

## Multi-functional wool fabric by graft-copolymerisation with polystyrene sulfonate: Enhanced fire retardancy, mechanical properties, and stain-resistance

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Multi-functionalisation of textile fibres is quite important to extend their range of applications. In this respect, a single treatment that offers multi-functional properties to textile fibres is highly desirable because of the low cost of the treatment. In this work, wool fibres were graft copolymerised with poly(styrene sulfonate) or pSS to enhance their fire-retardancy, antibacterial activity, antistatic properties, stain-resistance, and tensile strength. The pSS-grafted-wool fabrics were characterised by Fourier transform infrared spectroscopy, elemental analysis, differential scanning calorimetry, and tensile strength measurement. The fire retardancy was assessed by measuring limiting oxygen index and the thermal stability by thermogravimetric analysis. The pSS-grafted wool fabrics showed enhanced fire retardancy, as the LOI value of 24.5 shown by the untreated control fabric increased to 28.0 after grafting with 25% of pSS. The pSS-grafted fabrics also showed improved tensile strength and stain-resistance against C.I. Acid Red 40. The pSS-grafted fabric treated with 0.5% on-weight-of-wool fibre AgNO<sub>3</sub> not only showed excellent antibacterial activity against *Staphylococcus aureus* and *Klebsiella pneumonia* measured according to the AATCC Test method 147-1999 but the antibacterial activity was durable to at least 20 washes and also showed enhanced antistatic properties. Thus, the developed treatment could be used to make wool fabric multi-functional.

### Introduction

Wool fibres are versatile natural polyamide fibres with excellent moisture management and some levels of antistatic, stain-resist and flame-resist properties.<sup>1</sup> However, some of these properties are not sufficient to allow the wool to be used in more high-performance applications. For example, wool fibres have some levels of flame retardance properties but not enough to use them in automobile and aircraft upholstery. They are relatively stain-resistant but not good enough to match competing fibres for used in floor coverings. Like other fibres, they may allow growth of bacteria on their surface and may act as a vector for spreading bacterial diseases. Wool fibres are weaker than silk and other natural fibres. Therefore, they often need blending with synthetic fibres to support their use in many applications. Textile fibres are chemically modified to enhance their various properties, such as physicochemical, antibacterial, and stain-resist properties, and also to widen their applications beyond traditional areas. It was reported that the corona plasma treatment followed by the treatment with 2,3-epoxypropyltrimethylammonium chloride enhanced the mechanical and antistatic properties of wool fabrics.<sup>2</sup> The phosphorylation of wool enhanced the dyeability of wool with basic dyes.<sup>3</sup> A wool fabric treated with banana pseudostem sap medium at pH 5.5 showed enhanced thermal stability and acid dye absorption.<sup>4</sup> The reduction treatment

of wool fabrics with tris(2-carboxyethyl)phosphine followed by the binding of glycidyltrimethylammonium chloride by click reaction increased the antibacterial, antistatic and the dyeability of wool fabrics.<sup>5</sup> The treatment of wool fabric with boron-doped silica sol increased its flame retardancy and thermal stability.<sup>6</sup>

A single treatment that makes a fabric multi-functional is highly attractive. Polymeric grafting is an attractive tool to modify the surface of fibre introducing new functionality, which can help in further addition of a polymer or organic compound to impart new properties. Fibres are graft-copolymerised to improve their surface interfacial property,<sup>7</sup> UV protection,<sup>8</sup> hydrophilicity,<sup>9</sup> hydrophobicity,<sup>10</sup> and biocompatibility for biomedical applications.<sup>11</sup> Polymeric grafting has also been investigated for wool fibres to make them antibacterial,<sup>12</sup> antistatic,<sup>2</sup> and hydrophobic.<sup>13</sup> The internal and surface deposition of variable amounts of polymer may result in changes in physical, mechanical and chemical properties of wool.<sup>14,15</sup> Arai and co-workers have made extensive work on the graft copolymerisation of vinyl monomers onto wool fibres by means of a free radical initiation mechanism.<sup>16</sup> The free radical sites formed on the peptide chain's backbone may interact with the monomer and initiate the propagation of a grafted chain. Studies on virgin and modified wool fibres showed that thiol groups are the preferred grafting sites.<sup>17</sup> Different vinyl monomers including benzyl methacrylate, acrylic acid, methacrylamide, hydroxyethyl methacrylate, methyl methacrylate have been extensively investigated for grafting onto wool fibres.<sup>13,18,19</sup> We previously reported that the deposition of poly(methyl methacrylate) onto wool fabric surface by chemical vapour deposition polymerisation enhanced the hydrophobicity as well as the dyeability of wool fabrics with disperse dyes.<sup>13</sup> The deposition of acryl and acrylamide

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sulfonates by 'thiol-ene click' reactions enhanced the antistatic and liquid moisture management properties of wool fabrics.<sup>20</sup>

Metallic silver and silver ions have a long history in the treatment of burns and wounds as an effective antimicrobial agent.<sup>21</sup> Multi-functionalisation of wool fabrics with silver nanoparticles enhanced their antimicrobial properties.<sup>22–24</sup> However, silver nanoparticle-based treatments are the subject of controversy as their release into the environment can contaminate watercourses.<sup>25,26</sup> The binding of thioglycolic acid-capped silver nanoparticles enhanced the antimicrobial properties of wool fabric and enhanced the durability of the treatment to multiple washing.<sup>27</sup>

It has been reported that a thin coating of polyvinyl sulphonic acid greatly improved the fire-retardancy of polyurethane foam.<sup>28</sup> The addition of pSS-grafted silica nanoparticles to polypropylene improved its thermal stability and fire retardancy.<sup>29</sup> However, to the best of our knowledge, no published literature reported the fire retardancy and stain-resistance properties of wool fabrics grafted with pSS. Ionic silver treatment of wool fabrics has rarely been considered for antimicrobial applications. No article has reported the antibacterial activity and the durability of the treatment to washing of the pSS-grafted wool fabrics treated with ionic silver. In this work, for the first time, we are reporting antibacterial, stain-resistance and fire retardancy of wool fabrics graft-copolymerised with pSS. Usually to prepare the polystyrene sulfonate (pSS) grafted polymer, at first polystyrene is grafted to the polymer and then sulfonate groups are introduced in the polystyrene by treating with a strong sulphuric acid. In this work, wool fabrics were graft copolymerised with pSS by the direct graft copolymerisation of wool keratin fibre and styrene sulfonate in a single step to enhance their fire-retardancy, antibacterial activity, electrical conductivity, stain-resistance, and tensile strength. The pSS-grafted wool fabrics were characterised by differential scanning calorimetry, thermogravimetric analysis, elemental analysis, and Fourier transform infrared spectroscopy. Fire retardancy, stain-resistance, and antibacterial activity were evaluated by standard methods.

## Results and discussion

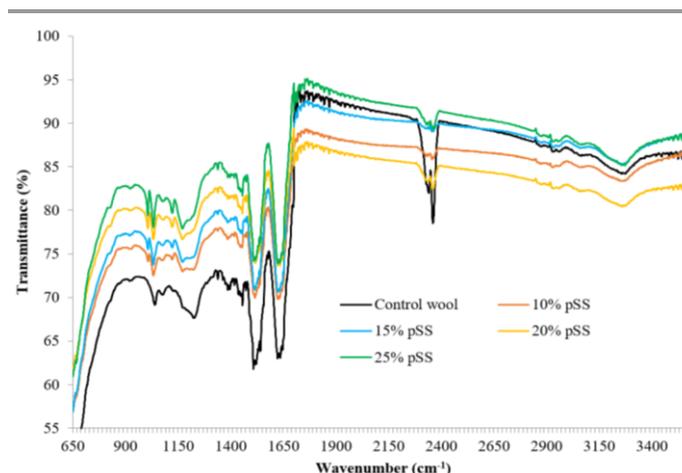
### Elemental analysis, FTIR and grafting efficiency.

Table 1 shows the elemental analysis of untreated and treated wool fibre, and reduction of nitrogen content and increase in sulphur content was observed as expected. The sulphur content of the graft wool increased to 3.94% compared to 3.25% sulphur content observed for the control wool because of the grafting of a sulfonated polymer (pSS) with wool. The change in sulphur content indicates the grafting of pSS onto wool fibres. As several researchers already observed in the case of pSS grafting with cotton and poly(benzyl methacrylate) grafting on wool, the optimum time and temperature for exhaustion-based grafting are 90 minutes and 65 °C, we used the same time and temperature as a standard.<sup>30,18</sup>

**Table 1.** Elemental analysis of control wool and also 25% pSS-grafted wool fabric.

Sample	Carbon %	Hydrogen %	Nitrogen %	Sulphur %
Control wool	48.23	7.20	16.22	3.25
25% pSS-g-wool	48.55	6.88	15.59	3.94

Fig. 1 shows the ATR-FTIR spectra of control wool fabric and also wool fabrics treated with various weight% of pSS. The FTIR spectrum of control wool shows typical wool keratin IR bands of amide III, amide II and amide I at 1227, 1545, and 1635  $\text{cm}^{-1}$ , respectively. The amide I band at 1635  $\text{cm}^{-1}$  is indicative of the  $\alpha$ -helical structure of wool and is associated with the C=O stretching vibration. The amide II band at 1545  $\text{cm}^{-1}$  is related to the N-H bending and C-N stretching vibrations. On the other hand, the amide III band at 1227  $\text{cm}^{-1}$  corresponds to the in-phase combination of C-N stretching and N-H bending. The small band at 1040  $\text{cm}^{-1}$  could be attributed to the cysteic acid. The broad peak at 3150–3350  $\text{cm}^{-1}$  could be attributed to the hydroxyl groups of certain amino acids (e.g. serine and tyrosine) of wool keratin.<sup>31</sup> On the other hand, the spectra of wool fabrics grafted with various weights (%) of pSS show four additional IR bands as shown in Fig. 1 and the intensity of these bands increased with an increase in the applied concentration of styrene sulfonate. These four bands observed at 1172, 1122, 1033 and 1006  $\text{cm}^{-1}$  are all representative of stretching vibrations associated with sulfonation.<sup>32</sup> These four bands are also available in the spectrum of pSS. The in-plane bending vibrations of the aromatic ring styrene para substituted with the sulfonate group and the sulfonated anion attached to the aromatic benzene ring are represented at 1006 and 1125  $\text{cm}^{-1}$  respectively, while the bands at 1035  $\text{cm}^{-1}$  represent the symmetric and asymmetric stretching vibrations of the sulfonated group respectively. None of these bands was observed in the case of untreated wool fibre. The ATR-FTIR spectra of the control and pSS-grafted wool fabrics suggest that pSS was successfully grafted to wool fibres.



**Fig. 1.** ATR-FTIR spectra of control wool fabric and also wool fabric grafted with various concentrations of pSS.

Fig. 2 shows grafting yield and grafting efficiency (the percentage of SS monomer polymerised and grafted with the wool fibres) of wool fabrics samples graft-copolymerised with pSS as a function of the applied concentrations of the SS monomer. It can be seen that the grafting yield increased proportionally with an increase in the monomer concentrations. On the other hand, the grafting efficiency decreased with an increase in the concentration of the monomer. The grafting yield increased from 5.0% for the applied concentration of 10% to 18.0% for the 40% of the applied concentration of monomer. From Fig. 2, it can also be observed that at lower concentrations of monomer, grafting efficiency was high as at 10% concentration of monomer 52% applied monomer reacted with the fibre but when the applied monomer concentration was 40% owf, only 45% of it reacted with the fibre. The decrease in the grafting

efficiency with an increase in the applied concentration of SS indicates that homopolymerisation increased with an increase in the monomer concentration causing a decrease in the grafting efficiency.

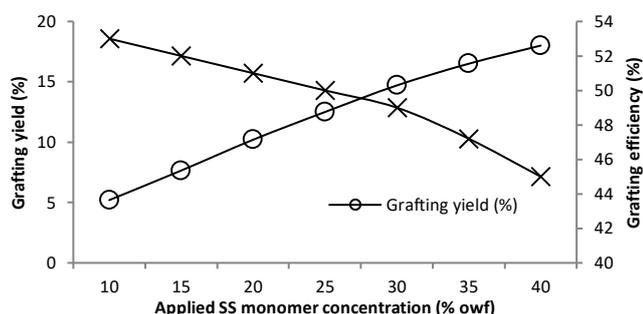


Fig. 2. Effect of SS monomer concentration on the grafting yield and grafting efficiency of the monomer reacted with wool fibre.

### Thermal stability and fire retardancy

The study of the thermal properties of the grafted wool fibres is very important as these properties have scientific and technological significance. Thermal analysis permits detection of changes in physical (melting point, crystallisation temperature, the degree of crystallinity, etc.) and chemical (crosslinking, degradation, and other reactions) structure brought about by the interactions between the grafted polymer and wool keratin. The response to a thermal treatment mainly depends on the structure and morphology of all phases forming the fibrous polymer. Fig. 3 shows the thermogravimetric analysis and DTG curves of control wool fabric and also wool fabric grafted with 25% pSS. It is evident that the pSS-grafted wool fabric sample showed slightly better thermal stability than the untreated control wool fabric.

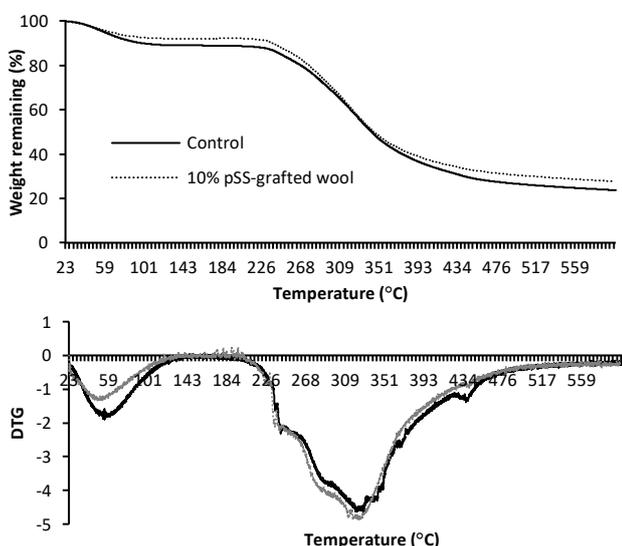


Fig. 3. Thermogravimetric analysis and DTG curves of control wool fabric and also wool fabric grafted with 25% pSS.

It can be seen that the weight loss occurs at several stages for both untreated and pSS-grafted wool fabrics, from room temperature to 108 °C, 229 to 437 °C and 437 to 600 °C. For the control wool fabric, in the first stage, approximately 10.5% weight is lost, and this weight loss is mainly due to the loss of moisture absorbed by wool fibres. Subsequently, up to 229 °C, the weight loss is quite stable and only

1.8% weight is lost and some volatiles are removed at this stage. The highest weight loss occurred at the third stage from 229 to 437 °C and approximately 57.5% weight loss lost at this stage due to the formation of various volatiles due to the thermal degradation of wool fibres. In the last stage, another 6.5% weight is lost up to 600 °C and char yield is 23.7%. On the other hand, in the case of the pSS-grafted wool fabric, in the first stage, 7.6% weight is lost compared to the 10.5% weight loss observed for the control wool fabric indicating that the grafting of wool with pSS reduced its moisture content. In the second stage up to 229 °C, only 1.1% weight was lost. In the third stage, up to another 57% weight was lost. In the final stage, another 8.5% weight was lost producing char yield 27.7%, much higher than the char yield produced by the control fabric at that temperature. The results indicate that the grafting of pSS onto wool fabric reduced wool fabric's thermal degradation increasing the char yield. The DTG curve shows that the peak degradation temperature for the control and pSS-grafted wool is almost same but the temperature for the 10% weight loss of the control and the pSS-grafted fibre is quite different, 98.0 and 238.1 °C respectively. The corresponding figure for the 50% weight loss is 340.7 and 345.8 °C respectively. Therefore, it can be concluded that the grafting of pSS onto wool affected its thermal stability.

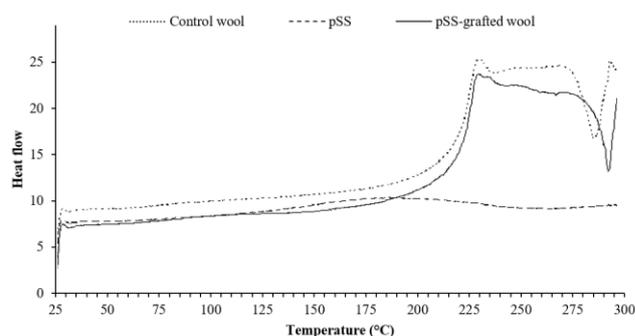


Fig. 4. DSC curves of second heating cycle of control wool fabric, pSS and pSS-grafted wool fabric.

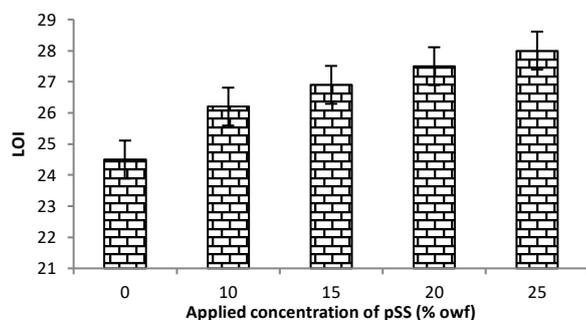
### Differential scanning calorimetry.

The differential scanning calorimetry profiles of the second heating cycle of untreated wool, pSS-grafted wool and pSS are shown in Fig. 4. Free radical polymerisation of styrene sulfonate produced an atactic polymer, which is fully amorphous and for this reason did not show any exothermic or endothermic peak. On the other hand, the control and pSS-grafted wool produced endothermic peaks at 291 and 298 °C respectively. The shifting of the endothermic peak towards higher temperatures from 291 °C for wool to 298 °C for the pSS-grafted wool, suggesting the positive effect of pSS grafting in enhancing the thermal stability of wool. The protection of wool from thermal degradation exerted by the pSS chains copolymerised within the fibre matrix may be related to both the intrinsic thermal properties of the grafted polymer and boundary interactions between the grafted polymers and the adjacent keratin chains.

### Fire-retardancy.

Wool fibres have the highest fire retardancy of the natural fibres, as the LOI of wool fibre is 24.5 compared to 18.0 for cotton. Fig. 5 shows the effect of the addition of pSS on the LOI value of wool fibre. It can be seen that the LOI value of wool increased with an increase in the grafted pSS add-on. The highest LOI was shown by the wool fabric

grafted with 25% pSS is 28.0, compared to 24.5 shown by the untreated wool fabric. It is evident the grafting of wool considerably increased the fire-retardancy of wool. This indicates that the grafted pSS produced sulphur species during the decomposition of pSS-grafted wool fibres, which slowed down the thermal degradation of wool through the destruction of free radicals formed during combustion. The achieved results are consistent with the results shown by pSS-g-silica nanoparticles in the case of PP/pSS-g-nanosilica composites and polyurethane foam coated with polyvinyl sulfonic acid.<sup>28,29</sup>



**Figure 5.** Effect of SS monomer concentration on the LOI value of pSS-grafted wool fabrics.

### Mechanical properties and moisture regain.

Moisture regain and tensile properties are two important parameters, which determine the properties and functional performance of textile fibres (e.g. handle and comfort properties). Grafting with pSS caused a significant change in moisture regain of the grafted wool fibres. Under standard atmospheric condition wool fibre shows moisture regain of 15% but in the case of pSS-grafted wool fibres, moisture regain dropped to 12%.

Table 2 shows the warp and weft-wise breaking strength and elongation at break of control wool fabric and wool fabric grafted with various concentrations of pSS. It can be seen that the control and pSS-grafted fabrics showed marginally lower tensile strength in weft direction compared to the warp direction strength. It is evident that the grafting of wool fabric with pSS increased wool fabric's tensile strength as well as breaking strength but the elongation decreased compared to the control fabric. In the case of pSS-grafted wool fabrics, the tensile strength and breaking strength increased, and the elongation at break decreased with an increase in the applied concentrations of pSS.

**Table 3.** The tensile strength, elongation and breaking strength of control wool fabric and also wool fabrics grafted with various concentrations of pSS.

Samples	Warp direction				Weft direction			
	Tensile Strength (MPa)	Elongation at peak (%)	Breaking strength (MPa)	Elongation at break (%)	Tensile strength (MPa)	Elongation at peak (%)	Breaking strength (MPa)	Elongation at break (%)
Control	14.5±0.2	44.4±1.1	4.8±0.1	55.5±0.8	14.12±0.2	49.3±1.1	4.2±0.1	60.6±1.6
10% pSS-grafted wool	15.3±0.1	43.0±0.8	5.1±0.1	54.6±0.5	14.6±0.1	50.9±0.8	4.4±0.1	56.4±1.1
15% pSS-grafted wool	15.8±0.1	44.8±1.2	5.2±0.1	53.6±0.9	15.0±0.1	48.9±0.5	4.5±0.1	59.7±0.9
20% pSS-grafted wool	16.0±0.1	46.35±1.1	5.3±0.1	52.3±0.4	15.3±0.1	45.8±0.7	4.7±0.1	58.5±1.3
25% pSS-grafted wool	16.2±0.1	43.03±1.5	5.4±0.1	50.6±0.5	15.5±0.2	45.2±0.6	4.9±0.1	53.8±2.1

The tensile strength of the control fabric was 14.53 and 14.12 MPa in warp and weft directions respectively. On the other hand, the wool fabric grafted with 25% pSS showed the tensile strength of 16.2 and 15.47 MPa in the warp and weft directions, respectively. Similar phenomena were observed for the breaking strength of the fabric as the pSS-grafted fabrics showed considerably higher breaking strength compared to the breaking strength shown by the control fabric in both directions. The peak elongation showed inconsistent results in both warp and weft directions but the elongation at break showed a trend as the elongation at break decreased with an increase in the applied concentration of pSS. The elongation at break shown by the control fabric was 55.52 and 60.59% in warp and weft directions respectively; the corresponding elongation at break values for the wool fabric treated with 25% pSS were 50.63 and 53.83 in warp and weft directions respectively. The grafted pSS polymer reinforced the wool fibres and therefore the tensile strength increased with an increase in the pSS concentrations. On the other hand, the grafting of pSS onto the macromolecular chains of wool fibres restricted their molecular chain mobility, which affected their

extensibility resulting in a decrease in the elongation at break of the pSS-grafted fabrics.

### Surface characteristics.

**Dynamic contact angle.** The surface contact angle measurement indicates the nature of the surface of the fibre, i.e. whether the surface is hydrophilic or hydrophobic. Table 3 represents the dynamic contact angle of water droplets deposited on the surface of control wool fabric, and wool fabric grafted with various levels of pSS. It can be seen that the control wool fabric is quite hydrophobic as the contact angle was 128.4° at 0 s of placing the water droplet, which reduced to 127.7° after 120 s of placing the water droplet. On the other hand, in the case of pSS-grafted wool fabrics, the contact angle only slightly decreased compared to the contact angle shown by the control fabric. The contact angle decreased with an increase in the concentration of the applied SS monomer but decreased to only from 128.4° for the control to the 121.8° for the 25% of SS monomer at 0 s, which did not decrease even after 120 s indicating

strong hydrophobicity. It is evident that the grafting of wool fabric with pSS has minimal effect on its contact angle and hydrophobicity.

Table 2. Dynamic contact angle ( $^{\circ}$ ) of water droplet placed on the surface of control and pSS grafted wool fabric at different times.

Samples	Contact angle ( $^{\circ}$ ) at				
	0 s	30 s	60 s	90 s	120 s
Control	128.4	128.2	128.0	127.7	127.7
10% pSS	129.6	126.1	125.9	125.5	125.2
15% pSS	123.1	122.9	122.6	122.5	122.3
20% pSS	124.0	123.1	122.8	122.5	121.9
25% pSS	121.8	121.9	122.1	122.4	122.3

The contact angle data showed that the contact angle of wool fabric dropped from  $128.4^{\circ}$  for the control to  $121.8^{\circ}$  for the wool fabric sample grafted with 25% of pSS indicating that the surface of the grafted fabrics has less hydrophobicity compared to the surface of control wool fabric. The pSS polymer is an anionic polymer having hydrophilic sulfonate moieties and therefore the pSS-grafted fabrics showed a lower contact angle compared to the surface of the control fabric. However, pSS has hydrophobic alkyl benzene groups and SS monomer has been absorbed into the amorphous regions of wool fibre and polymerised there, blocking the diffusion of water molecules into the interior of the fibre. Therefore, the pSS grafted fabric showed lower moisture regain than the moisture regain shown by the control wool fabric.

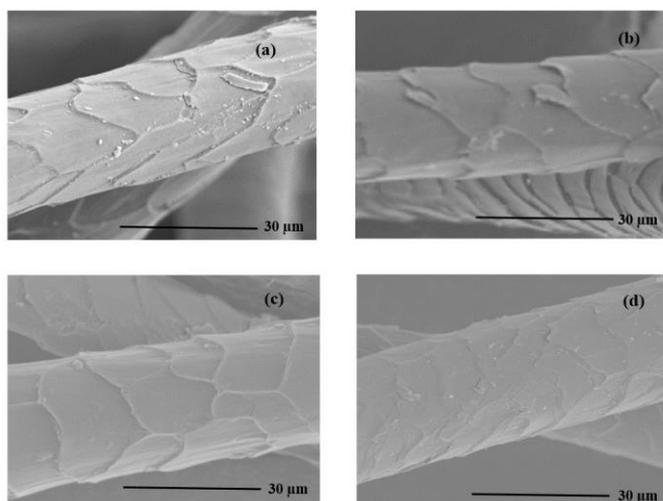


Fig. 6. SEM images of surface of untreated (a), and 10 (b), 20 (c) and 25% (d) pSS grafted wool fabrics.

**Surface morphologies.** The surface morphology of pSS-grafted wool fibres with different amount of polymer grafting was examined by scanning electron microscope (SEM) and is shown in Fig. 6. The SEM image of control wool fabric shows typical scaly surface of wool fibres. It can be observed that the typical scale pattern of untreated wool fibres underwent only slight modification with an increase in the concentration of SS monomer, which suggests that the majority of the polymer was internally grafted rather than depositing on the surface of wool fibres. Obviously, coverage of wool fibre surface by the pSS polymer increased with an increase in the applied

concentration of SS monomer. The coverage of fibre surface was more at 25% monomer application compared to 10% monomer application.

#### Stain-resistance.

The stain-resistance of control wool fabrics and also wool fabrics grafted with various concentrations of pSS against an acid dye-based stain (C.I. Acid Red 40) is shown in Fig. S1 (Supplementary content). The blank treated control fabric showed very poor stain-resistance and the intensity of the colour of the stain was quite high as the staining agent was confined to the circle corresponding to the size of the stain applicator in a limited area and did not spread, as the surface of the control wool fabric is quite hydrophobic. On the other hand, the stain spread on the pSS-grafted wool fabrics because of their increased hydrophilicity as evident by the water contact angle data. The grafted polystyrene sulfonate polymer forms an anionic layer on the surface of the fibre, which repelled anionic acid dye molecules and affected the absorption of the dye into the fibres. The increase in the surface hydrophilicity of pSS-grafted wool fabrics helped in the release of stains from the stained fabrics resulting in an increase in the stain-resistance.

In the case of control fabric, the colour difference between the stained and unstained control fabric is  $\Delta E=46.5$  as shown in Table S1 (Supplementary content). The value of colour difference considerably decreased for the pSS-grafted wool fabrics compared to the blank treated control fabric. In the case of pSS-grafted wool fabrics, the colour difference ( $\Delta E$ ) between the stained and unstained treated fabrics decreased from 39.2 for the fabric treated with 10% pSS to 37.1 for the fabric treated with 25% pSS. Therefore, the stain-resistance of the treated fabrics decreased with an increase in the concentrations of pSS. Table S1 (Supplementary content) also shows the  $CIE L^*a^*b^*$  values of stain control fabrics and also the fabric samples treated with various concentrations of pSS. The value of  $L^*$  shows lightness or darkness of the colour, i.e. the lower the lightness the darker is the colour. It can be seen that the control stained fabric showed the lowest  $L^*$  value but for the pSS-grafted wool fabrics, the value of  $L^*$  increased with an increase in the concentration of pSS. Similarly, the stained control fabric showed the highest colour strength, which decreased with an increase in the concentrations of pSS indicating that the intensity of the stain decreased with an increase in the pSS concentrations. Therefore, it can be concluded that the grafting of pSS onto wool fabric positively affected its stain-resistance against the acid dye-based stain.

#### Antibacterial properties.

The antibacterial performance and the durability of the treatment up to 20 washes of pSS-grafted wool fabrics treated with 0.5%  $AgNO_3$  against *Staphylococcus aureus* and *Klebsiella pneumoniae* are shown in Table 4. The antibacterial activity was compared with a wool fabric sample treated with  $AgNO_3$  at pH 9 (as in acidic conditions, Ag ions are hardly adsorbed into wool fibres). It can be seen that the control and the pSS-grafted wool fabric treated with  $AgNO_3$  showed excellent antibacterial activity against both the bacteria as 99 and 99.3% bacterial were killed respectively. However, after 5 cycles of washing, the killing of bacteria dropped to 85% for the control fabric but the pSS-grafted fabric still showed 99% killing of both bacteria. After 10 cycles of washing, the control fabric did not show any antibacterial activity but the pSS-grafted fabric showed excellent antibacterial activity even after 20 washing. Wool fabrics are washed less often compared to the fabrics made with other fibres

and therefore the test for 20 washes should be enough to provide lifetime antibacterial protection.

**Table 4** Antibacterial property of pSS-grafted wool fabric treated with 0.5% AgNO<sub>3</sub> measured according to the AATCC Test Method 100-1999.

No of cycles of wash	Ag (%) retained (measured by EDX)		% of bacteria killed			
			<i>Staphylococcus aureus</i>		<i>Klebsiella pneumoniae</i>	
	Control	pSS-grafted	Control	pSS-grafted	Control	pSS-grafted
0	1.35	1.82	99.6	99.8	99.0	99.3
5	0.83	1.43	98.0	99.5	49	99.2
10	0.17	1.12	0	99.9	0	99.3
20	0.05	0.60	0	98.5	0	98

The EDX results show that the pSS-grafted wool fabric absorbed considerably higher concentration of Ag<sup>+</sup> compared to the untreated control (Table 4). After 10 washes, the control fabric lost most of the absorbed Ag<sup>+</sup> ions and therefore did not show any antibacterial activity. On the other hand, the pSS-grafted wool fabric retained such a level of Ag<sup>+</sup> ions that even after 20 washes, still showed very strong antimicrobial activity. The grafting of pSS onto wool fabric samples enhanced their durability of the antibacterial treatment to multiple launderings.

#### Surface resistivity.

The surface electrical resistance and the 'guarded' volume resistance of control and pSS-grafted wool fabrics without and treated with AgNO<sub>3</sub> are represented in Table S2 (Supplementary content). It can be seen that the pSS-grafting had a marginal effect on the surface and volume resistivity of wool fabrics. At the lowest concentration of pSS (10%), a small decrease in resistance was observed but after which both surface and volume resistance increased with an increase in the pSS concentrations. It can be seen that the silver nitrate treatment had a considerable effect on the surface and volume resistance of untreated and pSS-grafted wool fabrics.

## Experimental

#### Materials.

The woven wool fabric of 26 ends cm<sup>-1</sup> and 26 picks cm<sup>-1</sup> of 150 g m<sup>-2</sup> made of merino wool fibres of average fibre diameter of 19 μm were procured locally. Sodium styrene sulfonic acid, potassium persulfate, silver nitrate and acetic acid were purchased from Sigma-Aldrich Chemicals (USA) and were of analytical reagent grade. Teric GN9, a non-ionic surfactant, was supplied by Huntsman Chemicals (USA). Sandozin MRN, a non-ionic non-silicone-based wetting agent, was supplied by Clariant Chemicals (Switzerland).

#### Graft-copolymerisation of wool with pSS.

Prior to grafting with pSS, wool fabrics were scoured with 2 g l<sup>-1</sup> Teric GN 9 and 0.25 g l<sup>-1</sup> Sandozin MRN at 50 °C for 30 min to remove the spinning lubricant used during spinning of wool fibres and also to remove dirt. Polymerisation was carried out in an Ahiba sample dyeing machine (Ahiba Turbomat 1000, Datacolour A.G., Dietlikon, Switzerland) using materials to liquor ratio of 1:30. The dyeing pot was filled with sufficient water and the wool fabric was placed in suitable carriers and placed inside the dyeing pot. Then, 0.5 ml l<sup>-1</sup> Sandozin MRN and the monomer solution were added, pH was set at

4.5 using sodium acetate and acetic acid buffer, and the temperature was increased to 45 °C and held for 15 min. The required quantity of an aqueous solution of a suitable initiator (potassium peroxydisulphate) was added and the temperature increased to 65 °C at 2 °C min<sup>-1</sup> and held for 90 min. The polymerisation bath was then cooled to 40 °C and the treated wool was washed with cold water, followed by soaping with 0.5 g l<sup>-1</sup> Teric GN 9 at 60 °C for 20 min. The treated fabric samples were washed with hot water at 60 °C for 10 min then rinsed with cold water to remove the unreacted monomer and oligomers adhering to the surface of the fibres.

#### Characterisation of pSS-grafted-wool fabrics.

**Physicomechanical characterisation.** Elemental analysis of the untreated and polymer treated wool was carried out at the Campbell Micro-analytical Laboratory, University of Otago (New Zealand) using Europa Hydra coupled to a Carlo Erba NC 2500. The IR spectra of the untreated and treated samples were recorded on a PerkinElmer FTIR (Model: System 2000, PerkinElmer Corporation, USA) with an attenuated total reflectance (ATR) attachment using a Zn/Se ATR crystal. The fabric samples were placed flat on the upper side of the crystal. Good fibre to crystal contact was ensured by applying 50 N force using a calibrated torque wrench. 64 scans were carried out for each sample and the averages are reported here. Graft yield (G<sub>y</sub>) was calculated by accurately measuring the dry weight of wool fabrics samples before and after polymeric grafting using the following formula:

$$G_y = \frac{W_t - W_0}{W_0} \times 100 \quad [1]$$

where, G is grafting yield, W<sub>0</sub> and W<sub>t</sub> are the weight of the wool sample before and after polymer grafting. The grafting efficiency (G<sub>e</sub>) was calculated by the polymer added to the fabric divided by the weight of the monomer applied according to the following formula and expressed as a percentage:

$$G_e = \frac{W_t - W_0}{W_s} \times 100 \quad [2]$$

where, W<sub>s</sub> is the weight of applied SS monomer.

#### Thermal analysis.

Thermogravimetric analysis (TGA) was carried out to evaluate the effect of grafting of pSS onto wool fibres on their thermal stability and degradation temperatures. TGA was carried out using a TM thermogravimetric analyser (Model: Thermo Electron Corporation, Waltham, USA) at room temperature to 600 °C at a heating rate of 10

°C/min under nitrogen environment. All TGA runs employed nitrogen (99.99% pure and food grade) as a purge gas for the furnace with a constant flow rate of 100 ml min<sup>-1</sup>. For each run, 10 mg of the sample was loaded in a platinum pan and was heated to 500 °C at a linear rate of 5 °C min<sup>-1</sup> under constant nitrogen gas flow (100 ml min<sup>-1</sup>), held for 10 min, and slowly cooled down to room temperature by switching off the heater. The TG curves and differential thermal analysis curves were recorded simultaneously along with temperature rise.

The differential scanning calorimetry (DSC) of control wool fabric, pSS and pSS-grafted wool (25% owf) was carried out on a Perkin-Elmer DSC-6 instrument (PerkinElmer Corporation, Waltham, USA) to assess their thermal response to heating. The scanning was started at 25 °C and increased to 150 °C at the rate of 10 °C min<sup>-1</sup> and hold at that temperature for 5 minutes to remove any thermal history of the sample. Then cooled to 25 °C at the same rate of heating and holding 25 °C for 5 minutes followed by again heated to 300 °C at the previous rate of heating and all scanning was carried out under a nitrogen atmosphere.

### Mechanical properties and surface morphology.

140 × 25 mm size samples were cut from the control and various pSS-grafted wool fabrics. The tensile strength and elongation at break of wool control wool fabrics and also wool fabrics treated with 10, 15, 20 and 25% pSS were measured using an Instron Universal Tensile Testing machine (Instron Inc., USA) using a crosshead speed 20 mm min<sup>-1</sup> and gauge length 100 mm. At least 10 samples were tested for each treatment and the averages are reported here.

### Surface characterisations.

The contact angle was measured in dynamic mode by using a KSV CAM 100 Contact Angle Measurement Apparatus (KSV Instruments, Helsinki, Finland). For each sample, the contact angle was measured at 10 places and the average contact angle was reported. The Young-Laplace equation was used to quantify the contact angles. For each sample, the first measurement was taken immediately after placing the drop of water and then at 10 seconds interval measurements were taken until 40 s.

The surface of the treated and untreated wool fabrics was characterised by scanning the fabrics sputter-coated with gold on a scanning electron microscope (Model JEOL JSM-7000F, JEOL Corporation, USA) at an accelerating voltage of 15 kV. The surface and the volume resistivity of the untreated and various pSS-grafted wool fabrics with and without silver nitrate treatment was assessed according to the AATCC Test method 76-2000: Electrical Surface Resistivity of Fabrics using Trek Surface Resistivity Meter (Model 152-1, Trek Inc., Lockport, USA). The volume resistivity was measured in 'guarded' state. All measurements were carried out at the standard atmospheric condition (20 ± 2 °C and 65 ± 25 relative humidity). The samples were conditioned at those conditions for 48 h prior to conducting the test.

### Evaluation of stain-resistance.

Stain resistance of the untreated and the pSS-grafted wool fabrics was assessed against C.I. Acid Red 40 according to AATCC Test Method 175-2008 Stain resistance: Pile Floor Coverings. This test method has been developed for measuring the stain-resistance of floor coverings but we have found it suitable for measuring the stain-

resistance of thick wool fabric. For each treatment two fabric samples of 100 × 100 mm size were placed into a conditioned room (65 ± 2%RH, 20 ± 1 °C) for 24 h. For blank staining, distilled water with pH 2.8 ± 1.0 adjusted by citric acid was used. One fabric sample was blank-stained and two samples were stained with C.I. Acid Red 40 solution. The stain applicator was placed at the centre of each fabric sample, 20 ml of stain solution was poured into the centre of the applicator and the top 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 the oven at 80 °C and returned to the conditioned room. Colour measurements of unstained and stained conditioned samples were carried out with a Mahlo spectrophotometer under D65 illuminant and 10° observer. At least two samples were tested for each treatment and the averages are reported here.

### Evaluation of fire retardancy.

The fire retardancy of the untreated and pSS-grafted wool fabrics were evaluated by measuring limiting oxygen index (LOI) according to the ASTM Test Method D2863 – 2009: Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics. In the LOI test, a small sample of 13 × 6 cm fabric was supported vertically in a mixture of oxygen and nitrogen flowing upwards through a transparent chimney. When the upper end of the sample was ignited, the subsequent burning behaviour of the sample was observed to compare the period for which burning continued or the length of the sample burned. The minimum concentration of oxygen was determined by testing a series of samples in different oxygen concentrations. The minimum oxygen concentration that caused candle-like burning of the fabric was treated as the LOI value.

### Treatment with ionic silver and the assessment of antibacterial properties.

The untreated and pSS-grafted wool fabrics were treated with AgNO<sub>3</sub> (0.5% owf) at pH 3 for 30 min at 70 °C and the fabric samples were dried without any washing. The antibacterial properties of control wool fabric and also the wool fabric graft-copolymerised with 25% pSS were assessed by a quantitative method according to the AATCC Test Method 100-1998. A fabric sample was placed in individual sterile Petri dishes. The nutrient broth was prepared with 5 g l<sup>-1</sup> peptone and 3 g l<sup>-1</sup> beef extracts and the pH was adjusted to 6.8 ± 0.1 with 1N sodium hydroxide solution. The bacterial culture of appropriate type diluted 100 times was transferred to the nutrient by using a 4 mm inoculating loop and was incubated at 37 ± 2 °C for 24 hours. 1.0 ± 0.1 ml inoculum was added to the sample in each petri dish. The Petri dishes were then incubated at 37 ± 2 °C for 48 h. The number of bacteria before and after the incubation is measured by a colony counter and the reduction in bacteria is measured which is expressed in percentage. This method provides a quantitative assessment of the antimicrobial performance of antibacterial textile materials as it provides a percentage of killing of a particular bacteria. The bacteria used were *Staphylococcus aureus* (ATCC 6538), and *Klebsiella pneumoniae* (ATCC 4352).

## Conclusions

We have demonstrated that pSS can be grafted onto wool fabric by an aqueous free-radical polymerisation process. The grafting efficiency was quite good but decreased with an increase in the

applied concentration of the monomer. Elemental analysis and ATR-FTIR spectra confirm that pSS has been grafted to wool fabric. The tensile strength and stain resistance against acid dye-based stain of the fabric considerably increased with an increase in the applied concentrations of the SS monomer. The warp and weft-wise tensile strength increased from 14.5 to 16.2 MPa and 14.1 to 15.47 MPa respectively for the wool fabric grafted with 25% pSS. The DSC, TGA and LOI measurements show that the thermal stability of wool fabric considerably increased after grafting with pSS, which increased with an increase in the pSS add-on. The LOI value increased from 24.5 for the control to 28.0 for the wool fabric grafted with 25% pSS indicating an excellent increase in the fire retardancy of the wool fabric. The pSS-grafted wool fabric followed by treatment with Ag<sup>+</sup> ions showed excellent antibacterial activity against *Staphylococcus aureus* and *Klebsiella pneumonia* and the treatment was durable to at least 20 washings carried out on a Wasicator, which is equivalent to 100 home laundering. The surface resistance of wool fabric grafted with pSS decreased with an increase in the pSS concentrations but increased after the treatment with Ag<sup>+</sup> ions. The developed treatment could be used in industry to make wool fabric multi-functional, i.e. to make wool fabric stain-resist, antibacterial, and fire retardant.

### Conflicts of interest

There are no conflicts to declare.

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