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A simultaneous antimicrobial and shrink resistance treatment of wool woven fabrics using the polymeric biocide polyhexamethylene biguanide

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Abstract Recently, a novel, effective, and commercially viable antimicrobial treatment for wool was reported that used a peroxymonosulfate/sulfite pretreatment and the biocide polyhexamethylene biguanide (PHMB). Given the polymeric nature of PHMB used in this antimicrobial treatment, this study investigated whether the treatment would also lead to shrink resistance of woven wool fabrics. It was shown that up to 5% PHMB (on mass of fabric) could be exhausted onto the pretreated wool at 40 °C. Under scanning electron microscope, PHMB was observed to coat the wool surface with no obvious interfiber bonding. PHMB finishing was durable to laundering, had little effect on the tensile strength of the fabrics and only slightly increased the bending rigidity. The finishing conferred strong antimicrobial activity to the fabrics and at the same time reduced felting shrinkage after laundering to an acceptable level. Thus, a single finishing process achieved two important functionalities for wool fabrics, antimicrobial activity and shrink resistance.

Introduction

Antimicrobial treatments of textiles have attracted considerable attention in recent years, both in academic research and in commercial products [1, 2]. The treatments, which inhibit the growth of or kill microorganism on the textiles, not only provide health and hygienic benefits, but also protect the textiles from discoloration and physical deterioration that can arise from bacterial growth. It is estimated that antimicrobial textiles are one of the fastest growing sectors of the textile market [2].

Commercial antimicrobial treatments of textiles use biocides such as silver (or its salts), quaternary ammonium compounds (QAC), polyhexamethylene biguanide (PHMB), and triclosan [1, 2]. These agents can be incorporated into the dope before extrusion of synthetic fibers (e.g., polypropylene, polyester, and nylon) or applied to synthetic and cellulosic fibers using an exhaustion or pad-dry-cure process [3–6]. Antimicrobial treatments of wool are more difficult to achieve due to its unique surface properties. In laboratory studies, wool has been exhausted with QAC [7, 8], covalently linked to thiol-containing QAC [9], adsorbed with metallic salts (Ag^{+} and Cu^{2+}) [10, 11] or coated with chitosan [12–14]. However, these finishings cause pollution of the environment, adversely affect fabric handle or have poor washing durability, and have therefore not been adopted for commercial productions of antimicrobial wool fabrics.

One issue with wool fabrics is their tendency to shrink due to felting upon laundering. The shrinkage results from the differential friction caused by the overlapping cuticle cells on the fiber surface and a good review of the mechanism is provided by Makinson [15]. For wool top, shrink resistance is commonly achieved by the chlorine-Hercosett process [15]. In this process, oxidation with chlorine partially degrades the cuticle cells and removes the outer lipid layer. Subsequent exhaustion and deposition over the entire fiber surface of the cationic, water swellable polymer, Hercosett, reduces the differential friction and hence felting shrinkage. Shrink resistance treatments can also be performed at fabric stage. Wool fabrics can be coated, for example, with a water soluble pre-polymer Synthappret

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BAP that crosslinks upon drying and curing [16]. Alternative fabric treatments include pretreatment with peroxide under alkaline conditions [17, 18], plasma [19–21], and enzymes [22–24] followed by coating with a polymer such as chitosan [18, 25, 26] or protein [27]. In these fabric-based treatments, the polymer tends to form bridges between individual fibers preventing their movement and hence conferring shrink resistance.

Denning et al. [28] reported that oxidation of wool with peroxymonosulfate (PMS; also known as Caro's acid, H_2SO_5) was very effective as a shrink resistance treatment. In this process, wool is first oxidized with PMS and then treated with a reducing agent such as sodium sulfite [28–30]. As with chlorination, application of a polymer is still needed if adequate shrink resistance is to be achieved. Recently, it was demonstrated that this PMS/sulfite pretreatment, in addition to achieving shrink resistance, also enabled the otherwise unreceptive wool to take up a large amount of PHMB by exhaustion [31, 32]. PHMB is a strong, fast acting, and broad spectral biocide against bacteria. This formed the basis for a novel, effective, and durable antimicrobial treatment for wool textiles. As PHMB is a polymer, its deposition on wool, like other polymers, may also lead to shrink resistance of the fabrics. This study investigates the shrink resistance as well as antimicrobial ability of PHMB exhausted on PMS/sulfite-pretreated wool and shows that a single process can simultaneously achieve these two functionalities in wool fabrics.

Experimental

Materials

The wool fabric used in this study was an untreated, square sett, plain weave of 152 g/m^2 (R60/2 tex yarn; 495 tpm Z; 385 tpm S for the ply; 11.4 end and 10.9 picks/cm) produced from Australian Merino wool (19 µm in diameter) with minimal finish. PMS (trade name Oxone) was obtained from DuPont. Sodium sulfite, and Triton X-100 and reagents for *Escherichia coli* culture (i.e., yeast extract, tryptone, and agar) were obtained from Sigma. PHMB in 20% (w/v) aqueous solution was purchased from Arch Chemicals and adjusted to pH 7–7.5 with NaOH solution before use.

Pretreatment with PMS and sulfite

The pretreatment was adopted from the wool shrink resistance treatment [28] and consisted of two sequential steps. The fabrics were first treated with PMS (2 g/L) solution containing 1 mL/L of the non-ionic surfactant Triton X-100 as a surfactant at room temperature for 15 min, rinsed thoroughly in water and squeezed to remove excess water. Subsequently, the fabrics were treated with 10 g/L sodium sulfite (pH adjusted to 8.2–8.5 with 2 M sulfuric acid) at room temperature for 15 min, again rinsed with water and squeezed. The liquor to wool mass ratio for both PMS and sulfite treatments was 40:1 (v/m). The fabrics were dried at 80 °C for 45 min and stored at room temperature before use.

Determination of PHMB exhaustion

Untreated and PMS/sulfite-pretreated fabrics, 0.40 g each, were immersed individually in 20 mL solutions containing 0.1% Triton X-100 with the designated amount of PHMB, i.e., 2, 4, or 8% solid on mass of fabric (omf) at 40 °C with continuously shaking for up to 60 min as previously described [31]. At specific times, 50 µL solutions were withdrawn from each treatment and diluted with deionised H_2O by 50 or 100 fold. The absorbance of the diluted solutions was measured in a UV–Visible spectrophotometer at 236 nm, at which PHMB had a strong absorbance proportional to its concentration [31]. The exhaustion of PHMB was calculated from the initial absorbance and the absorbance at the sampling time point.

Polyhexamethylene biguanide uptake was also determined by mass gain. PMS/sulfite-pretreated fabrics (160 × 155 mm, ~4.5 g) were accurately weighed (to ±1 mg) after conditioning (20 °C and 65% relative humidity, 48 h) and then treated with 0, 2, 4, or 8% (omf) PHMB by exhaustion in a bath at 40 °C for 60 min, thoroughly rinsed in deionized water (for 1 h with three changes of water), conditioned and the mass gain determined as above. PHMB uptake was calculated from the mass difference before and after the treatment.

Area felting shrinkage testing

Fabrics were cut to 160 × 155 mm in size with a marked area of 100 × 95 mm in the center. They were either untreated, pretreated with PMS/sulfite or pretreated and further exhausted with 2, 4, or 8% (omf) PHMB in the bath at 40 °C for 60 min as described above. A THOR washing machine was used in this study. The S (synthetic) cycle on this machine had been previously shown to induce similar felting shrinkage to the ISO 5A cycle on the fabric used in this study. For wool fabrics, the ISO 5A cycle is used as an accelerated test method, being equivalent to 8–10 wool wash cycles (ISO 7A cycle). The fabrics were relaxed first using the wool wash J cycle and then repeatedly washed for five cycles using the S cycle at 40 °C (i.e., accelerated testing equivalent to ~40–50 wool wash cycles). Ten grams of laundry powder and polyester fabrics to make the total load to 1 kg were included in the wash. After each wash, the dimensions of the central marked area were measured at three points each in the warp and weft directions. The fabrics shrank to a similar extent in the warp and weft directions. Area shrinkage was expressed as average ± standard error of mean of three independent replicates.

Antimicrobial test

Antimicrobial tests were performed according to the Assessment of Antibacterial Activity on Textile Materials (AATCC Test Method 100-1999). *E. coli* (ATCC-8739) was grown overnight in sterile LB broth (5 g/L Yeast extract, 10 g/L Tryptone, and 10 g/L NaCl, pH 7.0–7.2). The overnight culture was diluted to 1×10^7 cells/mL in the nutrient broth before use. Untreated, PMS/sulfite pretreated and PHMB treated (exhausted with 2, 4, and 8% PHMB omf in the bath) fabrics (~0.4 g, 50 × 50 mm in size) were wetted in 0.1% Triton X-100, rinsed in water, padded dry with absorbent tissue, cut into four small squares and stacked together. The damp squares were inoculated with 250 μL of the diluted culture. Care was taken so that the inoculum was fully absorbed without leaving any free fluid. The stack of fabrics was then transferred to a 250-mL wide-mouth jar, sealed and incubated in an oven at 37 °C for 5 h. After the incubation, 100-mL sterile distilled water was added to each jar which was then shaken vigorously by hand for 1 min to elute bacteria from fabrics. The number of colony forming units (CFU) were determined by serial dilution and plating on nutrient agar plates. "Time zero" assays were performed by eluting the cells immediately after the inoculation of untreated fabrics. The efficacy of antimicrobial activity is expressed as: bacterial reduction (%) = $100\% \times (B - A)/B$, where A is the number of CFU after the 5 h incubation from test samples, B is the number of CFU at zero contact time. If $A > B$, there was no reduction (N.R.).

Scanning electron microscopy (SEM) and FT-IR

Scanning electron microscopy was performed using a Hitachi S4300 SE/N at 1.2 kV accelerating voltage at 400, 2500, and 5000 magnifications. Before examination, a Pt/Pd sputter coating was applied to the sample surface. A Perkin Elmer Spectrum 100 FT-IR Spectrometer using an attenuated total reflection accessory was used to examine PHMB on the surface of treated wool fabrics.

Physical testing

All treatments, each with three replicates, were conditioned at 20 °C and 65% relative humidity for up to 48 h before physical testing. Bending tests were performed on the KES-FB2 Pure Bending Tester on samples of 200 × 200 mm in size. Tensile test was performed according to the ASTM D5034-09 test method using an Instron at an extension rate of 80 mm/min on samples of 50 × 200 mm in size in the weft orientation.

Results

PHMB is a polymeric biocide

Polyhexamethylene biguanide is a potent biocide with broad spectral activity against both gram positive and negative bacteria, yet with low toxicity to higher organisms. The minimal inhibitory concentrations range from 0.5 (e.g., against *Staphylococcus aureus*) to 10 ppm (e.g., against *Klebsiella pneumoniae*) (Arch Chemicals technical information). As such, it has long been used as a disinfectant in the food industry, sanitization of swimming pools [33] and more recently applied to cotton to produce antimicrobial textiles [2]. PHMB is also one of the very few polymeric biocides and its commercial preparations have an average molecular weight of ~2,500 Da (Fig. 1). In a previous study of antimicrobial treatment of wool, it was reported that large quantities of PHMB (e.g., up to 5% omf) could be exhausted onto wool after pretreatment with PMS/sulfite [31]. As polymer coatings are often used for wool shrink resistance treatment, we investigated here whether PHMB exhaustion would also confer shrink resistance.

PHMB exhaustion on PMS/sulfite-pretreated wool

In this experiment, untreated or PMS/sulfite-pretreated wool fabrics were exhausted with 2, 4, or 8% (omf) PHMB in the bath at 40 °C. The absorbance of PHMB at 236 nm was used to quantify exhaustion from the solutions, as described previously [31, 34]. Figure 2 shows that untreated fabrics hardly exhausted any PHMB at any of these concentrations. On the other hand, the PMS/sulfite pretreatment enabled the fabrics to take up PHMB from the solutions (Fig. 2). The amount of PHMB exhaustion increased sharply in the first 10 min and reached a plateau at around 40 min. After 1 h treatment, the fabrics exhausted 1.7, 3.7, and 5.5% of PHMB (omf) from the 2, 4, and 8% (omf) solutions, respectively, as calculated from absorbance change in the solutions.

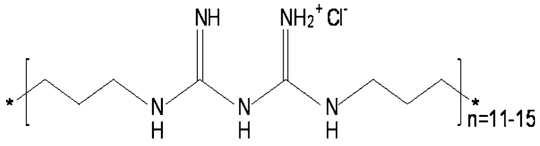

Fig. 1 Structure of PHMB showing its cationic and polymeric nature

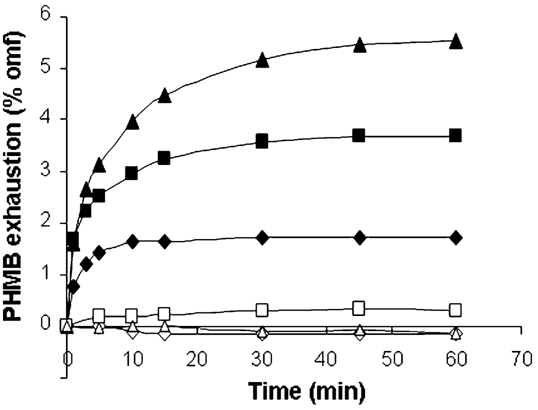

Fig. 2 PHMB exhaustion onto untreated (*open symbols*) and PMS/sulfite-pretreated (*filled symbols*) wool fabrics at 2% (*diamond*), 4% (*square*), or 8% PHMB (*triangle*) (omf) in the bath at 40 °C

The exhaustion was also determined by direct mass gain of the fabrics. The uptake of the PMS/sulfite-pretreated fabrics treated with 2, 4, or 8% (omf) PHMB in the bath at 40 °C for 60 min was 2.2, 3.9, and 4.7% omf PHMB, respectively, when corrected for the small mass loss of 0.3% in the absence of PHMB (i.e., 0%; presumably due to the loss of a small amount of protein) (Fig. 3). These results agreed reasonably well those determined by the absorbance method described above (Figs. 2, 3), and confirmed that the PMS/sulfite-pretreated wool fabrics were capable of taking up large amounts of PHMB.

Effect of PHMB on shrinkage

The PMS/sulfite pretreatment has been reported to be a very effective non-chlorine method for wool shrink resistance, reducing fabric shrinkage from 42 to 3% after one wash cycle [28]. However, it alone was inadequate to meet the requirement for adequate shrink resistance as stipulated by Woolmark Test Methods, and a polymer coating was still needed.

The shrink resistance effect of the PHMB treatment was investigated using a plain woven wool fabric which, if untreated, had area shrinkage up to 48% after one wash cycle. The PMS/sulfite pretreatment reduced the shrinkage to 5.3% after one wash and to 17.5% after five washes on the S cycle of the THOR washing machine (Fig. 4). Further finishing the pretreated fabrics with PHMB reduced the shrinkage in a dose dependent manner. The fabrics exhausted with 2, 4, or 8% (omf) PHMB in the bath had shrinkages of 5.4, 3.8, and 2.1% after one wash and 14.2, 11.7, and 7.1% after five washes (which were equivalent to 40–50 × ISO 5A washes), respectively, (Fig. 4). It appeared that exhaustion with 8% PHMB in the bath (which led to 4.5–5.0% PHMB add-on, Figs. 2, 3), in conjunction with the pretreatment, was able to reduce area shrinkage to <10% after 5 × ISO 5A washes. The requirement for adequate shrink resistance as stipulated by Woolmark Test Methods is less than 3% shrinkage in both the warp and weft directions after 5 × ISO 5A washes for woven shirts or blouses (W1, August 2000).

Characteristics of wool surface

Scanning electron microscope was used to examine the wool surface at low and high magnifications after PHMB finishing (Fig. 5). The untreated wool showed sharp cuticle cell edges which were responsible for creating the differential friction and hence fabric shrinkage during laundering. The PMS/sulfite pretreatment produced winkles on the surface and evidently softened the scales and their edges. The pretreated wool exhausted with 8% PHMB (omf) in the bath at 40 °C for 5 min (by which time the wool had taken up around 3% PHMB, see Fig. 2), showed evidence of a polymer covering the surface of the wool and partially

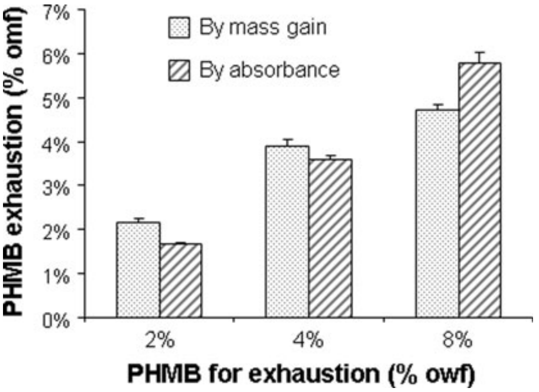

Fig. 3 Determination of PHMB exhaustion onto wool by mass gain and by absorbance at 236 nm. PMS/sulfite-pretreated wool fabrics were exhausted with 2, 4, and 8% PHMB in the bath at 40 °C for 1 h

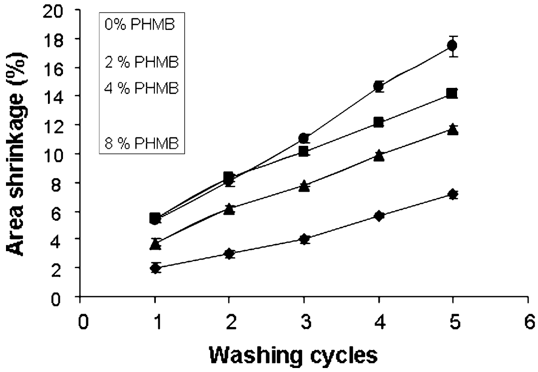

Fig. 4 Effect of PHMB exhaustion on wool fabric shrinkage. Fabrics were pretreated with PMS/sulfite, exhausted with 0, 2, 4, or 8% PHMB in the bath and then repeatedly washed for five cycles. Untreated fabrics shrank by ~45% after a single wash

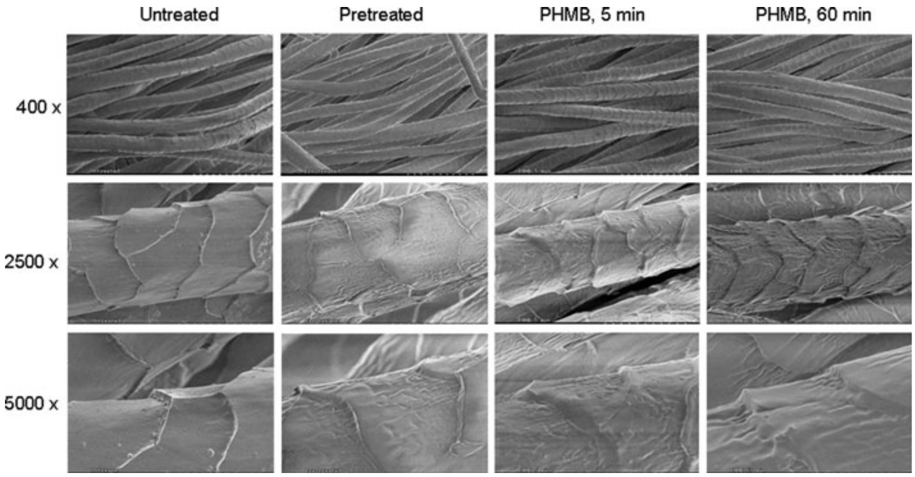

Fig. 5 SEM images of untreated and PMS/sulfite-pretreated wool and wool after pretreatment and further finishing with 8% PHMB in the bath for 5 and 60 min. Magnifications: ×400, ×2500, and ×5000

filling the edge of the cuticle cells. By 60 min (at which time the wool had taken up nearly 6% PHMB, see Fig. 2), these effects became even more striking (Fig. 5). PHMB appeared to produce an even coating on the fiber. No lumps, particles, or filaments were observed on the fiber surface or between individual fibers in any of the SEM images, indicating no inter-fiber bonding after the PHMB treatment.

FT-IR analysis

Fourier Transform Infrared Spectroscopy (FT-IR) analysis was carried out to confirm the presence of PHMB on the PMS/sulfite-pretreated wool as well as to examine its durability to washing. PHMB had a strong absorbance between 1200 and 1700 cm^{-1}, with a sharp peak at 1550 cm^{-1} (Fig. 6a). Untreated and pretreated wool had two major absorptions in this region, amide 1 (*A*) at 1633 cm^{-1} and amide 2 (*B*) at 1537 cm^{-1}, with the former slightly larger (the ratio of *A/B* was 1.06) (Fig. 6b). Further treatment with PHMB reversed their relative sizes, changing their ratio to 0.90 (Fig. 6d), due to the PHMB absorbance overlapping more with peak *B* in the wool.

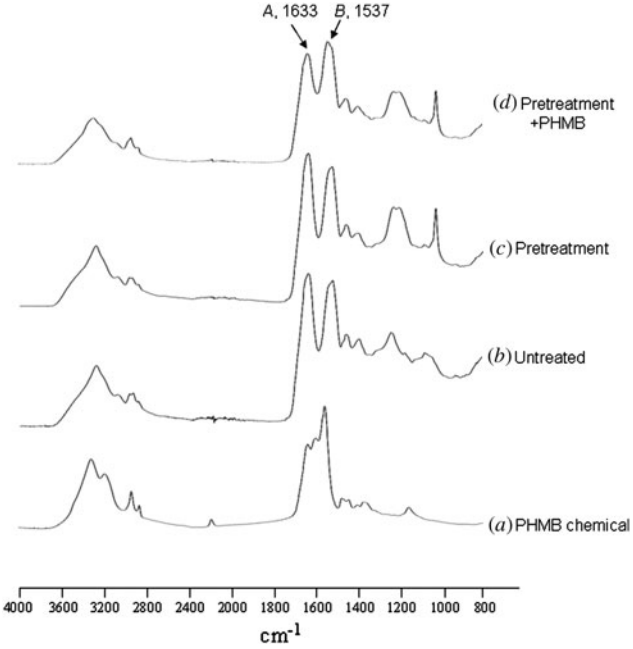

Fig. 6 FT-IR spectra of PHMB (*a*), untreated wool (*b*), wool after PMS/sulfite pretreatment (*c*), and wool after the pretreatment and PHMB exhaustion (*d*) showing the change in peak *A* (1537 cm^{-1}) and peak *B* (1633 cm^{-1}) after PHMB treatment

The ratio could therefore be used as an indication of PHMB presence on the wool. The spectra of PHMB-finished wool fabrics after washing for up to five S cycles were essentially identical, and the ratio between peaks *A* and *B* remained unchanged during the washing process (Fig. 7). This indicated that the PHMB treatment was not lost during laundering.

Antimicrobial activity

After exhaustion with different amounts of PHMB (0, 2, 4, or 8% omf in the bath), the wool fabrics were washed up to five S cycles in the THOR washing machine to determine the washing durability of antimicrobial activity using the gram negative bacteria *E. coli*. The pretreated fabrics (i.e., with 0% PHMB finishing) did not display any antimicrobial activity (Fig. 8) while the fabrics finished with 2, 4, or 8% (omf) PHMB in the bath all had strong antimicrobial activity before washing, reducing bacteria counts by >99%. However, antimicrobial activity of the fabrics finished with 2% PHMB decreased rapidly with washing and was essentially lost after three washes. Fabrics finished with 4% PHMB maintained 94% bacterial reduction after five washes while those finished with 8% PHMB showed very good durability to washing, maintaining 99% bacterial reduction after five washing cycles (Fig. 8).

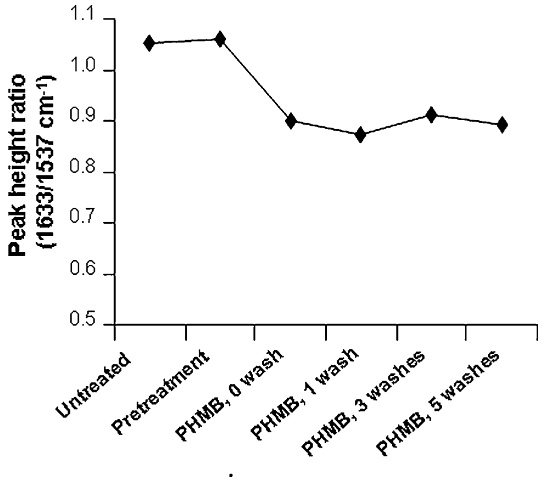

Fig. 7 The ratio of absorbance at peak *A* (1633 cm^{-1}) and *B* (1537 cm^{-1}) in FT-IR analysis. Pretreated fabrics were finished with 8% (omf) PHMB in the bath at 40 °C for 60 min and then washed for up to five cycles

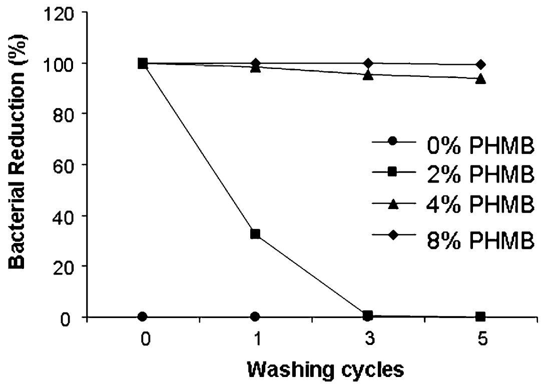

Fig. 8 Antimicrobial activity, expressed as percentage bacterial reduction, of wool fabrics exhausted with various amounts of PHMB in the bath and washed up to five cycles. The AATCC 100-1999 method and *E. coli* bacteria were used in the test

Physical properties

One important consideration both in antimicrobial and shrink resistance treatments is that they should not adversely affect the physical properties of the fibers or fabrics to an unacceptable degree. Critical physical parameters include tensile strength and bending rigidity (an important component of fabric softness and handle). Table 1 shows that the PMS/sulfite pretreatment slightly decreased tensile strength and bending rigidity, most likely due to the loss of some protein from the fabrics and chemical bond scission during the wet treatment. Further finishing with PHMB increased tensile strength by up to 8% and bending rigidity by up to 13% over untreated fabrics. These small increases were expected because of the presence of PHMB on the fabrics. Subjectively, the appearance and handle of PHMB-finished fabrics were almost indistinguishable to untreated or pretreated fabrics.

Discussion

This study has demonstrated that the previously reported antimicrobial treatment for wool also imparts shrink resistance to woven fabrics. The process uses the PMS/sulfite pretreatment, which is adopted from wool shrink resistance treatment, to render the otherwise unreceptive wool to take up large quantities of PHMB. As a polymeric biocide, PHMB on the wool fabrics provides strong and durable antimicrobial activity and at the same time further enhances shrink resistance. Thus, a single process simultaneously confers two important functionalities.

The PMS/sulfite pretreatment was originally developed for wool shrink resistance [28]. The treatment with PMS partially oxidizes disulfide bonds to cysteic acid, cystine-S-monoxide and cystine-S-dioxide groups while the reduction with sulfite causes nucleophilic fission of disulfide or partially oxidized residues. Both PMS and sulfite are essential, as neither alone conferred any significant shrink resistance [28–30]. Similarly, neither of these two chemicals alone was effective in generating wool highly receptive for PHMB exhaustion [31]. When used as sequential treatments, the PMS/sulfite pretreatment enabled wool to rapidly take up large amounts of PHMB (i.e., >4.5% omf) under mild exhaustion conditions (i.e., at neutral pH and 40 °C) (Figs. 2, 3). Several observations from the treated fabrics, such as PHMB's ability to kill bacteria by direct contact in antimicrobial assays, its detection by surface analysis of FT-IR, together with relatively fast exhaustion at 20–40 °C, suggested that the PHMB was largely located on the fiber surface rather than having diffused into the fiber. This was confirmed by direct SEM imaging (Fig. 5).

As PHMB was a potent biocide, its deposition on the wool fiber surface conferred strong and durable antimicrobial activity to the wool fabrics. Unwashed fabrics that contained 2% (omf) PHMB or more were able to deactivate almost all of the *E. coli* bacterial cells in standard assays (Fig. 8). Although fabrics containing 2% (omf) PHMB had poor washing durability, those containing >3% (omf) PHMB maintained >90% bacterial reduction after five washes (Fig. 8). This excellent durability to washing was confirmed by FT-IR analysis and was consistent with previous reports that antimicrobial activity could be effectively maintained after 25 washes (S cycle) using a higher sett fabric with less propensity for felting shrinkage [31, 32]. The PHMB on the fabrics should therefore be 3% omf or more for durable finishing but could be 2% or less for items that are not to be washed repeatedly. These

Table 1 Physical properties of wool fabrics after exhaustion with PHMB

	Untreated	Pretreated	2% PHMB	4% PHMB	8% PHMB
Bending rigidity (μN m)	7.92 ± 0.11	7.17 ± 0 .06	7.97 ± 0.22	8.8 ± 0.14	8.95 ± 0.05
Tensile strength (N)	259.5 ± 1.0	243.1 ± 1.8	266.7 ± 2.3	280.6 ± 6.8	281.0 ± 7.8

amounts are comparable to the 2–4% (omf) for durable finishing and 0.25–1% (omf) for disposable items recommended for cotton [2].

Like other polymers used on wool, PHMB also imparted shrink resistance to the wool fabrics. The coverage of the wool surface by PHMB was expected to reduce the differential friction of the fibers within the yarn during washing and, as a result, reduce felting shrinkage in a dose dependent manner (Fig. 4). The high solubility of PHMB in water and the exhaustion method used in its application contributed to the formation of an even coating on the fibers. It is highly unlikely that crosslinks would form between PHMB molecules or with the fiber surface as there are no reactive groups in PHMB and the conditions used for the exhaustion process were mild. No sign of PHMB aggregates on the surface of the fibers or between fibers were observed under SEM, thus eliminating interfiber bonding as part of the mechanism for the shrink resistance.

Finishing fabrics with polymers can severely impair their handle (i.e., softness), as in the case with chitosan or proteins [25, 27]. However, PHMB treatment had only a small effect on the bending rigidity of the wool fabrics (Table 1), and the handle was almost indistinguishable before and after the treatment. The lack of any adverse effect on the handle may be attributed to the relatively small size and the lack of interfiber bonding after PHMB coating.

Conclusion

This work has demonstrated that the PMS/sulfite pretreatment enables wool to take up the polymeric biocide PHMB in large quantities. PHMB coverage on wool not only provides effective and durable antimicrobial activity but also enhances shrink resistance.

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