but also increased their hydrophilicity and also the stain resistance against acid dye-based stain but also negatively affected their dyeability and stain resistance against red wine, especially at lower BSTP concentrations.
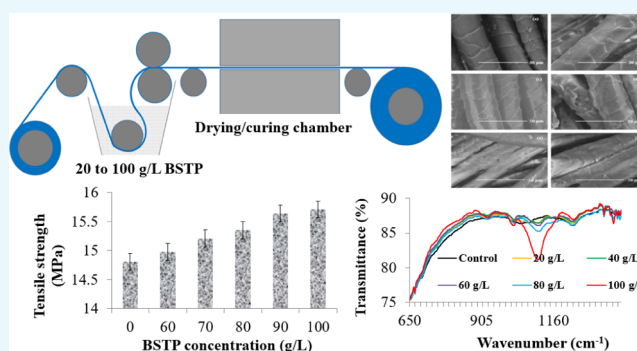
INTRODUCTION

Wool fiber is a keratin fiber, which is composed of 18 amino acids including arginine, cystine, glutamic acid, and glycine. The wool fiber-made fabrics have excellent antistatic, fire-retarding, wrinkle-resist, heat insulation, and moisture management properties. The interior of wool fiber is highly hygroscopic, and therefore it has some levels of antistatic properties.[1] The wool fiber surface contains a polyethylene-like hydrophobic layer, which is made of 18 methyl eicosanoic acid (18-MEA) bonded to the cuticle surface via thioester linkages, and therefore the wool fiber surface is quite hydrophobic providing some levels of stain resistance. However, wool fibers have several deficiencies including very high shrinkage during laundering. The fabrics made from them show poor dimensional stability and the felting of the fibers make the surface of the fabric esthetically unpleasant.

The physical structure of the outer scaly surface of the wool fiber is mainly responsible for its shrinkage and felting. During mechanical agitation, friction, and pressure in the presence of moisture and heat, the edge of the scales present on the surface of one fiber locks into the inter-scaling space of another fiber like a "ratchet" mechanism. As a result, wool fibers interlock and cannot return to their original position and the shrinkage

that takes place become permanent. Felting is sometimes advantageous, such as for fabrication of blankets and felted rugs but can be a serious problem for apparel as it changes the appearance of the fabric.[2,3] To make wool fabric shrink-resistant, the edge of epicuticles needs to be etched or the inter-scale spaces will need to be covered so that no interlocking of fibers can take place. Additionally, the removal of 18-MEA is necessary, to make the fiber surface compatible with polymers that are used to cover the scales so that they can uniformly spread on the fiber surface. The polymers used are usually cationic so that they do not affect the dyeability of wool fiber. However, they negatively affect the inherent stain-resist properties of the wool fiber.[4]

The most popular shrink-resist treatment for wool fiber in wool industry is the so-called "chlorine-Hercosett" treatment. In this method, wool fibers are initially treated with chlorine in acidic conditions followed by coating with a cationic epichlorohydrin-modified-polyamide resin containing reactive azetidinium groups.[5] Chlorination not only removes the bound
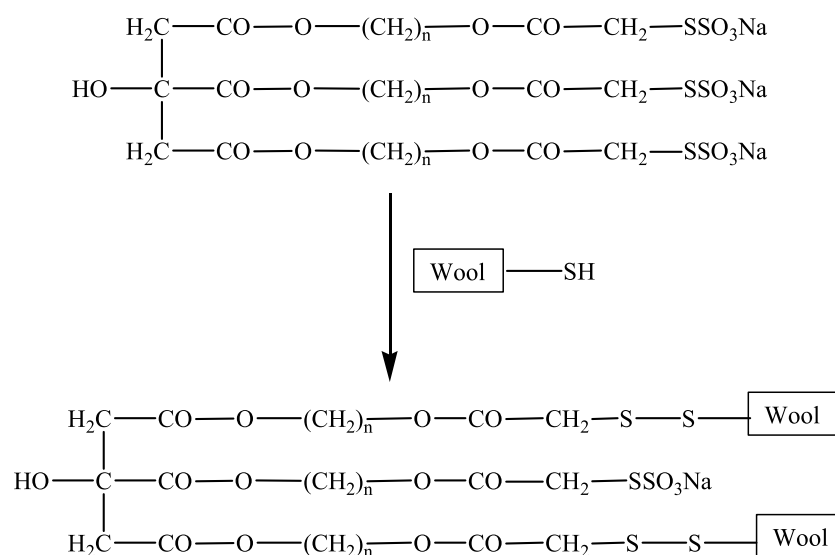
Figure 1. Mechanism of reaction of BSTP with thiol groups of wool fiber.
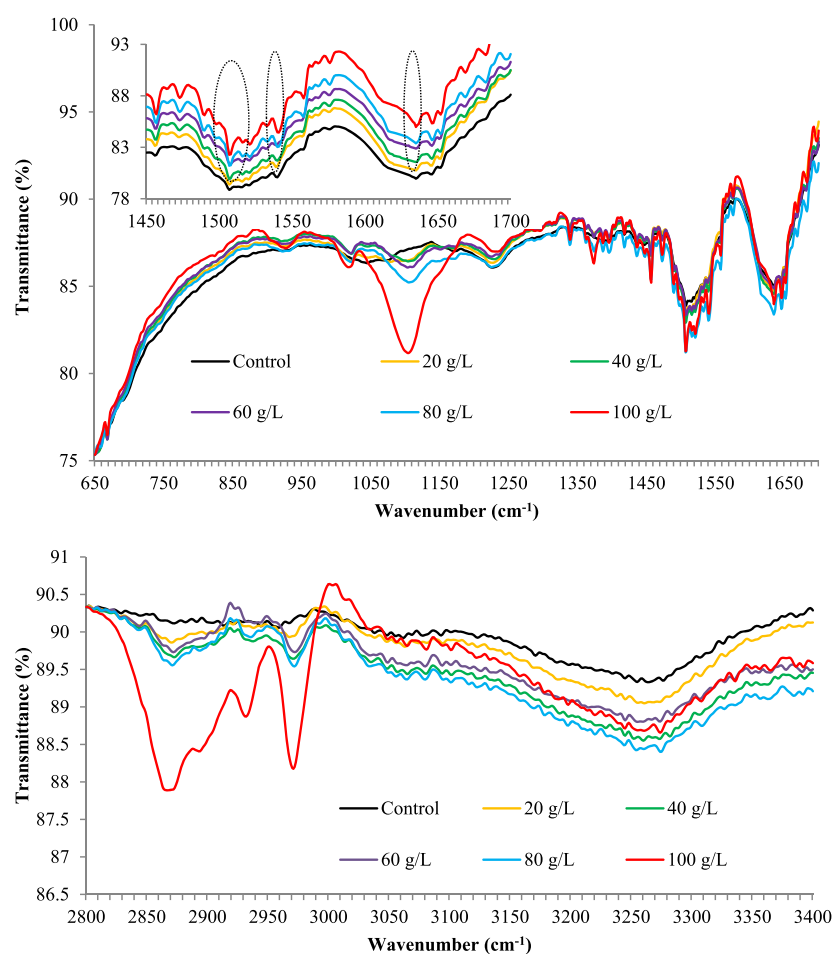

Figure 2. ATR-FTIR spectra of control wool fabric and also wool fabrics treated with various concentrations of BSTP.

lipids, such as 18-MEA, from the surface of wool fiber but also makes the surface hydrophilic and compatible with the polyamide resin coating. The chlorination treatment etches the scale edges, allows the formation of a uniform polymer coating on the surface of wool fibers in the subsequent resin treatment, and prevents the treated fibers from felting by stopping interlocking of fibers. One of the main advantages is

that it is a continuous process and so far is the most effective and the cheapest method to make wool fiber shrink-resistant. However, if the chlorination treatment is uneven, it may cause formation of uneven coating on the chlorinated wool fibers, and may also cause failure in the shrink resistance test.[6] Moreover, the chlorination process is potentially hazardous as it liberates chlorine gas to the environment and produces

Table 1. Whiteness, Yellowness, Dimensional Stability, and Felting Tendency of Control Fabric and BSTP-Treated Fabrics at Various BSTP Concentrations

BSTP concentrations (g/L)	whiteness index (Berger)	yellowness index (D1926)	wettability[a] (s)	area felting shrinkage (%)	felting tendency
0	24.00	23.97		41.60	severe felting
20	24.17	23.58	7.00	37.43	negligible felting
40	24.75	23.49	8.25	31.43	no felting
60	25.67	23.09	6.33	27.78	no felting
80	26.85	22.68	6.20	20.66	no felting
100	26.14	22.32	5.83	13.99	no felting

[a]The wettability was measured at 20 ± 2 °C and $65 \pm 2\%$ relative humidity (RH) by placing a droplet of water (2.82 mg) on fabric samples from 5 cm above. The control sample did not wet even after 120 min.

absorbable organic halogen (AOX) residues in effluent, which need treatment before discharging to watercourses.[7] As a result, in some countries, chlorination treatment is restricted, which demands the development of an eco-friendly alternative shrink-resist treatment for wool. Therefore, investigation of nonchlorine-based shrink-resistant treatments has gained momentum. A range of nonchlorine-based shrink-resist treatments, such as enzymatic,[8−12] sol−gel coating with silanes,[13] oxidation treatment followed by coating with a silicone resin,[14] and plasma-based coatings,[15] have been developed over the years to make wool fabric shrink-resistant. However, these treatments have several demerits, such as enzyme treatments are difficult to control causing uneven treatment, sol−gel coatings affect the handle properties of the fabric, and plasma treatments are expensive. Therefore, other simple and cheap alternatives have been investigated.

Initially, covering of wool fiber scales by coating with polybutadiene, collagen, and diacrylates has been studied as a means to provide shrink resistance to wool fiber-made apparels.[16−18] However, these coatings were unable to provide durability of shrink resistance to multiple washing, because in these coatings no bonding occurs between wool fiber and the polymer coating. A range of crosslink forming polymeric resins including polyurethane containing free isocyanate groups (Synthappret LKF), polyurethane with a bisulfite adduct (Synthappret BAP), Bunte salt-terminated polyether (Lankro-lan SHR3), and poly(dimethylsiloxane) diols in combination with an amino functional silane crosslinking agent, have been investigated to make wool fabric shrink-resistant.[19−21] However, poor spreading of hydrophilic polymers on the hydrophobic wool fiber surface produces uneven coating and poor handle properties causing their commercial failure.

The coating of wool fibers with BSTPs has been developed as an eco-friendly shrink-resist treatment for wool by Lewis.[20] In this method, no strong oxidation treatment, such as chlorination, is used that may damage the fiber. The wool fibers are reacted with a reducing agent to form thiol groups on the wool fiber surface and the BSTP then forms a polymeric coating on the treated fiber surface by forming covalent disulfide bonds between the thiol groups of wool fiber and the $-SSO_3Na$ groups of BSTP. The synthesis, curing mechanism, and application of bi and trifunctional BSTPs for the shrink resistance of wool fiber have been reported by Lewis.[22,23] To the best of our knowledge, no published literature reported the effect of the coating of BSTPs on wool fabric's dyeability, hydrophilicity, shrink resistance, stain resistance, and other physicomechanical properties. In this work, we are reporting the dyeability, hydrophilicity, stain resistance, shrink resistance, bending rigidity, and other physicochemical properties of wool

fabrics treated with a commercially available BSTP at various concentrations.

RESULTS AND DISCUSSION

The mechanism of reaction of the BSTP with wool fiber is shown in Figure 1. The wool fabric was pre-treated with a reducing agent (sodium sulfite) to break down the disulfide bonds of wool to produce free thiol groups. It can be seen that the $-SSO_3Na$ groups of BSTP reacts with these thiol groups and covalently binds to wool fibers by forming sulfur linkages.

**Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) Characterization of the Treated Wool Fabrics.** The ATR-FTIR spectra of control and BSTP-treated wool fabrics are shown in Figure 2. The FTIR spectrum of control wool shows various bands including wool keratin-related IR bands of amide III, amide II, and amide I peaks at 1227, 1350, 1540, and 1635 cm^{-1}, respectively. The peak at 1506 cm^{-1} could be attributed to the C−N stretching and also to the N−H in-plane bending vibrations (amide II) and its intensity increased with an increase in the applied concentration of BSTP. The broad peak at 3150−3350 cm^{-1} could be assigned to the hydroxyl groups of some amino acids of wool keratin, such as serine and tyrosine.[24] In contrast, all BSTP-treated fabrics show new peaks at 668, 926, 1020−1026 (broad peak), 1100 (broad peak), 1363, 2865, 2932, and 2971 cm^{-1}. The IR bands at 2865 and 2932 cm^{-1} could be assigned to the methylene groups $(-CH_2)$ of BSTP and their intensity increased with an increase in the concentration of BSTP.[25] The absorption peak located at 2971 cm^{-1} observed for all the fabric samples treated with BSTP is due to the stretching vibrations of C−H of the $-CH_2$ group of BSTP.[26] The BSTP-treated wool fabrics show a new band at 1020 cm^{-1}, which could be attributed to the Bunte salt of BSTP, and its intensity increased with an increase in the concentration of BSTP.[24,27] The bands at 668 and 1100 cm^{-1} are due to the $-CH_2$ groups of the long chain and $-C-O$ of ether groups of BSTP, respectively. The FTIR spectra indicate the presence of BSTP in the treated wool fabrics.

Wettability, Yellowness, and Shrink Resistance of the Treated Fabrics. Table 1 shows whiteness and yellowness indices of the control and fabrics treated with BSTP at various concentrations. The whiteness index shown by the control fabric was lower than the whiteness index shown by various treated samples. The whiteness index progressively increased with an increase in the concentrations of BSTP up to 80 g/L BSTP, beyond which the whiteness index slightly decreased. In contrast, the BSTP-treated samples showed a lower yellowness index compared to the control fabric, which is advantageous as the increase in the yellowness index is undesirable. The yellowness index decreased with the increase in the

Table 2. Bending Rigidity and Bending Modulus of Wool Fabrics Treated with Various Concentrations of BSTP

| BSTP conc. (g/L)	bending length (mm)		weight/m² (g)	sample thickness (mm)	bending rigidity (N m)		bending modulus (N/m²)	
	warp-way	weft-way			warp-way	weft-way	warp-way	weft-way
0	15.90	15.30	194.35	0.41	7.66	6.83	6335.21	5648.77
40	15.85	14.88	195.93	0.41	7.65	6.32	6326.94	5226.97
60	15.00	14.32	196.74	0.41	6.51	5.66	5384.10	4681.11
80	14.45	13.94	198.00	0.42	5.86	5.26	5209.87	4676.43
100	14.10	13.55	201.75	0.42	5.55	4.92	4934.26	4374.15
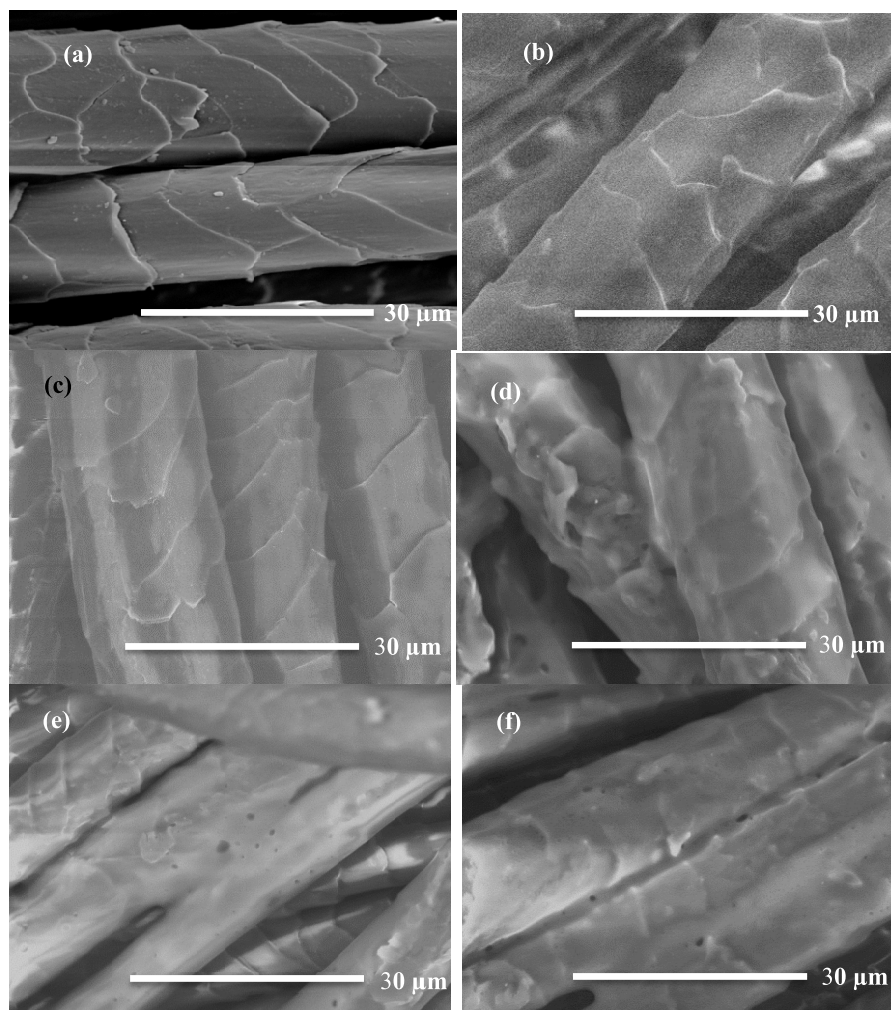
Figure 3. SEM micrographs of control wool fabric (a) and also wool fabric treated with 20 g/L (b), 40 g/L (c), 60 g/L (d), 80 g/L (e), and 100 g/L (f) BSTP.

concentrations of BSTP. The control fabric showed very low wettability compared to the wool fabrics treated with various concentrations of BSTP. The water droplet remained almost unchanged even after 120 min of the test. In contrast, the treated fabrics showed excellent wettability (Table 1) and the water droplet was absorbed by the fabric within a few seconds. The hydrophilicity of the fabric increased with an increase in the concentrations of BSTP. The treatment with sodium sulfite produced thiols, some of which reacted with thiol groups of the BSTP and the rest were oxidized to hydrophilic sulfonic acid groups. The BSTP itself is hydrophilic because of the presence of hydrophilic, hydroxyl, and thiosulfonate groups resulting in an increase in the hydrophilicity of the treated fabrics.

Table 1 also shows felting shrinkage and felting tendency of control and BSTP-treated fabrics. The blank-treated control fabric showed severe felting and shrinkage of 41%, which is consistent with the shrinkage observed by other researchers.[16,18] On the other hand, felting tendency and felting shrinkage of the BSTP-treated fabric progressively decreased with an increase in the concentration of BSTP. The fabric treated with 100 g/L BSTP showed the lowest shrinkage, which was only 14% after 3×5A washes.

Flexural Rigidity and Bending Modulus. Table 2 shows the bending rigidity and the bending modulus of wool fabric treated with various concentrations of BSTP. It can be seen that the coating with BSTP greatly affected the bending stiffness of the fabric as the flexural rigidity and bending modulus considerably decreased with an increase in the
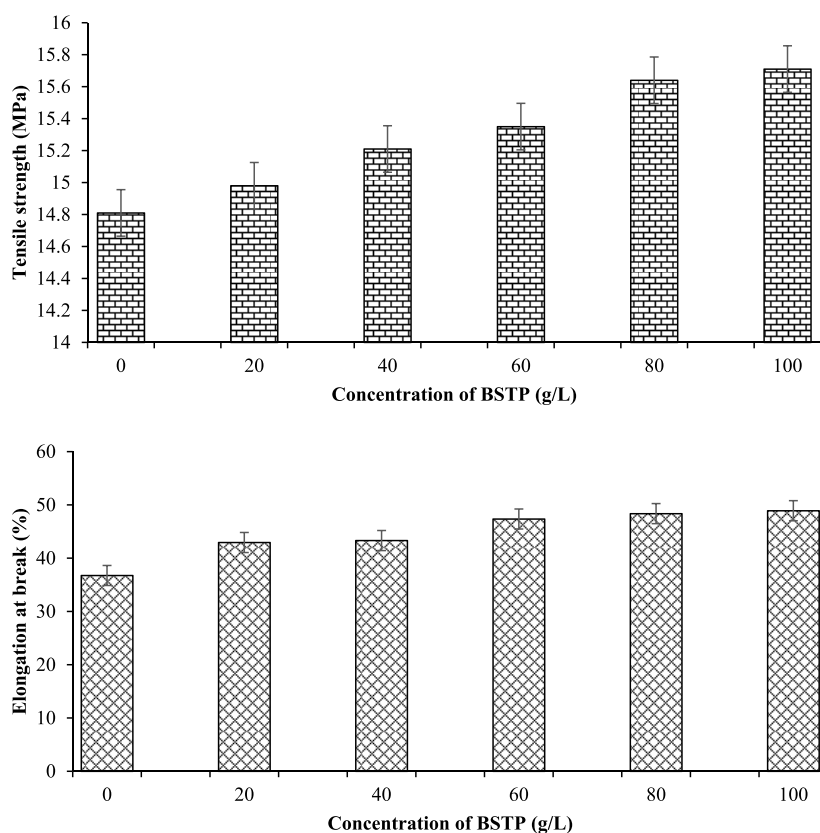
Figure 4. Effect of BSTP concentration on the tensile strength and the elongation at break of the coated wool fabrics.

applied concentration of BSTP. The flexural rigidity in the warp and weft directions of the control fabric was 7.66 and 6.83 N m, respectively, which decreased to 5.55 and 4.92 N m, respectively, for the fabric treated with 100 g/L BSTP. Similarly, the bending modulus of wool fabric in the warp and weft directions decreased from 6335.21 and 5648.77 N/m^2 to 4934.26 and 4374.15 N/m^2, respectively. The results suggest that the softness of the wool fabric considerably improved with the BSTP treatment as the BSTP formed an elastomeric layer on the surface of wool fabrics.

**Surface Morphologies of the Treated Wool Fabrics.** Figure 3 shows the scanning electron microscopy (SEM) micrographs of the surface of the control and the BSTP-coated wool fabrics. The image of untreated wool fabric shows the characteristic scaly structure of the wool fiber. There is also some debris produced by the damaged scales visible on the surface of the wool fiber. However, it is evident that the BSTP formed a uniform coating on the wool fiber surface covering the scales at higher concentrations than at the lower concentrations. The scaly structure of wool fibers is visible at the lower concentrations of BSTP, indicating that a very thin layer of coatings were formed. The fibers were not bonded together, and therefore they were free to move to cause some levels of shrinkage. Therefore, the achieved shrink resistance at these concentrations was poor. At 60 g/L of BSTP concentration, some bonding between fibers was observed but the coatings formed were uneven at this concentration. However, at BSTP concentrations of 80 g/L and higher, smooth and even coatings were formed which covered the scales of fibers, and fibers were bonded together. The results are consistent with the decrease in shrinkage that was observed with an increase in the concentration of BSTP.

Mechanical Properties of the Treated Wool Fabrics. The tensile strength and elongation at the peak of control and wool fabric treated with various concentrations of BSTP are shown in Figure 4. It is evident that all the treatments increased the tensile strength of the treated fabrics but the level of increase in the tensile strength is quite small. The average tensile strength shown by the control fabric was 14.8 MPa, which increased to 15.7 MPa for the wool fabric treated with 100 g/L of BSTP. Similarly, the elongation at peak also increased with an increase in the BSTP concentrations. The control and the treated fabrics both showed quite good extensibility. The elongation at peak increased from 36.75% for the control to 48.91% for the wool fabric treated with 100 g/L of BSTP. In summary, the tensile strength and the elongation at break increased with an increase in the concentration of BSTP.

Usually, the fabric coated with a polymer shows an improved tensile strength due to the reinforcement but the elongation is decreased as the extensibility of the fabrics is limited by the bonded polymeric coating. However, in our case, we observed that the BSTP coating increased the elongation of fabric, which increased with an increase in the concentration of BSTP. The results suggest that the BSTP formed an elastomeric coating on the surface of fiber resulting in increasing the elongation of the fabric.

Contact Angle of the Surface of the Treated Wool Fabrics. Figure 5 shows the shape and contact angle of water droplets placed on the surface of wool fabrics treated with various concentrations of BSTP and detailed results are shown in Table 3. The contact angle shown by the control wool fabric was 120.6° at 0 s which only marginally decreased with an increase in time suggesting that it is reasonably hydrophobic.
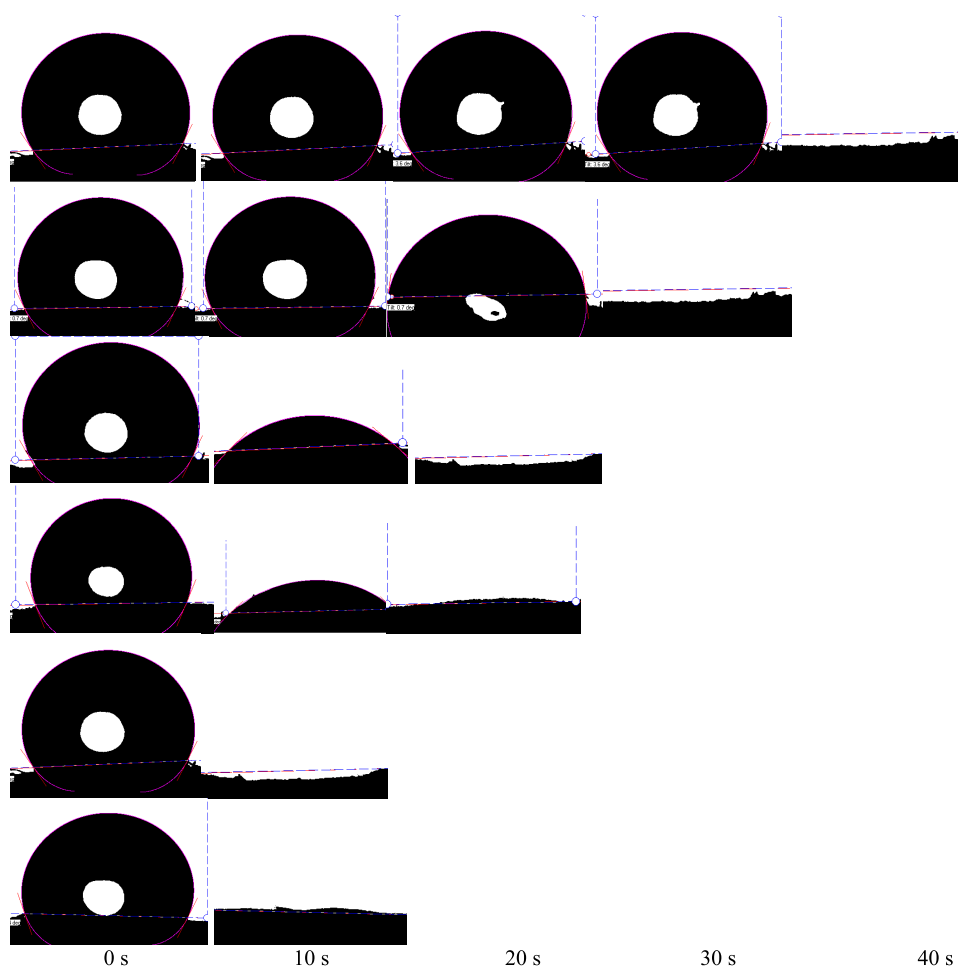
Figure 5. Dynamic water contact angles of the surface of wool fabric treated with 0 g/L (1st row), 20 g/L (2nd row), 40 g/L (3rd row), 60 g/L (4th row), 80 g/L (5th row), and 100 g/L (6th row) BSTP at 10 s intervals up to 40 s.

Table 3. Dynamic Contact Angle of Water Droplets Placed on the Wool Fabric Treated with Various Concentrations of BSTP

concentrations of BSTP (g/L)	contact angle (deg) at				
	0 s	10 s	20 s	30 s	40 s
0	120.6 ± 1.7	118.2 ± 2.1	118.03 ± 1.8	117.9 ± 2.2	118.0 ± 2.1
20	115.9 ± 1.1	116.0 ± 1.6	82.0 ± 1.1	0	0
40	117.6 ± 1.8	43.9 ± 0.9	0	0	0
60	111.7 ± 0.9	41.8 ± 1.5	0	0	0
80	120.9 ± 1.5	0	0	0	0
100	112.5 ± 0.7	0	0	0	0

The contact angle observed for the control wool fabric is consistent with the contact angle shown by untreated wool fabric reported in other published literature.[28,29] It can be seen that only in the case of control fabric, the contact angle only marginally reduced after 40 s, showing good hydrophobicity. On the other hand, all the treated fabrics showed moderate to good hydrophilicity as the contact angle proportionally decreased with an increase in the concentration of BSTP. In the case of wool fabric treated with 20 g/L, the contact angle became 0 after 30 s, whereas for the wool fabrics treated with 40 and 60 g/L, the contact angle went down to 0 after 20 s of the test. For higher than 60 g/L concentrations, the contact angle became 0 after 10 s of test showing excellent hydrophilicity. The results show that the BSTP coating made wool fabric highly hydrophilic.

Dyeability of BSTP-Treated Wool Fabrics. The reflectance vs wavelength curves of wool fabric dyed with three acid dyes are shown in Figure 6. It can be seen that the reflectance curves of the dyed fabrics show a trend, and the reflectance values increased with an increase in the applied concentration of BSTP at the wavelength of maximum absorption for each particular dye. The CIE $L*a*b*$ values and color strength of control and BSTP-treated wool fabrics dyed with three acid dyes are shown in Table 4. It can be seen that the lightness value ($L*$) of the dyed fabrics for all three dyes increased with the increase in the concentration of BSTP suggesting that the depth of the shade decreased with an increase in the concentration of BSTP. Similarly, for all three dyes, the color strength value also decreased with an increase in the BSTP concentration. The highest color strength was shown by the control fabric for all dyes indicating that the
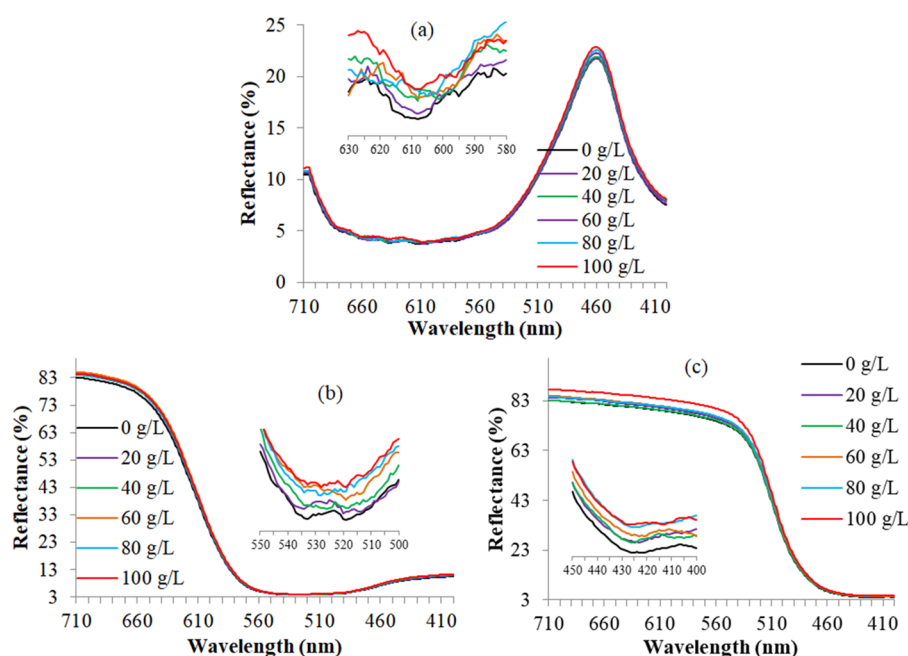
Figure 6. Reflectance vs wavelength curves of wool fabrics dyed with Tectilon Blue GRL (a), Tectilon Red F2G (b), and Tectilon Yellow 2G (c) dyes.

Table 4. CIE *L*a*b** Values of Wool Fabrics Treated with Various Concentrations of BSTP Dyed with Three Acid Dyes

| concentration of BSTP (g/L)	CIE *L*a*b** values			color strength (K/S)
	L*	*a**	*b**	
Tectilon Yellow 2G				
0	42.6	57.71	26.51	11.29
20	42.75	57.78	26.39	10.75
40	42.75	57.78	26.42	10.66
60	42.91	57.68	26.58	10.38
80	42.97	57.68	26.35	10.02
100	43.14	57.61	26.43	9.89
Tectilon Blue GRL				
0	25.48	1.24	−33.18	12.46
20	25.51	1.39	−33.06	12.34
40	25.55	1.54	−33.06	12.02
60	25.72	1.34	−32.92	11.95
80	25.81	1.62	−32.98	11.78
100	26.16	1.62	−32.85	11.75
Tectilon Red F2G				
0	84.71	1.12	93.24	12.26
20	85.45	1.06	92.53	12.06
40	85.5	1.15	93.05	11.99
60	85.5	1.08	92.37	11.80
80	85.65	1.77	92.42	11.61
100	86.01	0.85	91.06	11.52

control dyed fabric produced the deepest shade. The color strength of control wool fabric dyed with Tectilon Red F2G, Tectilon Blue GRL, and Tectilon Yellow 2G was 12.26, 12.46, and 11.29 respectively, which decreased to 11.52, 11.75, and 9.89 respectively.

The wool fabric treated with 100 g/L shows the lowest color strength of all the three dyes investigated. The results indicate that the color strength of the stained fabric is related to the applied concentration of BSTP, which decreased with an increase in the applied BSTP concentration. The increase in the concentration of BSTP adversely affects the dyeability of wool, although the level of change in color strength compared to the control fabric dyed with the same dyes was small.

Stain Resistance of Treated Wool Fabrics. The stain resistance of control wool fabrics and also wool fabrics treated with various concentrations of BSTP against an acid dye-based stain is shown in Figure 7. The blank-treated control fabric showed very poor stain resistance as the intensity of the color of the stain was high. The spreading of the staining agent was restricted to a circle to the size of the stain applicator in a limited area, as the surface of the control wool fabric is quite hydrophobic. On the other hand, for the BSTP-treated fabrics, the stain spread all over the fabrics because of their increased hydrophilicity with an increase in the BSTP concentrations, which is evident by the low water contact angle data. The increase in the hydrophilicity increased the stain release properties of the fabric, and therefore the stain resistance against the acid dye-based stain increased with an increase in the concentration of BSTP. The control fabric showed the poorest stain resistance as the color difference (ΔE) between the stained and unstained control fabric is very high (59.84) as shown in Table 5. However, for the BSTP-coated fabrics, the value of color difference considerably decreased in comparison with the control fabric. In the case of BSTP-treated fabrics, the color difference (ΔE) between the stained and unstained samples decreased from 59.84 for the control to 45.29 and 40.35 for the fabric treated with 20 and 100 g/L BSTP, respectively. Therefore, the stain resistance of the treated fabrics decreased with an increase in the BSTP concentration.
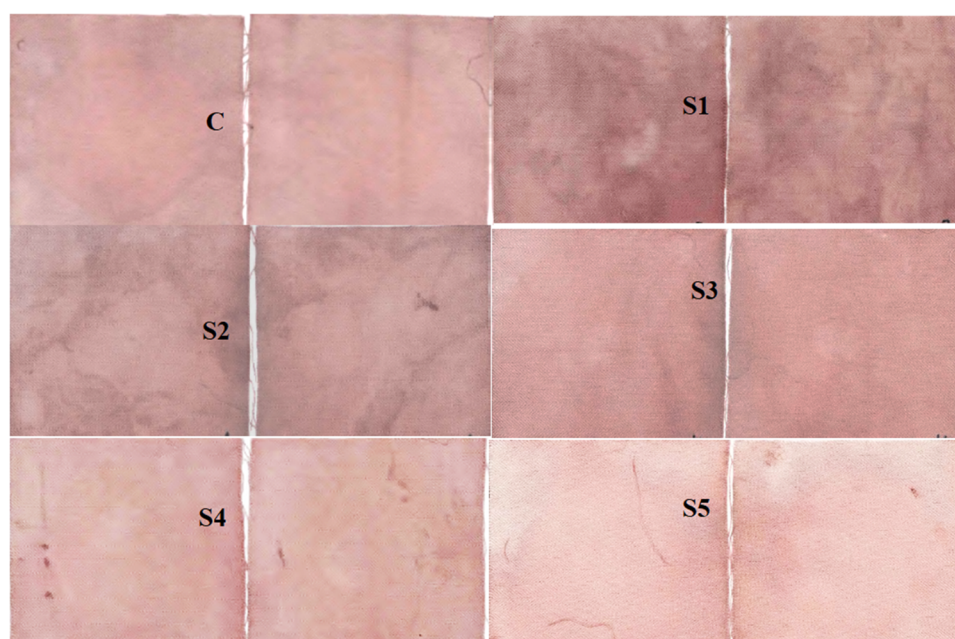
However, wool fabrics treated with BSTP showed mixed results against the red wine stain compared to the stain resistance observed against C.I. Acid Red 40 as shown in Figure 8. At lower concentrations of BSTP, the stain resistance of wool fabric against red wine was worsened compared to the control fabric but improved with an increase in the concentrations. The wool fabric treated with 20 g/L BSTP
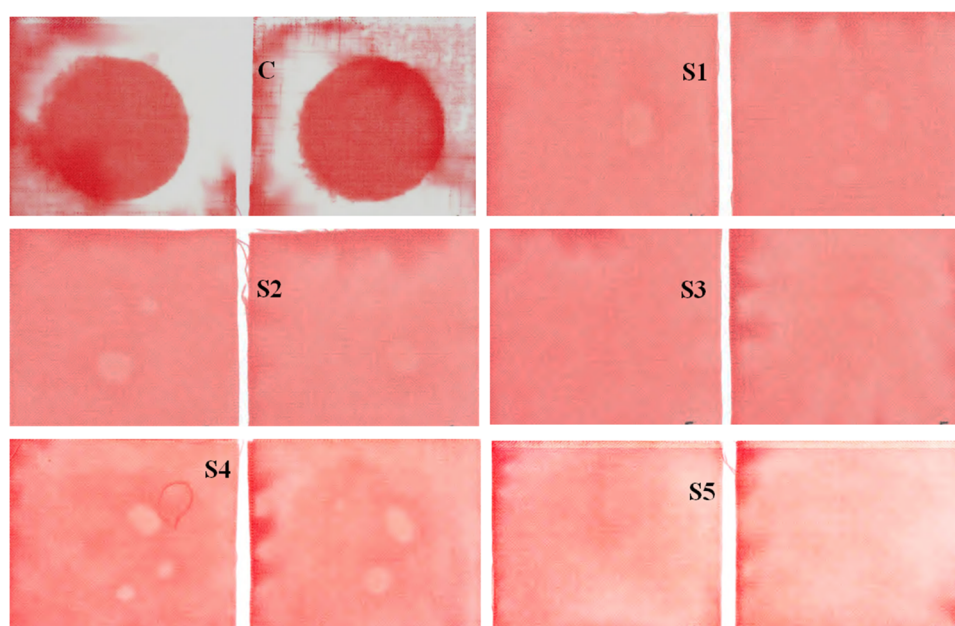
Figure 7. Stain-resist performance against C.I. Acid Red 40 of control wool fabric (C) and also wool fabrics treated with 20 g/L (S1), 40 g/L (S2), 60 g/L (S3), 80 g/L (S4), and 100 g/L (S5) BSTP.

Table 5. CIE $L^*a^*b^*$ Values and Color Difference (ΔE) of the Stain Samples Compared to the Untreated Standard Sample for C.I. Acid Red 140 and Red Wine

concentration of BSTP (g/L)	C.I. Acid Red 40				red wine			
	L^*	a^*	b^*	ΔE	L^*	a^*	b^*	ΔE
0	60.07	43.1	16.97	59.84	64.64	9.58	5.28	31.22
20	69.57	38.4	17.54	45.29	62.53	10.39	6.11	39.53
40	67.65	32.84	13.68	44.85	60.02	11.5	5.95	36.70
60	70.61	37.38	16.35	43.72	58.81	11.32	5.59	35.77
80	68.46	39.54	17.48	45.08	58.33	11.34	5.19	33.27
100	68.42	39	18.1	40.35	58.2	11.24	5.14	29.27

Figure 8. Stain-resist performance against red wine of control wool fabric (C) and also wool fabrics treated with 20 g/L (S1), 40 g/L (S2), 60 g/L (S3), 80 g/L (S4), and 100 g/L (S5) BSTP.

showed quite a poor stain resistance against red wine compared to the control fabric as the color difference increased from 31.22 for the control to 39.53 for the treated fabric. The increase in the BSTP concentration from 40 to 80 g/L decreased the color difference value but it was still higher than the color difference value shown by the control fabric. The wool fabric treated with 100 g/L BSTP only slightly decreased the color difference value compared to the control fabric. The application of BSTP negatively affected the stain resistance of wool fabric against red wine.

The red wine contains several polyphenols including anthocyanidin and tannin, and also the natural pigments of the skin of the grapes dissolved in the ethyl alcohol.[30] The treatment with BSTP affected wool fabric's natural resistance against red wine and the stain resistance decreased when the fabric was treated with a low concentration of BSTP. However, the stain-resist performance increased with an increase in the concentration of BSTP. The effect of BSTP coating of wool fabrics on stain resistance of wool fabrics was considerably less compared to the other polymers [such as poly-(chlorohydroxypropyl-diethylene adipamide ammonium chloride) or Hercosett 125] used for the shrink resistance of wool fabrics.[4]

Discussion. The coating treatment with BSTP increased the tensile strength and decreased the shrinkage of wool fabric during laundering. The coating formed on the wool fiber surface by BSTP contributed to the strength of the untreated fiber as reinforcement. The SEM images of wool fabrics coated with BSTP (Figure 3) show that at lower concentrations of BSTP, the increase in tensile strength and the shrink-resist performance of wool fabrics were quite low up to 40 g/L of BSTP as no inter-fiber bonding formed at that concentration and the reinforcement by coating of fibers with BSTP played the major role in increasing the tensile strength. However, at 60 g/L and above, a very uniform coating of BSTP was formed on wool fibers, and also the fibers were bonded together by the BSTP coating as shown in Figure 3. The inter-fiber bonding did not permit the movement of wool fibers, and therefore the tensile strength, as well as the shrink-resist performance, increased with an increase in the concentration of BSTP.

It can be seen that the stain resistance against the C.I. Acid Red 40, as well as the hydrophilicity of wool fabrics, increased with an increase in the BSTP concentrations. The surface tension of water, ethyl alcohol, and the wool fiber surface are 72.8, 22.39, and 30.95 mN/m respectively.[31] Therefore, it is much easier for ethyl alcohol to wet the wool fiber surface compared to water. From Tables 1 and 3, it can be seen that the time required to wet the fabric and the water contact angle of the surface of wool fabrics decreased with an increase in the concentrations of BSTP. However, an increase in the hydrophilic groups on the wool fabric surface by an increase in the concentration of BSTP should progressively increase the surface tension of the fiber. Therefore, the wettability by ethanol should be decreased and the stain resistance of wool fabric against red wine should increase with an increase in the concentration of BSTP. However, polyphenols are anionic but the wool fiber surface is strongly cationic at a pH below 5. The thin coating of weakly anionic BSTP formed on the wool fiber surface can only slightly reduce the cationic charge of the surface of wool fibers at these conditions. Therefore, at lower concentrations, BSTP coating cannot prevent the adsorption of polyphenols into the wool fiber. When red wine is left in air for 48 h for the stain-resist test, under aerobic conditions bacteria

in the wine slowly converts ethyl alcohol into acetic acid,[31] which reduces the pH of the red wine, and therefore the adsorption of polyphenol into wool fiber increased as the pH of the red wine decreased. It is known that wool fiber can electrostatically bind polyphenols.[32] Therefore, the increase in the wettability of the treated fabric in water did not increase their stain release properties either, resulting in a decrease in the stain resistance against red wine with an increase in the concentration of BSTP.

In the case of the acid dye-based stain, the increase in the hydrophilicity of wool fiber with an increase in the concentration of BSTP should increase the wettability of wool fabric by the aqueous acid dye-based stain, and therefore more staining acid dye should be absorbed into the fiber, thereby decreasing the stain resistance. Although acid dyes are strongly anionic, BSTP also forms an anionic surface layer on the fiber surface, which prevents the penetration of acid dyes into the interior of the fiber. The increase in the hydrophilicity of the fiber with an increase in the concentration of BSTP increased the stain release properties of the fabric as the fabric became easier to wash by water and the penetration of the staining dye was limited near the surface of the fibers. Therefore, the stain resistance of the treated wool fabrics increased with an increase in the BSTP concentration. In summary, the treatment with BSTP positively affected wool fabric's stain resistance against C.I. Acid Red 40 but negatively affected stain resistance against red wine, especially at lower concentrations.

Table 4 shows that the color strength of wool fabrics treated with BSTP decreased with an increase in its concentration. The BSTP contains weakly anionic hydroxyl groups and also the unreacted anionic Bunte salt groups that together affect the dyeing of wool with anionic acid dyes. Therefore, for all acid dyes investigated in this work, the depth of shade produced on the dyed fabrics decreased with an increase in the concentration of BSTP.

■ CONCLUSIONS

The effect of the coating of wool fabric with a BSTP on its dyeability, shrink resistance, mechanical properties, felting, and stain resistance was systematically evaluated. It was found that the treated fabric showed very good shrink resistance and very little felting tendency compared to the blank-treated control fabric. The shrink-resist performance improved with an increase in the concentration of BSTP. The treated fabric showed better whiteness and lesser yellowness compared to the control fabric. The BSTP coating had a positive effect on the tensile strength, breaking tenacity and elongation at break, and negatively affected the flexural rigidity and bending modulus of the treated wool fabric. The hydrophobic wool fabric surface became quite hydrophilic with the coating with BSTP, which increased with an increase in the concentration of BSTP. The treated fabric showed better stain resistance against C.I. Acid Red 40 but had little effect on the stain resistance against red wine, especially at high concentrations. These findings will help to develop a polymeric resin for providing shrink resistance to wool fabrics that will not affect the dyeability of wool fibers negatively.

■ EXPERIMENTAL SECTION

Materials. The wool fabric used was a 2/2 twill woven of 210 g/m² having 34 ends/cm and 24 picks/cm. The BSTP
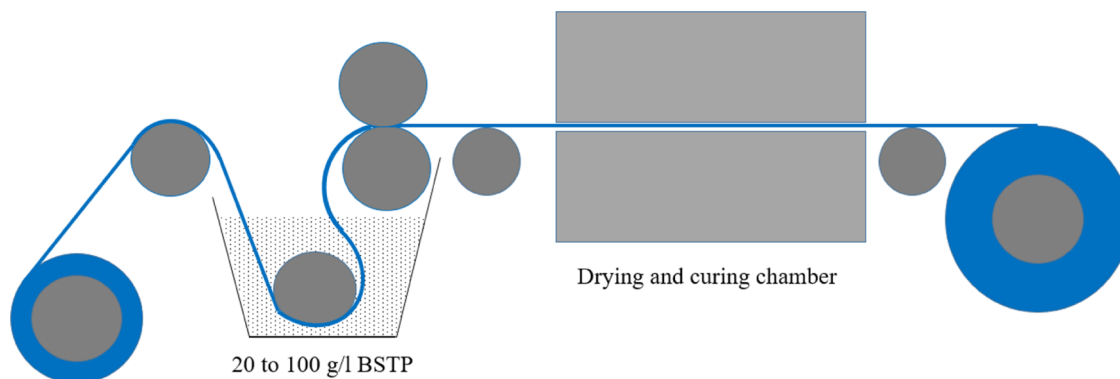
Figure 9. Schematic diagram of the coating of wool fabrics with BSTP by the pad-dry-cure process.

used in this work is a commercial product called 'Securlana K', which is a 40% aqueous solution of sodium salt of glycerol tri(polypropyleneoxide)ether tris(sulfothioglycolate), and it was purchased from Pulcra Chemicals (Germany). Hostapal MRN (a wetting agent) and Sandoclean PC (a non-ionic detergent) were procured from Clariant Chemicals (Switzerland). Sodium sulfite, acetic acid, and sodium acetate were supplied by Sigma-Aldrich Chemicals. Albegal FFA, a defoaming and leveling agent was supplied by BASF Chemicals (Germany). The standard phosphate-free detergent used for the shrink resistance of wool fabric was purchased from the Society of Dyers and Colorists (SDC), U.K. Three acid dyes, Tectilon Red F2G (C.I. Acid Red 337), Tectilon Blue GRL (C.I. Acid Blue 25), and Tectilon Yellow 2G (C.I. Acid Yellow 17) were purchased from Huntsman Chemicals Inc. for evaluating the dyeability of the BSTP-treated wool fabrics.

Pretreatment of Wool Fabrics. Lubricants are sprayed on wool fibers during the spinning process to reduce the damage of fiber due to the friction with various metallic parts of the spinning machine, which remains in the fiber even after weaving. Therefore, prior to the coating with BSTP, the wool fabric was scoured with a 2 g/L Sandoclean PC at 50 °C for 20 min using a 9-L capacity Vald Henriksen dyeing machine to remove the spinning lubricants. The fabric was then rinsed once in warm water at 45 °C and rinsed several times with cold water to completely remove the used detergent from the fiber.

Treatment of Wool Fabric with BSTP. Wool fabrics were soaked in aqueous solutions of 20, 40, 60, 80, and 100 g/L BSTP containing 0.25 g/L Hostapal MRN and 15 g/L sodium sulfite for 5 min. The wet fabrics were then passed through the two squeeze rollers of a padding mangle at 2 m/min speed and at 3.4 kPa pressure. The schematic diagram of the treatment of wool fabric with BSTP is shown in Figure 9. The treated fabrics were then dried at 90 °C for 3 min followed by curing at 140 °C for 3 min. They were then washed with hot water (60 °C) followed by rinsing with cold water until the pH of the water became neutral. After which, the treated fabrics were dried at 60 °C for 30 min.

Characterization of BSTP-Treated Wool fabric. The untreated and BSTP-treated wool fabrics were characterized by various methods as mentioned below.

Assessment of Shrink Resistance, Felting, Wettability, and Color Change. The shrink resistance measurement was carried out according to the Woolmark Test Method TM 31. In this method, the wool fabric samples were repeatedly washed five times according to the Woolmark 5A washing protocol at 50 °C for 60 min using three different concentrations of standard

phosphate-free detergent (SDC detergent) in a Wascator (SDL Atlas, Rock Hill), using a liquor ratio of 1:20. The washed fabrics were dried and their dimensions were measured compared to the original dimension of the fabric samples to quantify the felting shrinkage and shrink resistance performance. Felting of fabric samples was visually evaluated. The whiteness and yellowness indices were spectrophotometrically assessed by using a hand-held spectrometer (model: 45/0, BYK-GARDNER GmbH, Geretsried, Germany). The wettability of the control and BSTP-treated wool fabrics was evaluated after conditioning the samples in the standard atmospheric conditions (20 ± 2 °C and 65 ± 2% relative humidity) for 48 h according to the AATCC Test Method 39-1998: Evaluation of Wettability by placing a droplet of ultrapure water (2.82 mg) on various fabrics from two cm above. The time taken for the water droplet to completely disappear is considered as the wettability of the fabric and the lower value is considered as the better wettability. The samples were preconditioned under the above-mentioned conditions for 48 h prior to testing. At least 10 measurements were taken for each fabric sample and the averages are reported here.

Mechanical Characterization. An Instron Universal Tensile Testing Machine (model 4204, Instron Testing Systems, Inc., Norwood) was used to measure the tensile strength and elongation properties of the treated wool fabrics. The measurements were carried out at 20 °C and 65% relative humidity (RH) according to the ASTM Test Method D5035-06: A Standard Test Method for Breaking Force and Elongation of Textile Fabrics (Strip Method). The sample size was 25.4×152.4 mm^2, and the gauge length was 100 mm. The samples were conditioned at the above-mentioned conditions for 3 days before the testing was carried out. At least 10 samples were tested for each treated fabric and the averages are reported here. The bending stiffness of the wool fabric treated with various concentrations of BSTP was carried out using a Shirley Fabric Stiffness Tester (Shirley Developments Limited, Stockport, U.K.) according to the ASTM Test Method D1388-14: A Standard Test Method for Stiffness of Fabrics. The fabric samples were conditioned at 20 ± 2 °C and 65 ± 2% relative humidity for 48 h and the test was also carried out at these conditions. The flexural rigidity was calculated according to the following equation

$$\text{flexural rigidity, } G \text{ (N m)} = W \times C^3 \times 9.80 \times 10^{-6} \qquad (1)$$

where W = weight of fabric (g)/m^2, and C = bending length (mm). The bending modulus was calculated according to the following equation

$$\text{bending modulus (N/m}^2) = \frac{12 \times G \times 10^3}{T^3} \qquad (2)$$

where G = flexural rigidity (N m) and T = fabric thickness (mm).

Attenuated Total Reflectance-Fourier-Transform Infrared Spectroscopy (ATR-FTIR). Infrared studies were used to characterize the surfaces of the control and BSTP-treated wool fabrics. A PerkinElmer FTIR (model: System 2000, PerkinElmer, Inc., Waltham) spectroscopy was used for recording the FTIR spectra of various fabrics. The spectroscope was equipped with an ATR attachment and a zinc–selenium (Zn/Se) crystal. A fabric sample was placed over the Zn/Se crystal and 64 scans at a resolution of 4 cm^{-1} were performed for each sample and the averages are reported here.

Contact Angle Measurement. The contact angle was measured by using a KSV CAM 100 Contact Angle Measurement Apparatus (KSV Instruments, Helsinki, Finland) and was calculated by using the Young–Laplace equation. The contact angle was measured at 10 places for each treatment and the average contact angle was reported. For each sample, the first measurement was taken immediately after placing the droplet of water and then at 10 s interval measurements were taken until 40 s.

Scanning Electron Microscopy. To assess whether a change in surface scales of wool fiber took place during the treatment with BSTP, the treated fabrics were scanned under a Hitachi scanning electron microscope (model: TM3030 Plus, Hitachi Corporation, Japan) at 15 kV. The fabric samples were scanned without any conductive coating.

Evaluation of Dyeability. The dyeability of the fabric was evaluated by dyeing the control fabric and BSTP-treated fabric samples with three acid dyes, namely Tectilon Blue GRL, Tectilon Yellow 2G, and Tectilon Red F2G at 2% on the weight of the fiber (owf). All dyeings were carried out in an Ahiba laboratory dyeing machine (model: Turbomat 1000, Datacolor International, Switzerland) using tap water and with a material to liquor ratio of 1:30. The dye bath was prepared with the required quantity of dye, 10% owf sodium sulfate (as an electrolyte), 1.0 g/L Albegal FFA, and 0.25 g/L Sandozin MRN. Five grams of fabric was cut from the control fabric as well as from each treated fabric, and all of them were dyed in the same bath to compare their dyeability. The pH was adjusted to 4.7 with acetic acid and sodium acetate solution. The bath was then heated from ambient room temperature at 2 °C/min to 98 °C and held for 60 min followed by cooling at 2 °C/min to 40 °C. The bath was then dropped, the dyed samples were rinsed in warm water (60 °C) for 15 min, and then also with cold water for two times to remove the dyes adsorbed to the surface of wool fibers. The fabric samples were then dried and various color measurements were carried out.

Color Measurement. The color measurements of wool fabrics dyed with three acid dyes were carried out under illuminant D65, using a 10° standard observer with UV component and specular excluded by using a Datacolor reflectance spectrophotometer (model: Spectraflash SF 600, Datacolor International, Switzerland) interfaced to a personal computer.[33] The reflectance values of the dyed samples were measured at the appropriate wavelength of the maximum absorption for each dye and the color strength (K/S) was measured according to the Kubelka–Munk equation. The samples were folded three times and four measurements were made on each sample. The average value is reported here. The

color difference was calculated by measuring CIE L^*, a^*, b^* color difference (ΔE) at different places of each dyed fabric under illuminant D65, using a 10° standard observer by a BYK-Gardner Spectro-Guide 45/0 gloss Color Spectrophotometer (BYK-GARDNER, Germany).

Evaluation of Stain Resistance. The stain resistance of the control and treated wool fabrics was assessed according to the AATCC Test Method 175-2008 Stain resistance: Pile Floor Coverings against C.I. Acid Red 40 and red wine staining agents. For each treatment, two samples of 100×100 mm^2 size were used. The samples were conditioned at the standard atmospheric conditions (65 ± 2% RH, 20 ± 2 °C) for 24 h. For blank staining, distilled water with a pH of 2.8 ± 1.0 (adjusted by citric acid) was used. One fabric sample was blank-stained and two samples were stained with either C.I. Acid Red 40 or red wine. The stain applicator was placed at the center of a fabric sample, and then 20 mL of C.I. Acid Red 40 solution or red wine into the center of the applicator. The top of the stain applicator was pressed with the flat of the inside of the hand. The applicator was carefully removed and the stained fabric samples were left in the conditioned room for 24 h, then rinsed under running tap water, dried in an oven at 80 °C and returned to the conditioned room. Color measurements of unstained and stained samples were carried out with a Mahlo spectrophotometer (under D65 illuminant and 10° observer). For each treatment, three samples were examined and the averages are reported here.

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Notes

The author declares no competing financial interest.

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