Modification of surface properties of wool fabric with Linde Type A nano-zeolite

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ABSTRACT: Wool is a naturally occurring composite fiber consisting of keratin and keratin-associated proteins as the key molecular components. The outermost surface of wool comprises a lipid layer that renders the surface hydrophobic, which hinders certain fabric processing steps and moisture management properties of wool fabrics. In this study, Linde Type A (LTA) nano-zeolite (a Na^+-, Ca^{2+}-, and K^+-exchanged type A zeolite) was integrated onto the surface of wool using 3-mercaptopropyl trimethoxy silane as a bridging agent. The resultant surface morphology, hydrophilicity, and mechanical performance of the treated wool fabrics were evaluated. Notably, the surface hydrophilicity of wool increased dramatically. When wool was treated with a dispersion of 1 wt % zeolite and 0.2 wt % silane, the water contact angle decreased from an average value of 148° to 50° over a period of approximately 5 min. Scanning electron microscopic imaging indicated good coverage of the wool surface with zeolite particles, and infrared spectroscopic evaluation demonstrated strong bonding of the zeolite to wool keratins. The zeolite application showed no adverse effects on the tensile and other mechanical properties of the fabric. This study indicates that zeolite-based treatment is potentially an efficient approach to increasing the surface hydrophilicity and modifying other key surface properties such as softness of wool and wool fabrics. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42392.

INTRODUCTION

A wool fiber is comprised predominantly of an inner cortex of keratin and associated proteins, surrounded by a cuticle layer of fatty acids.[1,2] The cuticle layer makes the wool surface hydrophobic, which significantly limits some potential applications in the moisture or water management capabilities of wool textiles, due to restricted heat and moisture transfer. This hydrophobicity can also create an unfavorable static charge on garments.[3–6] The hydrophobic nature of the wool fiber surface also reduces its amenability to wet chemical processing such as dyeing and anti-shrinkage finishing.[4,7] Synthetic polymers have traditionally been used to achieve these functionalities,[8] however, synthetic materials require energy-intensive processing which has an adverse environmental impact.[9] For example, nylon and polyester are non-renewable petrochemical-based materials that require high amounts of energy to synthesize, and also create serious waste management problems.[9] In contrast, wool is a natural, renewable, and biodegradable fiber. Various approaches using enzymes,[10–12] chemicals,[11,13,14] and plasma radiation[11] have been applied to improve surface wettability of wool, how-

ever, these led to undesirable mechanical performance due to associated wool damage. Therefore, the challenge is to add advanced functionalities to wool textiles without compromising critical mechanical properties, and thereby provide a robust basis for competing with synthetic fabrics.

Recent developments in nanotechnology may provide a solution to this hydrophobicity problem: by integrating nanomaterials into or onto wool, a wide range of functionalities may be introduced to create 'smarter' fabrics.[4,15,16] There has been some research on the use of silica nanoparticles as a hydrophilic coating on wool fibres.[4,15,17] Mineral nanomaterials such as zeolites have the potential to enhance moisture absorption, ultraviolet radiation, and antimicrobial protection, flame-proofing, mechanical strength, dyeing capability, and also to increase skin comfort.[18] However, there are few published reports on the use of zeolites for creating multi-functional coatings on wool textiles.[18–22]

Zeolites are aluminosilicate based minerals that form rigid and porous lattices. They contain alkali or alkaline earth metal ions, such as Na^+, K^+, Ca^{++}, Sr^{++}, and Ge^{4+} in order to maintain

electrical neutrality.[23–25] Each zeolite type has a unique lattice and framework structures, with pores, cavities, and channels of varying sizes and geometries.[20,23,24,26] This characteristic allows for a wide range of applications as catalysts, gas absorbents, and ion-exchange membranes or filters.[18,20,23,24,26,27] Modification of zeolites by introducing molecules or ions into their cavities can further increase their potential uses in creating smart textile products.[18,19,21,28] There are numerous types of zeolites available based on their size, framework structure, chemical compositions, and functionalities. In a previous communication,[22] the surface of wool was modified with a micron-sized zeolite molecular sieve 5A via breaking the chemical structure of zeolite particles using an acid treatment followed by coupling with a silane agent. The molecular sieve is a Na^+ and Ca^{2+}-exchanged zeolite type A with a 1 : 1 Si : Al ratio. Because of high level of Al^{3+} in the framework, this zeolite has a tendency to collapse its structure during chemical treatment, for example in low pH environment.[29,30] In contrast, Linde Type A (LTA) nano-zeolite (a Na^+-, Ca^{2+}-, and K^+-exchanged type A zeolite) has a high level of Si^{4+} (maximum Si : Al ratio of nine or more)[31] and thereby the structural framework of this nano-zeolite is resistant to chemical treatment. As the structure of LTA zeolite is retained, modified wool textiles may be applied for additional non-traditional applications such as chemical or gas filtration, energy harvesting, and controlled release of active agents, in contrast to molecular sieve 5A. In the present study, wool fabric was treated with LTA nano-zeolite (100 nm) to improve the fabric's surface hydrophilicity or wettability and associated performance, while retaining the intact zeolite structure. As silane effectively binds two otherwise poorly compatible surfaces with different functional groups,[32] 3-mercaptopropyl trimethoxysilane was used as a coupling agent to bind the inorganic zeolite to the organic wool fabric.

EXPERIMENTAL

Materials

NanoZeolite LTA (Na^+, Ca^{2+}, and K^+ ion exchanged type-A zeolite with 0.3–0.5 nm pore size and 100 nm particle size) was obtained from NanoScape AG, Germany. 3-mercaptopropyl trimethoxy silane (95%) and Fourier transform infrared (FTIR) grade potassium bromide were obtained from Sigma-Aldrich, St Louis, MO. A plain-weave fabric made from 100% New Zealand merino wool was used. This fabric was commercially scoured. It had average fiber diameter of 20 micron and dry weight of 124 g/m². The fabric consists of yarn with average diameter of 200 micron and the average number of yarns is 3 × 3/mm² in criss-cross pattern. The images of wool fabrics are provided in Supporting Information (Figure S1).

Wool Surface Treatment

Wool fabric samples with size of 10 cm × 10 cm × 0.02 cm were treated by immersion in 50 ml plastic tubes. Dispersions of 0.01, 0.05, 0.2, 0.5, and 1% (w/v) zeolite in 0.2% (w/v) silane solution (with pH 7.8–10) were prepared using distilled water, in which fabrics were immersed separately with a fabric-to-dispersion ratio of 1 : 30 (w/w). The fabrics were treated at 70°C for 3 h in an oscillating (90 rpm) water bath. The treated fabrics were washed thoroughly with hot water (70°C) five times; during each washing, the fabric was immersed in 100 ml distilled water and shaken for 5 min at 90 rpm in the water bath. This washing technique was used to remove any loosely bound or free silane and zeolite particles from the wool fabrics. The washed fabrics were dried in an air-circulated oven at 60°C for 16 h. In a separate experiment, untreated, silane (0.2%), zeolite (0.5%), and zeolite (0.5%)/silane (0.2%) treated washed wool fabrics were immersed in distilled water at 1 : 100 ratio (w/v) and pH values of corresponding samples were recorded after 2 h.

Measurement of Hydrophilicity

The hydrophilicity of wool fabrics was evaluated by means of water contact angle. It is known that the smaller the average contact angle, the greater the fabric's hydrophilicity. Contact angle measurements with distilled water (10 μl) on the fabrics were recorded using a contact angle meter (CAM 100, KSV Instruments, Finland). Measurements were taken after 5 min of contact. For each sample, three measurements were taken and the mean values obtained.

Measurement of Tensile Properties

The wool fabrics were conditioned and evaluated for their mechanical performances according to the ISO 13934-2 test method. The tensile properties of the wool fabrics were measured using a universal testing machine INSTRON 4204 (Instron, High Wycombe, UK) with a load cell of 100 N, gauge length of 10 mm, and extension speed of 20 mm/min. Each tested specimen had an average width of 10 mm and thickness of 0.20 mm. For each sample, five test specimens were tested and the stress–strain plot that represents the average results was reported. Prior to testing, all samples were conditioned under standard atmospheric conditions (60±2% relative humidity and 21±1°C) for 24 h.

Scanning Electron Microscopy

The surface morphology of the wool fabrics was observed at ×3500 magnification under a JEOL JSM 7000F field emission, high resolution scanning electron microscope (Tokyo, Japan). In preparation for microscopy, the fabrics were first coated with a thin layer of carbon.

Infrared Spectroscopy

Fourier transform infrared–attenuated total reflectance (FTIR-ATR) measurements of the wool samples were taken using a Nicolet 5700 FTIR spectrometer with an attenuated total reflectance (ATR) accessory. Measurements were taken in the 400–4000 cm^{-1} wavenumber range using 128 scans. Infrared measurements of zeolite, silane, and silane-treated zeolite were taken using a Perkin-Elmer System 2000 FTIR spectrometer. Transparent KBr disks of zeolite, silane, and silane-treated zeolite were made and spectra obtained. The wavelength range was set to 450–4500 cm^{-1} and 16 scans were used. Zeolite was treated with silane at 5 : 2 ratio (w/w) in an aqueous dispersion for 3 h at 70°C, and washed thoroughly and dried prior to FTIR analysis.

X-ray Diffraction Study

Wide angle x-ray diffraction measurements were carried out at 20°C using a X'Pert PRO diffractometer (PANalytical, The Netherlands) in the normal reflection mode with Ni-filtered Cu Kα
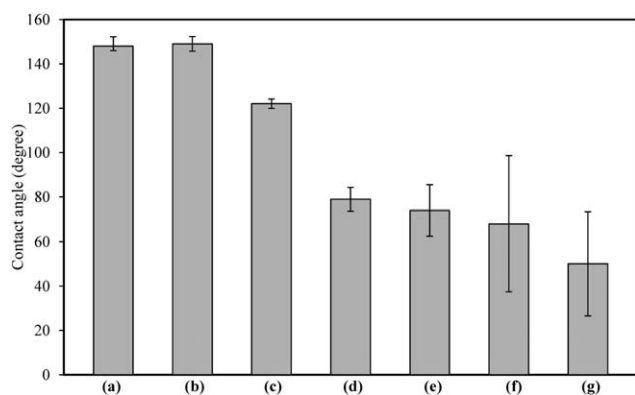
Figure 1. Water contact angle on fabric surfaces measured after 5 min: Untreated fabric (a), silane-treated fabric (b) and fabrics treated with dispersions in 0.2 wt % silane of 0.01 (c), 0.05 (d), 0.2 (e), 0.5 (f) and 1.0 (g) wt % zeolite.

radiation ($\lambda = 1.541$Å) in the 2θ range of 3° to 60°. After the samples were loaded, a careful alignment procedure was followed to ensure the accuracy of the θ angle. A scanning rate of 1.0°/min was used in each case.

RESULTS AND DISCUSSION

Surface Hydrophilicity

Increasing the surface hydrophilicity of wool was the primary focus of this investigation. Wool fabric with a highly hydrophilic surface has the potential for application in the clothing industry with regard to moisture management and wet chemical processing to improve dyeing and shrink resistance treatments. It is expected that because of the porous structure of zeolite, a coating of zeolite will change surface energy and roughness of wool fabric,[4,15] leading to improved capillary transport of absorbed water or moisture (wicking). The hydrophilicity of the treated fabrics was measured in terms of water droplet (10 µl) contact angle (shown in Figure 1). As anticipated, untreated wool had a high contact angle due to the hydrophobic surface bound fatty acid layer, and absorbed water very slowly. The average contact angle of 148° of untreated wool remained unchanged over the measurement time of 1 h (Supporting Information, Figure S1(a)). It indicated that the structure of plain-weave fabric has insignificant effect on contact angle values, which harmonizes with the values reported elsewhere.[7,33,34] However, when wool was treated with the aqueous dispersions of zeolite and silane, the surface hydrophilicity increased significantly. For example, after treatment with 0.5 and 1% zeolite (in 0.2% silane solution) respectively, the five minute contact angles were 68° and 50° (Figure 1). The images of water contact angles on wool are provided as Supporting Information (Figure S2). It also appeared that treatment with silane alone did not change surface wettability of wool fabric as water contact angle remained unaffected, similar observation is reported elsewhere.[35] Therefore, the reduced contact angles of zeolite+silane-treated fabrics are attributed to the capillary transport of absorbed water by porous zeolite layers only present on wool surfaces. Previous studies indicated that wool fabrics treated with silicone based particles using silane as a coupling agent, showed good washing fastness characteristics, demonstrating marginal changes of sur-

face wettability or water contact angles after 3×7A or 3×5A wash cycles in a Wascator laboratory washing machine.[33,35]

In the treated fabric, silane acts as a bridging agent between the zeolite and the wool. The increased hydrophilicity observed after zeolite+silane treatment aligns with the understanding of the surface morphology of wool (Figure 2), where zeolite nanoparticles are able to bond to the wool surface efficiently via the silane coupling agent. In another report,[22] wool fabric was converted into super-hydrophilic material via treating with dealuminated zeolite, causing the untreated wool contact angle of 148° to drop instantly to 0° on treatment with a dispersion of zeolite and silane in acetic acid solution. Treatment in the presence of an organic acid causes the regular framework structure of zeolite to collapse and surface bound zeolite to lose its intrinsic structural properties. However, the present study indicates that a moderate level of hydrophilicity of wool fabrics is achievable on surface treatment without breaking the structural integrity of nano-zeolite.

Wool Surface Morphology

Wool fabrics have a large surface area in relation to their bulk, and therefore surface morphology plays a critical role in influencing wool's behavior as a textile. As shown in the SEM images [Figure 2(a)], the untreated wool surface consists of flattened cellular sheets of cuticle cells that overlap each other from root to tip along the fiber. The cuticle cells are approximately 0.5 µm thick and form a protective sheath around an internal cortex. The cells have sharply defined scale edges, and at the junctions of cells, the surface drops to the level of the next underlying cuticle cell. The junction between the upper and lower scales is distinct and generally small compared to the cell thickness.[14,22,36]

After treatment with dispersions of zeolite and silane, the wool fabrics or fibers were coated with thin layers of zeolite and/or silane [Figure 2(b–d)]. Treatment resulted in accumulation of zeolite particles on the fiber surface; the observation of clumps (with dimensions of 1 µm or more) on the surface is attributed to zeolite nanoparticle self-polymerization and aggregation, facilitated by the reactive silane. The particle of original dimension (~100 nm) of zeolite was also observed on wool fabrics. However, this treatment produced a consistent surface coating and a decrease in water contact angle. This is consistent with zeolite hydroxyl groups on the surface reacting with silanol molecules, which interact strongly with exposed protein side chain moieties in the wool cuticle, forming a durable zeolite coating. The zeolite coating on wool surface was also supported by pH change of aqueous media where wool fabrics were immersed. It appeared that untreated and silane-treated wool showed pH of 6.24 and 5.78, respectively, whereas zeolite and silane/zeolite-treated wool showed pH values of 7.84 and 8.00, respectively. It indicated that the surface of zeolite or silane/zeolite-treated wool is basic in nature, which is attributed to the basic metal ions (Na^+, K^+, and Ca^{++}) present in zeolite framework. However, this zeolite treatment appeared to have no deleterious effects on the morphology of the native wool fiber, as the treatment did not remove surface components in the presence of alkaline dispersion (pH 10) of zeolite and silane.
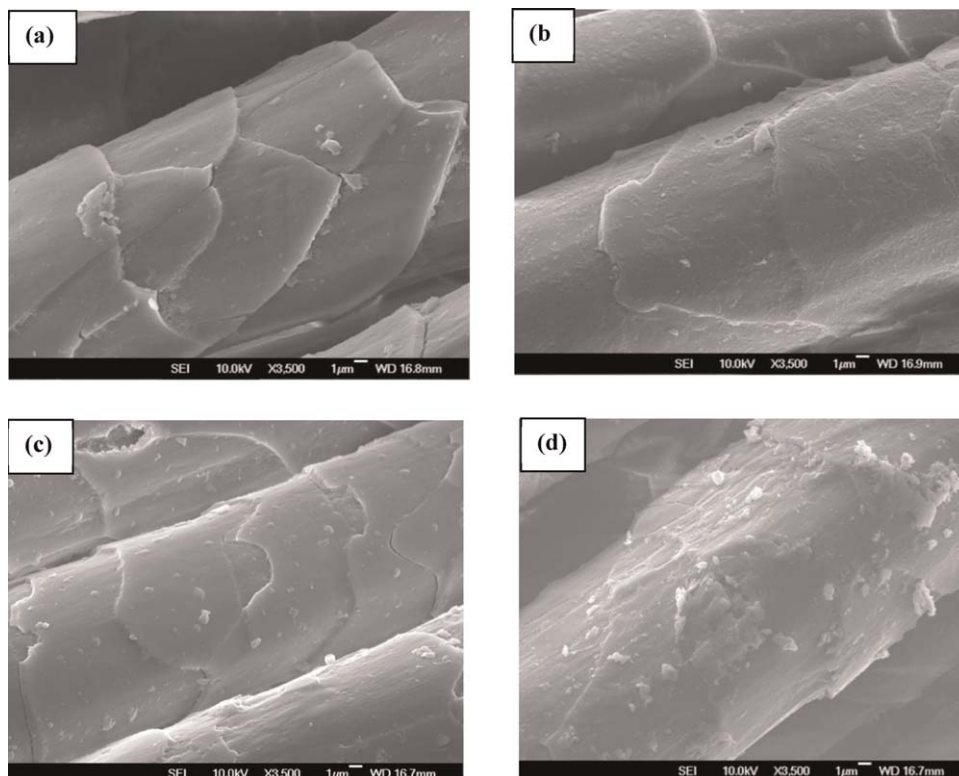
Figure 2. SEM morphology of wool fiber: (a) untreated wool; (b) wool treated with zeolite (0.5%); (c) wool treated with silane (0.2%); and (d) wool treated with zeolite (0.5%) and silane (0.2%).

Mechanical Performance

The tensile strength and modulus of the untreated and modified fabrics were evaluated to check if surface treatments had any adverse effect on mechanical performance. Tensile strength was obtained from measuring the maximum stress of stress–strain plots when the fabric starts to break, and the modulus was determined based on elastic modulus measurements (at 5% strain). Untreated wool had a mean tensile strength of 29 MPa and a modulus of 343 MPa. When silane and zeolite dispersions were applied separately, the tensile strength and modulus of the fabrics dropped as shown in Figure 3, which is attributed to the plasticizing effect of silane solution and alkaline effect of zeolite dispersion (with pH 7.8–10). The plasticization decreases tensile modulus, leading to decreased internal friction of fibers inside the fabrics and consequently reduces tensile strength of treated fabrics. In general, wool fabrics treated under alkaline pH show poor mechanical durability.[14] Alkaline reagents are used in soaps or detergents for wool processing steps such as the scouring of greasy wool, laundering of wool fabrics and dyeing. They can progressively cause hydrolysis of peptide bonds and amino acid side-chains in cell membrane complex (CMC) of keratin matrix,[37,38] facilitating the bridging of zeolite nanoparticles via silane agent in the current treatment. Therefore, treatment with a mixed dispersion of silane and zeolite had only a small effect on wool fabric tensile characteristics, with original strength largely retained. The fabrics treated with 0.5% zeolite in 0.2% silane revealed an average tensile strength of 27.8 MPa and strain-at-failure value of 28.5%. The tensile modulus decreased to 212 MPa (38% lower than that of untreated wool fabric),

indicating an improved fabric softness, often a highly desirable property for a textile product. The good mechanical properties of the silane and zeolite-treated fabrics are attributed to the reinforcing effect of the nano-scale zeolite bound to the wool surface via a silane bridging agent.

In general, when wool is treated with minerals or organic additives for improving functionality, the mechanical modulus increases.[39] However, a previous report demonstrated that dispersions of another form of zeolite (molecular sieve 5A) in acetic acid and silane enabled the mechanical performance of the original wool to be retained.[22] The zeolite treatments used in
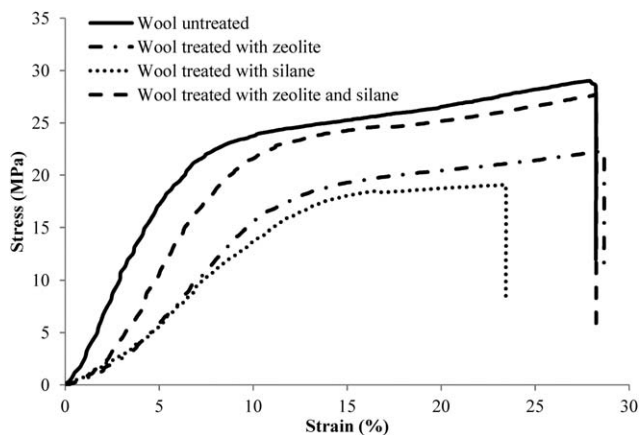

Figure 3. Representative stress–strain plots of untreated and treated wool fabrics.
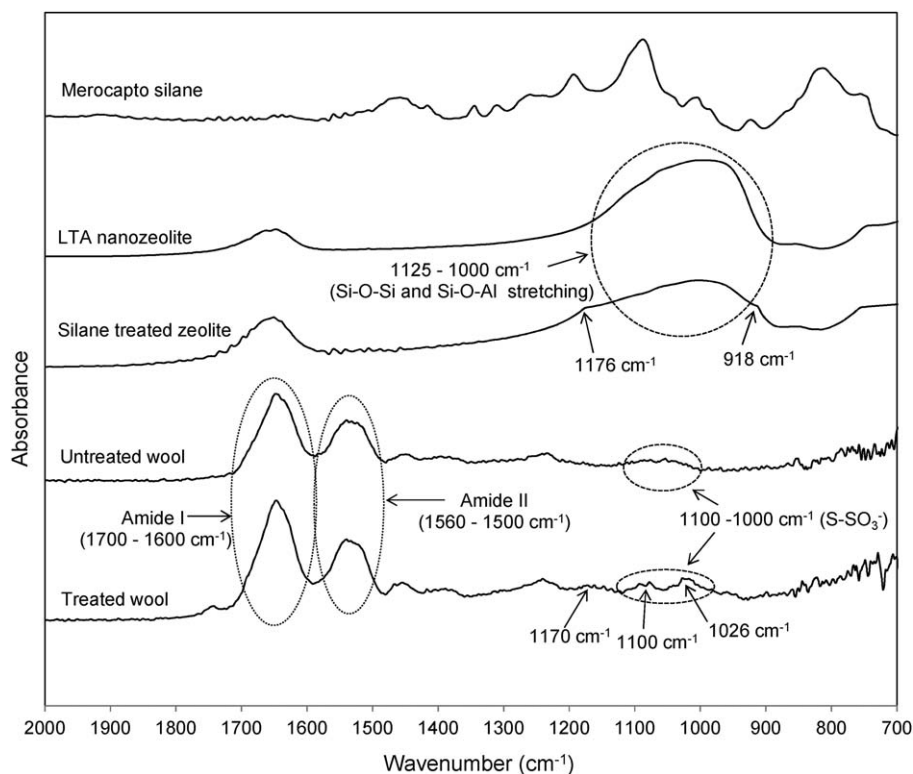
Figure 4. FTIR spectra of silane, zeolite, silane-treated zeolite, and untreated and treated wool (silane and zeolite dispersion).

the present study do not appear to produce any adverse effects on the mechanical performance of wool fabrics. In wool, CMC acts as a kind of molecular glue in retaining the mechanical integrity of the fiber. Compared to other regions, the CMC is particularly susceptible to chemical ingress and attack. It is anticipated that in an alkaline environment such as zeolite dispersions, the CMC phase is partially damaged and the mechanical integrity of fabrics is consequently reduced. In a mixed dispersion of silane and zeolite, wool's CMC phase undergoes physicochemical changes by alkaline agents (e.g., metal hydroxides) released from Na^+, Ca^{2+}, and K^+ exchanged LTA nanozeolite. It facilities the exposure of reactive groups (e.g., COO^-, SO_3^{2-}, SH, NH_2 or OH) of keratin protein, allowing the interaction at molecular level with nano-sized zeolite via silane as a bridging agent and retains the mechanical durability of the fiber.

Chemical Interaction

Infrared spectroscopy was used to evaluate the surface chemical characteristics of the wool fabrics before and after zeolite treatment (Figure 4). On its own, zeolite produced a broad band centered around 1000–1125 cm^{-1}, which is due to asymmetric stretching of the structural frameworks.[40] It also showed typical spectra of absorbed moisture around 1653 cm^{-1} (deformation band) and fundamental stretching bands above 3100 cm^{-1}. On its own, silane produced IR bands at 2841 cm^{-1} and 2942 cm^{-1}, assigned to –CH stretching vibration of –CH_3 and propyl chain[41] and strong bands at 1100 cm^{-1} and 1192 cm^{-1} which are attributed to Si–O stretching and deformation.[42] The IR spectrum of silane-treated zeolite revealed characteristic

bands of control zeolite with two additional weak bands centered at 1176 cm^{-1} and 918 cm^{-1}, which are likely to be originated from silane's Si–O stretching and vibration, and also –CH_2 rocking of silane moiety,[43] respectively. It indicated that zeolite surface's Si–OH group was chemically modified with silane via covalent and/or hydrogen bonding as reported elsewhere.[43,44] However, no obvious changes in the characteristic wavenumber range of zeolite (450–4000 cm^{-1}) were observed, indicating that the structural integrity of chemical framework remained unchanged after modification with silane. Figure 4 represents the characteristics absorbance bands in the range of 2000–700 cm^{-1}, where some synergisms of chemical interactions were observed.

Both untreated and treated fabrics (Figure 4) produced the characteristic bands of amide I (C=O stretching) and amide II (N–H bending and C–H stretching) in the range of 1700–1600 cm^{-1} and 1500–1560 cm^{-1}, respectively.[14,45–48] Untreated wool produced a broad band in the range of 1000–1100 cm^{-1} due to stretching vibration of cysteine–S–sulfonate (Bunte salt),[47–50] and intensity was increased on treatment with a dispersion of silane and zeolite, indicating strong interaction between zeolite with the S–S/SO_3^- groups of keratin via silane agent. In treated wool, the additional peaks around 1026 cm^{-1}, 1100 cm^{-1}, and 1170 cm^{-1} are assigned to the Si–O–Si bond[7,15] between the zeolite framework[29] and the silane linker. This indicated the strong association of zeolite with wool proteins using silane as a linker. Wool contains a particularly high level of cysteine residues (around 10 to 12 mol %),[45,50,51] which form disulfide bonds with other cysteine residues (forming
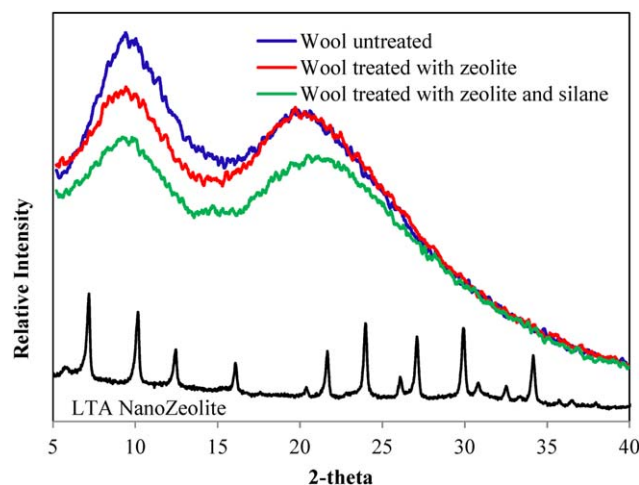
Figure 5. X-ray diffraction patterns of zeolite, and untreated and treated wool fabrics. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cystine). These bonds are the most reactive moiety of keratins and can be substantially altered by exposure to certain chemical environments.[47,49] For example, during wool product processing some of these disulfide bonds undergoes oxidative degradation to generate cysteic acid residues.[49] In addition, wool keratin contains around 20 mol % to 25 mol % of aspartic and glutamic acid residues, which contain –COOH side group. These abundant –COOH and –SO$_3$H groups facilitated the binding of zeolites onto wool keratin via a silane coupling agent.

X-ray Diffraction Study

The x-ray diffraction pattern (Figure 5) of LTA nano-zeolite showed specific reflections at $2\theta = 7.1°$, $10.1°$, $12.4°$, $16°$, $21.5°$, $23.4°$, $27°$, $29.7°$, and $34.2°$ with high relative intensities that correspond to (100), (110), (111), (210), (221)/(300), (311), (321), (322)/(410), and (332) planes, respectively. In addition, many minor peaks with small intensities were observed. Similar XRD patterns have been reported for other type A zeolites.[29,52] The relative positions of the diffraction lines indicate that the zeolite contains a simple cubic lattice with a lattice constant of 12.3 Å. It revealed that it is a crystalline and highly porous mineral based on a cubo-octahedral structural unit, similar to that in the mineral sodalite.[25,52–54]

Wool fiber is a kind of polymer consisting of crystalline and amorphous phases. The two strong peaks at $2\theta = 9°$ and $2\theta = 15–31°$ were assigned to α-helix and β-sheet structure, respectively.[55,56] The peak intensity at $2\theta = 9°$ decreases on treatment with the dispersions of zeolite and zeolite/silane (Figure 5), indicating reduction of α-helix structure. Wool is an amphoteric material with isoelectric point at pH 3.4–4.8 and exists as a negatively charged in a high pH solution.[57,58] However, under alkaline conditions of zeolite and zeolite/silane dispersions, the intermolecular interactions including di-sulfide and hydrogen bonding are disrupted, resulting in breakdown of crystalline α-helical structure of wool keratin. Similar observations of crystallinity changes of wool have been reported when wool was exposed to steam explosion or high temperature.[56,59]

CONCLUSIONS

The surface treatment of wool fabrics with aqueous dispersions of nano-zeolite and silane (linker) led to varied physicochemical changes to the wool. Water contact angle data demonstrated the transformation of hydrophobic wool surfaces into hydrophilic surfaces. The average contact angle of 148° for untreated wool, which was unchanged over the measurement time of 1 h (due to lack of absorption), reduced to 50° in 5 min on treatment with a dispersion of 1% nano-zeolite and 0.2% silane. This treatment did not have any limiting effects on the mechanical performance of the treated wool. Though the treatment led to a slightly lowered tensile strength, the modulus of the fabric was lowered – a desirable effect that should improve the softness and wearing comfort of the final wool product. Scanning electron microscopic images revealed good coverage of the wool surface with nano-zeolite. These positive attributes of treated wool fabrics are attributed to the chemical attachment of zeolite nanoparticles onto wool keratins via the silane coupling agent as evidenced by infrared spectroscopic changes and x-ray diffraction patterns. In conclusion, this study revealed that zeolite-like minerals can be integrated well with wool fabrics to create smart textiles with advanced functionality.

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