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Strong insect-resist property and wash-durability exhibited by wool fabric sustainably treated with a natural diterpenoid and a synthetic pyrethroid under subcritical CO_2

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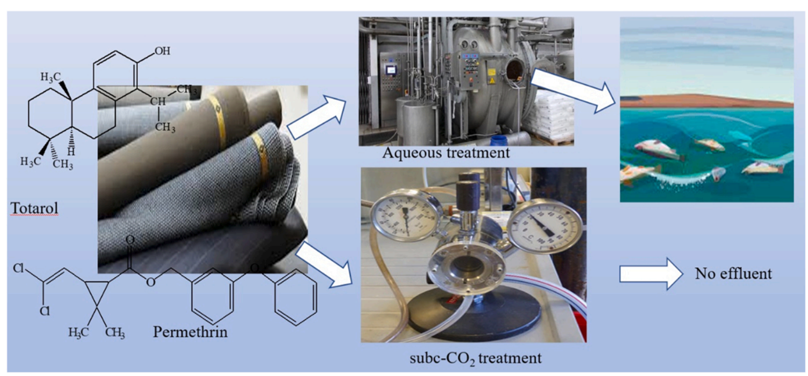
HIGHLIGHTS

- Wool fabrics were treated with torarol and permethrin insect-resist agents under subc-CO_2.
- The insect-resistance of treated fabric was compared with the aqueous-treated fabric.
- The totarol-treated fabric did not exhibit any insect resistance even at a very high dosage.
- The fabric treated with permethrin by the aqueous method lost insect resistance after 10 washes.
- The permethrin-treated fabric by the subc-CO_2 method showed insect resistance after 20 washes.

GRAPHICAL ABSTRACT



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ABSTRACT

To conserve wool textiles from insect attack, they are frequently treated with emulsions of natural and synthetic pyrethroid in an aqueous medium. Although the treatment is highly effective, it produces toxic effluent. In this work, insect-resist wool fabrics were produced by treating them with a natural diterpene (totarol), and a synthetic pyrethroid (permethrin) in a subcritical carbon dioxide (subc-CO_2) medium. The totarol treatment failed to provide any insect-resist activity but the permethrin treatment even at 0.03% on the weight of wool fiber (owf) showed excellent insect-resist properties and the mortality of the larvae was more than 98%. The wool fabrics treated with permethrin at 0.03% owf under subc-CO_2 only marginally lost insect resistance after 20 washes (equivalent to 80 domestic washes) but at 0.09% owf, still, the mortality of larvae was more than 98%. However, the fabric treated with 0.05% owf by the traditional aqueous treatment completely lost its insect-resistance property after 5 washes. The Soxhlet extraction of permethrin with dichloromethane from the treated fabric and GC-MS analysis of the extracted permethrin suggest that most of the permethrin was absorbed into the wool fiber. The developed process could be a durable and sustainable treatment for the conservation of wool textiles.

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1. Introduction

Wool fiber is a natural protein fiber made of keratin polymer that was in use for the manufacturing of textiles from ancient times as wool textiles production started in the fourth millennium BCE [1]. It is an important fiber as it has outstanding inherent characteristics including warmth, wrinkle-resistance, heat insulation, resilience, fire retardancy, and aesthetic properties, and is also easier to dye compared to other textile fibers [2]. Currently, wool fiber is used in the manufacturing of fabrics for luxury fashion apparel and suiting. However, apparels made with wool fibers are prone to insect attack, which affects their usability and longevity. Compared to the insects, their larvae are more damaging to the fiber as they live on feeding the fiber and they are more difficult to kill than the moths as they often remain hidden within food sources [3]. The larvae of the webbing clothes moth (*Tineola bisselliella*), and case-bearing clothes moth (*Tineola pellionella*) make tiny holes in the fabric and the size of these holes increases with time, making them unusable. In a keratin protein fiber like wool, polypeptide macromolecular chains are crosslinked by many disulfide bonds that provide the fiber high strength. However, microbes and insects can digest wool by secreting extracellular keratinolytic enzymes that catalyze and hydrolyze these disulfide bonds releasing peptides and soluble sulfhydryl-containing amino acids causing strength loss [4].

To prevent insect damage, wool fibers are usually treated with pesticides and insect-resist agents (e.g., pyrethroids) commonly known as a mothproofing agent but most of them are quite toxic and can be absorbed into the human body through inhalation of vapors and skin contact [5,6]. Pyrethroids (e.g., permethrin) bind to a voltage-gated sodium channel protein in nerves disrupting the nerve signal. The affected insects exhibit tremors and uncoordinated movement, and normal bodily functions are disrupted ultimately causing the death of insects [7,8]. Other than synthetic pyrethroids, organophosphorus compounds [9], azole derivatives [10], various natural biobased compounds, such as cedar oil [11], naturally occurring quinonoid, and flavonoids/heavy metal complex [12], have been studied with some level of success. Sunderland et al. studied the insect resist efficacy of wool fabrics treated with seven azoles including sulconazole nitrate, miconazole nitrate, tebuconazole nitrate, and propiconazole nitrate at 3% on the weight of fiber (owf) against *Tineola bisselliella* and *Anthrecenus australis* larvae [10]. They found that propiconazole provided the most effective protection of wool from these species by providing an anti-feeding effect disrupting the insect's utilization of cholesterol by inhibiting the cytochrome P450 enzymes, and at a concentration of approximately 0.4% on the weight of fiber (owf) predicted to give adequate insect resistance. However, the treatment is not durable to washing. Kato et al. studied the effect of the treatment of wool with various natural dyes on the insect antifeeding behavior against the larvae of *Anthrecenus verbasci* and found that the strength of the anti-feeding effect of natural dyestuffs was in the order of lac dye<gallnut< catechu<red cabbage [13]. Of them, natural agents showed quite limited success and almost all the studied alternatives to pyrethroids showed limited durability to washing. Therefore, synthetic pyrethroids are still being used in the wool industry for making wool fabrics insect-repellent. To prolong their effectiveness and to limit the negative effects of these synthetic pyrethroids on human skin, microencapsulation and binding microcapsules to wool fiber surfaces have been studied [14]. In our previous work, we reported that wool fabric treated with some natural polyphenols exhibited quite good insect-resist properties [15]. Totarol, a phenolic diterpenoid isolated from the sap of *Podocarpus totara*, has been reported to have a potent antimicrobial activity [16,17] and also it is used in several commercial products as an insect repellent. It also has a unique pungent smell and therefore the fabric treated with totarol may repel the insects.

Permethrin, a synthetic pyrethroid, is the mostly used insect-resist agent for wool treatment in the wool industry due to its high effectiveness, non-volatility, stability at wider pHs, low cost, and low toxicity to humans, which is also used for controlling wasps and bed bugs [18,19]. Permethrin is highly effective against carpet beetles (*Anthrenocerus australis*) and larvae of moths (*Tineola bisseliella*) [14]. Although several studies showed that permethrin ingestion can damage the liver and kidney of rats [20,21], until the present no published research reported any of its negative effects on human health. Therefore, it is generally recognized as safe for human at the level it is applied to wool fiber as an insect-resist agent [22–24]. Permethrin is virtually insoluble in water and for this reason, its aqueous emulsion is applied onto wool from an aqueous bath. However, the treatment has limited durability to washing as permethrin is not absorbed into the fiber, rather it deposits on the fiber surface [25] and may come in contact with human skin. The applied permethrin is slowly released from the fabric surface by abrasion during its use and washing causing water pollution and resulting in limited durability of the treatment. Moreover, the aqueous treatment of wool with permethrin produces effluent that contains a portion of the applied permethrin, and therefore it cannot be discharged to watercourses as the permethrin can cause toxicity to aquatic life [26]. Therefore, there is a need to develop an alternative effluent-free treatment. The wash-durability of the treatment can be extended if permethrin can be absorbed into the fiber instead of depositing it on the fiber surface.

Supercritical carbon dioxide (sc-CO_2) has been studied as an alternative medium to the aqueous medium for the sustainable dyeing of textiles as it is a zero-effluent and energy-efficient process [27–29]. The treated fabric does not need any drying which is common for aqueous treatments. Nguyen et al. reported that synthetic pyrethroids including cypermethrin are soluble in sc-CO_2 [30]. Therefore, we anticipated that permethrin also could be soluble in sc-CO_2 and sub-critical CO_2 (subc-CO_2). However, either sc-CO_2 or subc-CO_2 was ever studied for the insect-resist treatment of wool fiber with permethrin. Totarol was found effective against a wide range of bacteria [31,32] but never studied to make wool fabric insect-resist. The diterpenes extracted from various sources, such as ground coffee beans, were found soluble in sc-CO_2 [33,34], and therefore we assumed that totarol (a diterpene) also could be soluble in subc-CO_2. The sc-CO_2 treatment is carried out at very high

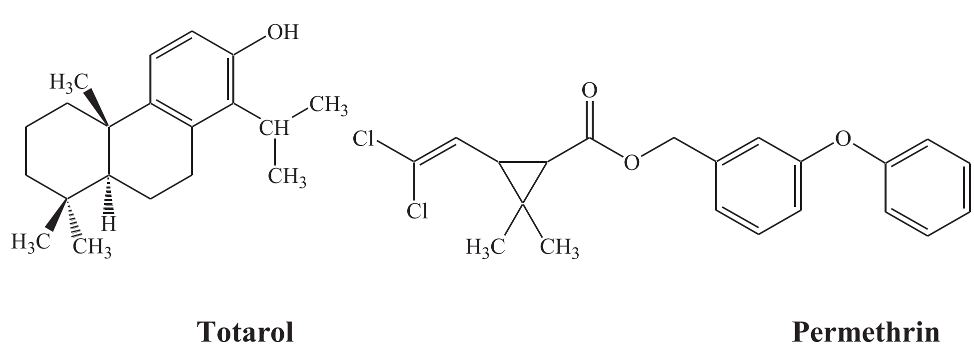


Fig. 1. The chemical structures of permethrin and totarol.

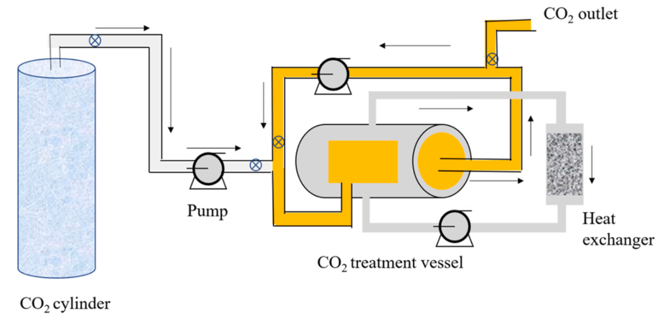


Fig. 2. Schematic diagram of the subc-CO_2 treatment set-up used for the treatment of wool fabrics with permethrin and totarol.

pressure (up to 20.0MPa) making such machinery highly expensive and risky but sub-critical CO_2 (subc-CO_2) equipment is less costly and less dangerous because of the lower pressure used compared to the sc-CO_2 process. In this work, for the first time, we are reporting the treatment of wool fabric with permethrin in a subc-CO_2 at 6.0 MPa to make wool fabric insect-resist and also reported the durability of the treatment to multiple washing. The developed treatment can be used in the textile industry as a zero-effluent insect-resist treatment for wool and other protein textiles.

2. Experimental methods

2.1. Materials

A piece of plain-woven wool fabric with 200 g/m^2 having 25 ends/cm and 23 picks/cm made from chlorine-Hercosett treated shrink-resist merino wool with an average diameter of 19 μm was used throughout this work. Before the subc-CO_2 treatment with totarol and permethrin, the fabric was treated with 2 g/L Sandoclean PC (a non-ionic detergent) and 0.2 g/L Sandozin MRN (a wetting agent) at 60 °C for 20 min to remove any dirt and spinning oil present in the fabric. Totarol powder extracted from a heartwood of a yew tree found in New Zealand (*Podocarpus totara*) was procured from Essentially New Zealand Limited (Auckland, New Zealand). Permethrin, cyclopropanecarboxylic acid, 3-(2,2- dichloroethenyl)− 2,2-dimethyl-,(3-phenoxyphenyl)methyl ester, was purchased from Sigma-Aldrich Limited (USA). Sandozin MRN and Sandoclean PC were purchased from Arkema Chemicals (Switzerland). The chemical structures of totarol and permethrin are shown in Fig. 1.

2.2. Treatment of wool fabric with permethrin in sub-CO_2 process

We used a 50 mL pressure vessel (Polaron Critical Point Dryer, Quorum Technologies Limited, UK) made of brass and chrome with glass windows and equipped with a CO_2 inlet pump and outlet tube connected with the inlet pump so that liquid CO_2 can be pumped and recirculated through the vessel. The schematic diagram of the subc-CO_2 treatment system used for the wool fabric is shown in Fig. 2. The wool fabrics were treated with 0.03, 0.06, 0.09, 0.15, and 0.20% owf of permethrin but for totarol, the applied dosage was 1% and 3% owf. The wool wrapped on the perforated steel cylinder was placed inside the vessel and fabric. The required quantity of permethrin or thymol was taken in a small metal boat, which was placed inside the perforated steel cylinder in the pressure vessel. Then the vessel was filled with liquid CO_2 at 6.0 MPa pressure and 40 °C and then the CO_2 outlet valve of the CO_2 gas cylinder was shut down and liquid CO_2 was recirculated through the vessel for various times. After the exhaustion of permethrin/thymol was completed, the pressure of the vessel was released, the treated fabric was recovered, and the vessel was cleaned for the next treatment. The treated fabrics were dried in a fume hood overnight at room temperature. For comparison, wool fabric was also treated with a permethrin emulsion (0.05% owf permethrin) in an aqueous medium.

2.3. Assessment of insect-resist performance of the wool fabric

The bioassays of wool fabrics treated with totarol and permethrin were conducted against *Tineola bisselliella* larvae according to the ISO Test method 3998–1977: Textiles — Determination of resistance to certain insect pests. The exposure period for the bioassay was 14 days. Plastic containers of 50 mm in diameter and 18 mm high, with a fine stainless-steel mesh aperture in the lid, were used as test cages. All test larvae were reared at the testing laboratory of AsureQuality (New Zealand) in a standard manner, where the tests were conducted. After 14 days, the mortality of the larvae and the weight loss of the test fabric samples were assessed. No mortality of the larvae and high weight loss of the fabric specimens indicate no insect resistance. On the other hand, no weight of test samples and mortality of larvae indicate high insect resistance. At least three samples were tested, and the averages are reported here. The statistical analysis of the data was carried out using ANOVA.

2.4. Assessment of durability of the antibacterial treatment to washing

The durability of the insect-resistance property of the wool fabric treated with permethrin in aqueous and subc-CO_2 media was measured according to the International Wool Secretariate (IWS) developed 7 A washing protocol by washing in a wascator at 40 °C using a commercial wool washing detergent (Softly®, marketed by Pental Products Limited, Australia). The washing in a wascator was severe compared to the domestic washing and each cycle of IWS 7 A washing is equivalent to four domestic washes. The fabric samples were washed for 5, 10, 15, and 20 cycles wet-on-wet basis without in-between drying.

2.5. Assessment of tensile strength of permethrin-treated fabrics

The tensile strength of wool fabric before and after the treatment with various concentrations of permethrin under subc-CO_2 was carried out according to the ASTM Test Method D5035–06: *Standard Test Method for Breaking Force and Elongation of Textile Fabrics (Strip Method)*. The tensile strength of the treated wool fabrics was measured by using an Instron tensile strength tester (Model 4204, Instron Corporation, USA) at 20 ± 2 °C and 65 ± 2% relative humidity. The sample size, gauge length, and speed were 25.4×152.4 mm, 100 mm, and 50 mm/min respectively. The samples were conditioned at the above-mentioned temperature and humidity for 3 days. At least 10 samples were tested for each treatment, and averages are reported here.

2.6. Determination of permethrin in wool fabric

A small quantity of treated fabric was placed in dichloromethane and Soxhlet extraction was carried out for a predetermined time. An Agilent 7010B triple quadrupole gas chromatograph mass spectrometer (Agilent Technologies, Inc., Santa Clara, USA) equipped with a high-efficiency EI source was used to measure the quantity of permethrin present in the treated wool fabrics. The advantages of EI ionization are a low influence of molecular structure on response and a large number of characteristic fragments. The GC/MS was employed with helium as the carrier gas at a constant flow of 1 mL/min. The oven temperature started at 75 °C and remained at this temperature for 3 min increasing to 120 °C at 25 °C/min ramp rate and then increased to 300 °C at 5 °C/min ramp, holding at 300 °C for 11 min. The injection port was adjusted at 250 °C and splitless injection mode was used.

After the acquisition of the total ion chromatogram for the mixed stock standard solutions in scan mode, peaks were identified by their retention time and mass spectra. The most abundant ion that showed no evidence of chromatographic interference and had the highest signal-to-noise ratio was selected for quantification purposes. The concentrations of permethrin were determined by interpolation of the relative peak area of permethrin to the internal standard peak area in the sample on the

Table 1
Bioassay of wool fabric treated with various PPs by the subc-CO_2 method against *Tineola bisseliella*.

Treatment	Mean mortality (%)	Mean pupation (%)	Mean mass loss (mg)	Mean mass loss (as a % of the mean voracity	Visual assessment (2 & 3)	Pass (p), fail (f), or borderline (b)
Control	0	0	59.3 ± 0.9	89.5	4D	f
0.05% owf permethrin	98.3	0	0.9 ± 0.6	1.6	1 A	p
1% owf Totarol	0	0	55.0 ± 6.6	92.9	4D	f
3% owf Totarol	0	0	53.1 ± 3.6	89.5	4D	f
F Test (P<0.05)	* **	ns	* **			
LSD = 0.05	10.4	n/a	8.5			

spiked calibration curve. To compensate for losses during sample processing and instrumental analysis, an internal standard (TPM) was used.

2.7. Surface characterizations

The surface of the permethrin-treated fabrics was characterized by Fourier transform infrared spectroscopy, contact angle measurement, and scanning electron microscopy. The presence of permethrin was identified by the Fourier transform infrared (FTIR) spectroscope and the spectra were recorded by a Nicolet FTIR (Model: Summit Pro, Thermo Fisher Scientific, USA) equipped with an attenuated total reflectance (ATR) attachment at a resolution of 4 cm^{-1} in the range from 450 to 4000 cm^{-1} by using a diamond crystal and 64 scans were signal-averaged. The contact angle of untreated and treated wool fabrics was measured at 10 places on the face and back surfaces by a KSV Contact Angle Measurement Apparatus (Model: CAM 100, KSV Instruments, Finland) and the average contact angle has been reported. The surface morphologies of permethrin-treated wool fabric samples were examined by a Hitachi scanning electron microscope (Model: TM 3030 Plus, Hitachi Corporation, Tokyo, Japan). The elemental analysis of C, O, N, and S elements of treated wool fabrics was carried out by an energy dispersive X-ray (EDX) using the same SEM equipped with Quantax75 energy dispersive X-ray attachment.

3. Results and discussion

3.1. Solubility of totarol and permethrin in subc-CO_2

Totarol is a yellowish-brown colored compound, but no published data are available about its solubility in sc-CO_2 or subc-CO_2 although several companies in New Zealand commercially extract totarol using sc-CO_2. We tested the solubility of totarol and permethrin in subc-CO_2 for the applied dosages we used in our work. The glass windows on both sides of the Polaron high-pressure vessel allowed us to clearly observe the state of the totarol and permethrin in subc-CO_2. Totarol produced a highly transparent clear golden color solution and no totarol particles were visible. The treatment of wool fabric with totarol under subc-CO_2 produced a uniformly golden-colored fabric confirming the high exhaustion of totarol by the wool fabric sample. In the case of permethrin, a clear solution was produced, and no permethrin particles were visible suggesting its good solubility in subc-CO_2.

3.2. Insect-resist performance

The insect-resist performance of wool fabrics treated with various dosages of permethrin and totarol by the subc-CO_2 method in terms of the killing of larvae and weight loss of tested wool fabrics against *Tineola bisselliella* is presented in Table 1. The untreated fabric did not show any insect resistance which is demonstrated by no killing of larvae and high weight loss of the tested fabric. The high weight loss suggests quite extensive damage to the tested wool fabric, which is consistent with previously published articles [5,10]. However, the fabric sample treated with 0.05% owf permethrin showed excellent insect-resist performance with 98.3% killing of larvae and negligible weight loss of the fabric. However, like the control fabric, the wool fabric treated with 1% owf totarol did not show at all any insect-resist behavior as the mortality of the larvae of *Tineola bisselliella* was 0% and the weight loss occurred was even more than the control fabric. Even three times increase in the totarol dosage also failed to kill any larvae of *Tineola bisselliella* and the weight loss that occurred was almost equal to the weight loss observed for the control fabric. Therefore, we can conclude that totarol did not exhibit any insect-resist property against *Tineola bisselliella* larvae, but permethrin showed excellent insect-resist performance. As the wool fabrics treated with even a high dosage of totarol did not show any insect-resist property, for further experiments, totarol was not considered.

3.3. Effect of permethrin concentrations on the insect-resist performance

The effect of applied dosages of permethrin on the insect-resist performance of wool fabrics treated with permethrin at the levels of 0.03–0.2% owf in the subc-CO_2 medium against *Tineola bisseliella* larvae is shown in Table 2. The wool fabric treated with the lowest applied dosage, 0.03% owf, also showed very good insect resistance as the mortality of insect larvae was 98.0% and the weight loss that occurred was only 8.7%. The increase in the applied dosage of permethrin to 0.06% owf increased the mortality of larvae to 98.6% and the weight loss decreased to 4.5%. A further increase in the dosage of permethrin to 0.09% owf increased the mortality of *Tineola bisseliella* larvae to 100% and the weight loss decreased to a negligible level (only 0.6%)

Table 2
Bioassay of *Tineola bisselliella* on wool fabric treated with various concentrations of permethrin by the subc-CO_2 method before washing.

Treatment	Mean mortality (%)	Mean pupation (%)	Mean mass loss (mg)	Mean mass loss (as a % of the mean voracity	Visual assessment (2 & 3)	Pass (p), fail (f), or borderline (b)
0.05% owf (aqueous treated)	98.3	0	4.5 ± 0.2	8.4	1A	p
0.03% owf permethrin	98.0	0	5.3 ± 1.4	8.7	1 A	p
0.06% owf permethrin	98.6	0	4.5 ± 0.5	8.3	1 A	p
0.09% owf permethrin	100	0	0.6 ± 0.4	2.7	1 A	p
0.15% owf permethrin	100	0	3.1 ± 0.4	6.1	1 A	p
0.2% owf permethrin	100	0	3.0 ± 0.2	5.5	1 A	p
F Test (P<0.05)	ns	ns	Ns			
LSD = 0.05	n/a	n/a	n/a			

Table 3
Bioassay of *Tineola bisselliella* on wool fabric treated with various concentrations of permethrin subc-CO_2 method after 20 times 7 A washing (the aqueous treated sample was 5 times washed).

Treatment	Mean mortality (%)	Mean pupation (%)	Mean mass loss (mg)	Mean mass loss (as a % of the mean voracity	Visual assessment (2 & 3)	Pass (p), fail (f), or borderline (b)
0.05% owf (aqueous treated)	0	0	57.3 ± 0.7	87.5	4D	f
0.03% owf permethrin	93.4	0	0.9 ± 0.3	1.5	1 A	p
0.09% owf permethrin	98.8	0	0.5 ± 0.1	0.9	1 A	p
0.15% owf permethrin	97.7	0	0.7 ± 0.2	1.2	1 A	p
0.2% owf permethrin	95.0	0	1.6 ± 0.2	2.7	1 A	p
F Test (P<0.05)	ns	ns	Ns			
LSD = 0.05	n/a	n/a	n/a			

Table 4
Quantity of permethrin identified in wool fabric by Soxhlet extraction with DCM and then by GC-MS treated with various concentrations of permethrin.

Applied dosage of permethrin (% owf)	Permethrin quantified in the fabric in (% owf)	
	Before washing	After 20 washing
0.05 (aqueous treated)	0.045	Not detected§
0.03	0.007	0.0005
0.09	0.021	0.0008
0.15	0.031	0.009
0.20	0.05	0.011

§ After 5 washes

suggesting almost no damage to the treated fabric. The increase in the dosage to 0.15% and 0.2% owf slightly increased the weight loss probably due to the displacement of the surface-bound permethrin in contact with the larval body surface and removal from the fabric resulting in increased weight loss. The results show that 0.09% owf permethrin was more than enough for the 100% mortality of *Tineola bisselliella* larvae, i.e., 100% insect resistance.

3.4. Durability of the insect-resist treatment to washing

Table 3 shows the durability of the wool fabrics treated with 0.05% permethrin after 5 washes and wool fabrics treated with various dosages of permethrin by the subc-CO_2 treatment after 20 washes. The wool fabric treated with 0.05% permethrin by the aqueous treatment showed very poor durability to washing as it did not show any insect resistance after 5 washes. The mortality of larvae was 0% and the weight loss was 87.5% suggesting that the applied permethrin was washed off from the surface of the treated wool fabric during washing. On the other hand, the wool fabric treated with 0.03% of permethrin by the subc-CO_2 treatment after 20 washing (equivalent to 80 domestic washes) exhibited a slight drop in the mortality of the larvae from 98.0% to 93.4% but the weight loss occurred was quite marginal. For a higher dosage, the mortality of the larvae increased to more than 98% and the weight loss also was negligible showing the high durability of the treatment to washing.

3.5. Determination of permethrin on wool fiber surface by GC-MS

The surface-bound permethrin from wool fabrics treated by the aqueous and the subc-CO_2 method was extracted by Soxhlet extraction with DCM and quantified by GC-MS, and the results are shown in Table 4. With the increase in the dosage of permethrin, the quantity of surface-bound permethrin increased. For the wool fabric treated with 0.05% owf permethrin by the traditional aqueous method, the detected quantity of permethrin present in the fabric before washes was 0.045%, i.e., almost 90% of the applied permethrin was adsorbed onto the fabric surface but after 5 washes no permethrin was detected in the washed fabric suggesting that the applied permethrin remained on the surface of fibers and washed off during washing. On the other hand, for the subc-CO_2-based treatment, the identified quantity of permethrin in the treated fabric before washing was very small compared to the applied dosages, and permethrin identified in the fabric after washing was very low but showed excellent insect resistance. For the fabric treated with 0.03% owf permethrin by the subc-CO_2 method, the total permethrin detected by the DCM extraction and detection by GC-MS was 0.007% and the permethrin detected in the 20 times washed fabric was only 0.0005% but the fabric still showed strong insect-resistance. Similarly, 0.021% permethrin was detected in the fabric treated with 0.09% owf but after 20 washing the fabric had only 0.008% permethrin but still

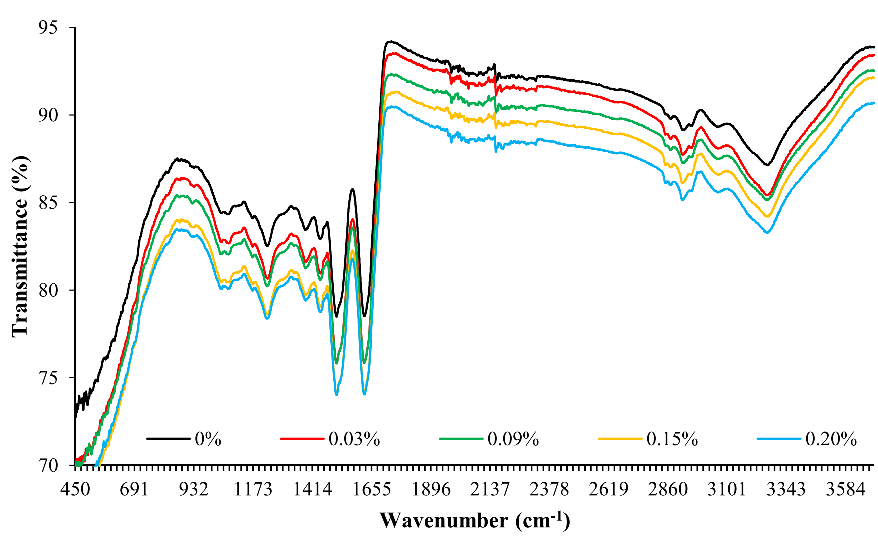


Fig. 3. ATR-FTIR spectra of wool fabrics treated with various concentrations of permethrin.

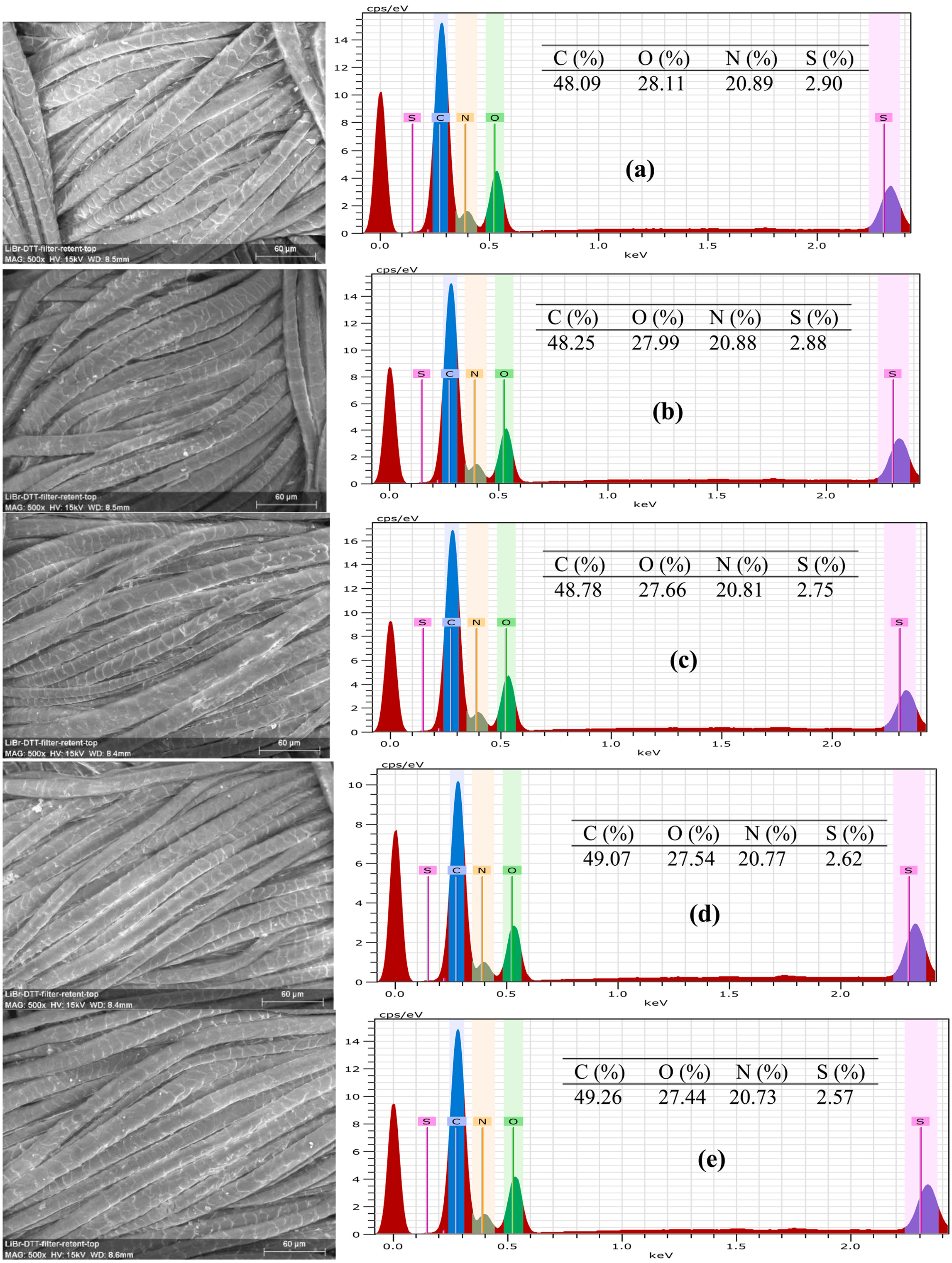
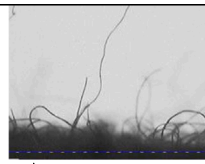
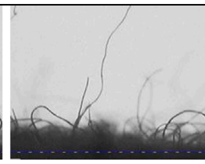
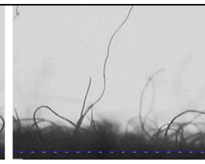
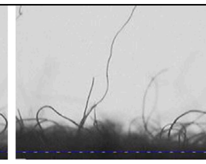
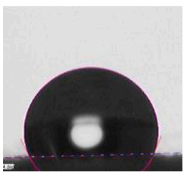
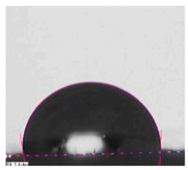
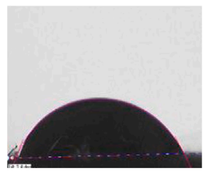
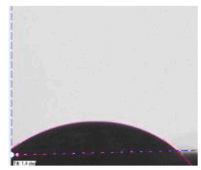
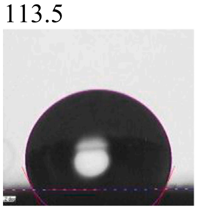
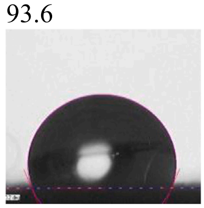
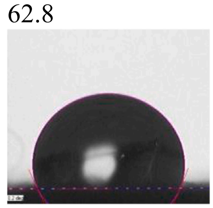
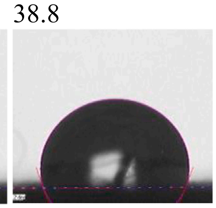
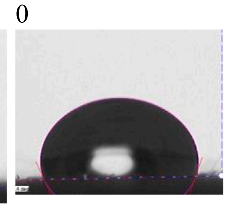
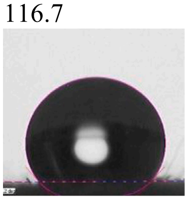
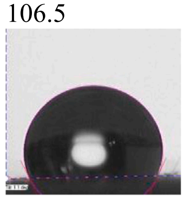
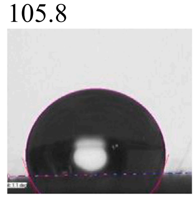
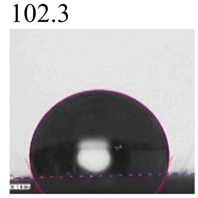
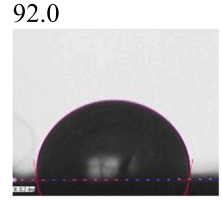
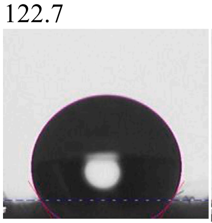
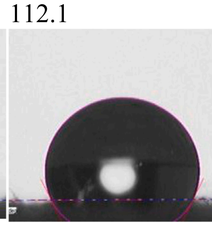
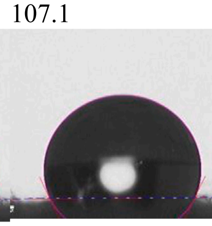
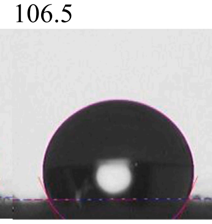
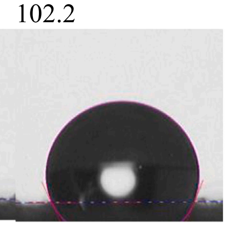


Fig. 4. EDX spectra of wool fabrics treated with 0 (a), 0.03 (b), 0.09 (c), 0.15 (d), and 0.20% (e) permethrin.

Table 5
Dynamic contact angle of surfaces of wool fabrics treated with various dosages of permethrin by subc-CO_2 treatment.

Samples ID.	Average contact angle (°) at				
	0 s	60 s	120 s	180 s	240 s
Control					
	102.2	0*	0	0	0
300 ppm					
	113.5	93.6	62.8	38.8	0
900 ppm					
	116.7	106.5	105.8	102.3	92.0
1500 ppm					
	122.7	112.1	107.1	106.5	102.2
2000 ppm					
	122.5	116.2	115.4	113.3	113.6

showed 98.8% killing of *Tineola bisselliella* larvae. The recommended concentration of permethrin for the protection of wool fiber against moths and larvae is 0.018% owf (recommended applied dosage is 0.1% owf) but the concentration of permethrin found in the wool fiber dust by Berger-Preiß et al. was 0.07%, suggesting that the applied permethrin remained on the surface of the fiber [35]. Veer et al. applied 0.1% (owf) permethrin to wool fiber in the scouring bath and then the fibers were dyed and converted into fabric. After 20 times of hand washing, the fabric had only 0.008% (owf) permethrin [36]. The results achieved by others also prove that the permethrin applied in the aqueous bath only deposits on the surface and has low durability to washing. However, in this work, even the fabric treated with 0.03% (owf) permethrin and washed in a wascator 20 times still showed excellent insect-resist property but the detected permethrin level even before washing was very small suggesting that most of the applied permethrin were absorbed into the fiber treated by the subc-CO_2 process and very little of that came out by DCM extraction and detected by GC-MS.

3.6. ATR-FTIR

Fig. 3 shows the ATR-FTIR spectra of wool fabrics treated with various concentrations of permethrin. The spectrum of untreated wool fabric exhibits IR bands at 1650, 1550, and 1350 cm^{-1} that are related to the amide I, amide II, and amide III of wool keratin. It also shows IR bands at 2850, 2930, and 3250 cm^{-1} related to the symmetric and asymmetric CH_2 and OH groups [37]. On the other hand, wool fabric treated with various concentrations of permethrin also shows similar bands as permethrin has methyl and hydroxyl groups like wool and the intensity of the various bands are also similar even with an increase in the concentrations of permethrin as the applied permethrin concentrations were very low and most of which were absorbed into the fiber.

3.7. Elemental analyses of wool fiber surface

Fig. 4 shows the elemental analysis of C, O, N, and S of untreated and also wool fabric treated with various concentrations of permethrin. Of the elements, C and H are present in permethrin, and therefore the application of permethrin to wool should increase the C content and decrease the S and N contents. The C, O, N, and S contents of the control wool fabric were 48.09%, 28.11%, 20.89%, and 2.90% respectively. From Fig. 4, it is evident that with an increase in the permethrin dosages, the C content increased, and the O, N, and S contents decreased. For the wool fabric samples treated with 0.2% permethrin, the C content increased to 49.26% but the O, N, and S contents decreased to 27.44%,

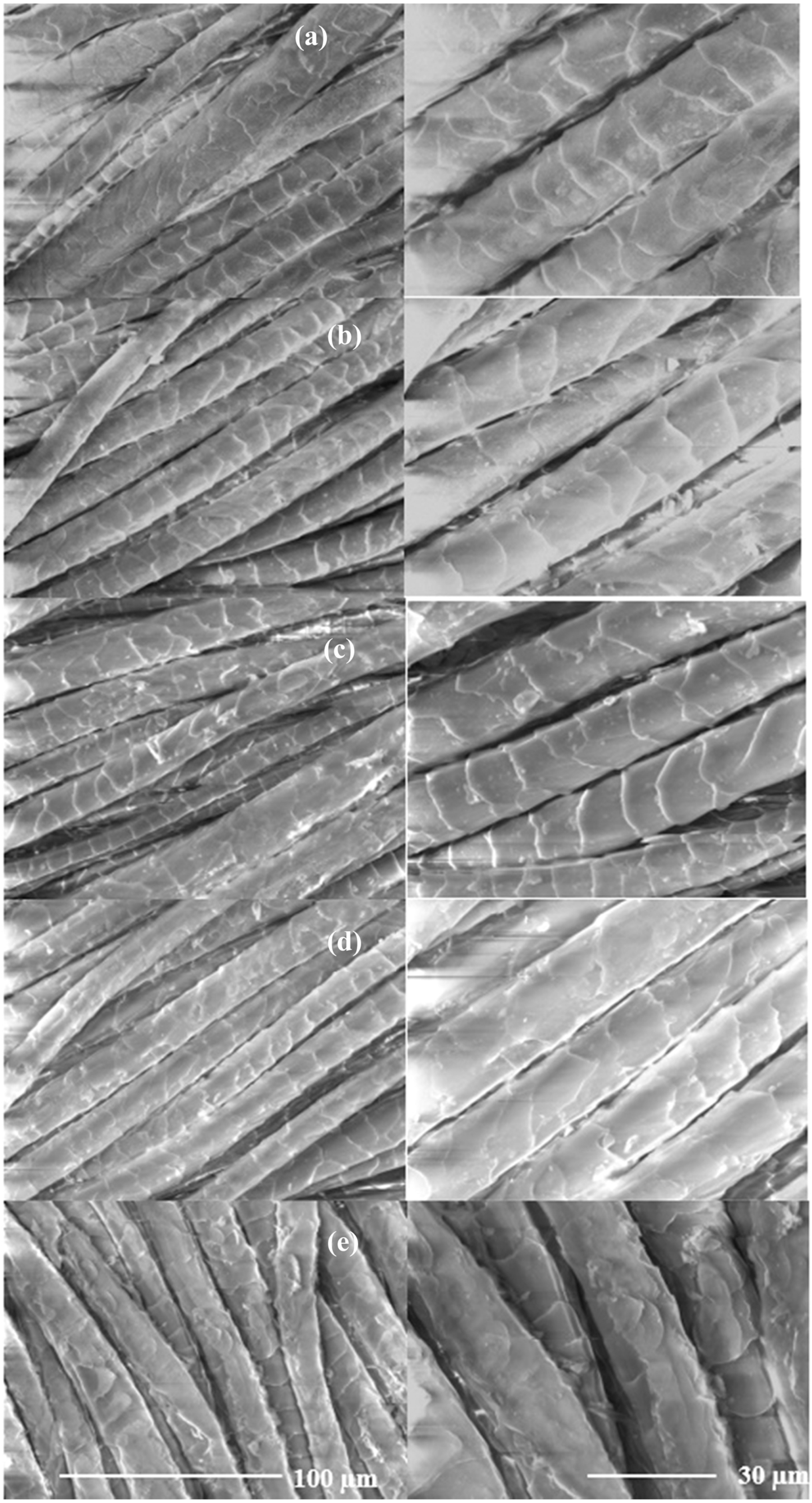


Fig. 5. SEM micrographs of wool fabric treated with 0 (a), 0.03 (b), 0.09 (c), 0.15 (d), and 0.2% (e) permethrin by the subc-CO_2 method.

20.73%, and 2.57% respectively. The increase or decrease in various elemental contents was small as the applied dosage of permethrin was also very small. The change in elemental contents of treated wool fabrics indicates the presence of permethrin in the fabric.

Fig. S1 (Supplementary Information) shows the distribution of various elements such as C, N. O, and S on the surface of wool fibers treated with various concentrations of permethrin. The uniform distribution of various elements suggests that the surface of wool fabrics was uniformly coated with permethrin.

3.8. Contact angle of surface of wool fabrics

Table 5 shows the dynamic contact angle of wool fabric surfaces treated with various concentrations of permethrin under the subc-CO_2 medium. The untreated control chlorine-Hercosett treated fabric showed quite good hydrophilicity as opposed to the untreated wool fabric which is reasonably hydrophobic. The water droplet vanished within a few seconds after placing it on the fabric surface, which is consistent with previously published results [38].

On the other hand, the hydrophilicity of the fabric slowly increased with an increase in the applied concentrations of permethrin. For the fabric treated with 0.03% permethrin, the contact angle at 0 s was 113° but at 180 s became 38.8°, after which became 0. The contact angle at 0 s slowly increased to 122° but more increase in contact angle was observed for the 240 s test as the contact angle increased to 113.6° for the fabric treated with 0.2% permethrin, which was almost similar to the non-shrink-resist treated wool fabric. Permethrin does not have any hydroxyl groups, rather it has several methyl groups making it quite hydrophobic. Therefore, the hydrophobicity of the fabric was increased with an increase in the permethrin dosage.

3.9. Surface morphologies

Fig. 5. shows the SEM micrographs of wool fabrics treated with various concentrations of permethrin. The control fabric shows typical wool fiber surface scales are subdued and the deposition of a thin coating of Hercosett resins. For the permethrin-treated fabrics, no surface deposition of permethrin is visible on the surface of wool fabric treated with various concentrations of permethrin up to 0.15% owf. However, for the fabric treated with 0.2% (owf) permethrin, some deposition of permethrin is visible on the surface of wool fibers, and therefore increased detection of permethrin was observed in the DCM extraction of permethrin for this fabric sample suggesting not all permethrin applied was absorbed into the fabric. The surface-deposited permethrin was removed during the DCM extraction.

3.10. Tensile strength

Fig. S2 (Supplementary Materials) shows the effect of permethrin dosage on the tensile strength of wool fabric treated with permethrin under subc-CO_2. It can be seen that the permethrin treatment did not show any trend and had a negligible effect on the tensile strength of the treated wool fabrics. The tensile strength loss of the permethrin-treated wool fabrics was marginal as the tensile strength decreased from 9.55 kgf for the control to 9.4 kgf for the 0.15% permethrin-treated wool fabric but again increased to 9.5 kgf when the applied dosage of permethrin was 0.2%. Although Kong et al. managed to increase the tensile strength of aramid fiber by crosslinking under sc-CO_2 via diffusing crosslinking agents into the amorphous regions of the fiber [39], several researchers observed quite the opposite, i.e., a considerable loss of tensile strength of ultra-high-molecular-weight polyethylene fiber when dyed in sc-CO_2 with disperse dyes [40], and hemp fibers treated in sc-CO_2 [41]. Long et al. observed serious etching effect or damage to wool fibers when the CO_2 pressure was 35 MPa and opined that pretreatment, dyeing, and finishing of wool fiber in supercritical carbon dioxide should not be carried out at more than 30 MPa pressure to avoid fiber damage [42]. As we used quite low pressure (6 MPa), no damage to the fiber occurred, which is evident from SEM micrographs of treated wool fibers shown in Fig. 5, and therefore the effect observed was negligible. Under pressure, permethrin penetrated the amorphous region of wool fiber, which increased the durability of the treatment to washing.

3.11. Sustainable conservation of wool textiles

It is necessary to conserve the environment as well as historical and contemporary wool textiles. The production of no effluent by the developed method will conserve the environment and also will enable the carrying out of such a kind of treatment in the wool industry of the developed world. Unlike hydrocarbon solvents, liquified CO_2 is a non-toxic and non-flammable solvent making it ideal for the sustainable treatment of textiles. The absorption of permethrin into the fiber rather than depositing on the fabric surface reduces the interaction of human skin with permethrin avoiding permethrin-related skin sensitization [40]. The subc-CO_2 media can not only be used for the treatment of wool fabrics with permethrin but also can be used for the extraction of permethrin from the used wool textiles as demonstrated by others [30] so that it will not affect the circularity of wool textiles for its reuse or its biodegradability. It also can be used for the conservation of historical textiles made of wool and other protein fibers.

4. Conclusions

In this work, highly wash-durable insect resist wool fabric was developed by treating it with permethrin under a subc-CO_2 medium, which produces no effluent that needs treatment. This work demonstrated that the durability of the permethrin-treated wool fabric to washing can be considerably improved by carrying out the treatment under a subc-CO_2 medium. The treatment also slightly improved the surface hydrophobicity of the treated wool fabric. The aqueous treatment of wool fabric with permethrin emulsion had a quite poor durability to washing. The DCM extraction and GC-MS analysis and SEM micrographs suggest that in the case of aqueous treatment, almost all of the applied permethrin remains on the surface of wool fiber but in the case of the treatment under subc-CO_2 medium most of the applied permethrin is absorbed into the fiber, resulting in increased durability of the treatment to washing. The treatment of wool fiber with permethrin enhanced its surface hydrophobicity, which is evident by the increase in the dynamic contact angle of the surface of the treated fibers. This developed method can be used in industry for the zero-effluent insect resist treatment of wool and other animal fibers with permethrin with enhanced durability of the treatment to washing.

CRediT authorship contribution statement

Mohammad Mahbubul Hassan: Conceptualization, Methodology, Experiments, Characterizations, Writing, Data analysis, Reviewing. Peter Brorens: Mechanical characterizations, Data curation, and Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2023.131595.

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