



Modification of wool by air plasma and enzymes as a cleaner and environmentally friendly process



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ABSTRACT

A big disadvantage of the traditional anti-felting modification of wool is the problem of environmental pollution. Low temperature plasma (LTP) and enzyme process are the two important cleaner technologies which have potential use in the textile industry. In this paper, transglutaminase, a protein cross-linking enzyme, combined with air low temperature plasma and protease was used to modify wool fiber. The influences of the combination treatment on wool knitgoods performances were discussed. It was shown that air low temperature plasma pretreatment, instead of conventional chemical pretreatment, improved wettability significantly and made enzyme molecule more accessible to protein chains of the wool. Protease treatment following air plasma impacted a significant reduction in fabric shrinkage and the loss of strength was under control. Transglutaminase remediated wool damage, resulting in an increase in bursting strength. The machine washable wool knitgoods are obtained and the damage to the wool fiber can be controlled by using the combination treatment of air plasma, protease and transglutaminase. TGase was demonstrated to catalyze cross-linking reaction in wool protein by analyzing the thermal behavior of wool.

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1. Introduction

Maintenance of a cleaner environment recently became one of the most important global concerns. Growing industrialization significantly contributed to an increase of pollution, but insufficient efforts have been made to continue further industrial progress by adopting cleaner production technologies. The dimensional stability of textile goods is of great importance, influencing clothing acceptability to the consumer by defining the fit, comfort, and look after repeated laundering. The scalar structure of the wool fiber cuticle influences the felting shrinkage tendency of wool goods. Chlorine or its derivatives is often used in traditional anti-felting modification of wool. However, chlorine-Hercosett treatment shows the easy absorption of chlorine, resulting in the yellowing of wool, and damage to wool fiber (Yao et al., 2009). Hypochlorite chlorine is an oxidizing agent, and wool is very sensitive to it. If the chlorine process (i.e., concentration) is not effectively controlled, not only would oxidation and scission of the numerous disulfide bonds in the exocuticle of wool occur, but also damage to the wool

cortex. A big disadvantage of the process is the problem of environmental pollution, for example, the disposal of absorbable organic halogens compounds (Du et al., 2007). Chen et al. (2010) pointed out that chlorination occurred simultaneously with oxidation when wool was treated by chlorine-contain reagents. The adsorbable organic halogens compounds were produced by the chlorination of amino acid residues, especially tyrosine residue. With the increase of ecological restrictions imposed on the textile industry, the industries are required to find environmentally favorable alternatives in wool treatment processes.

Low temperature plasma (LTP) treatment, a water-free dry clean process, provides a new access to chlorine-free fiber surface modification and the felting shrinkage is reduced because of the decrease in directional frictional effect (Kan and Yuen, 2006). However, wool area shrinkage treated by air plasma alone exceeded the maximum approved value. Radetic et al. (2007) found that it is necessary to use suitable polymer for subsequent treatment, and a considerable decrease in fabric area shrinkage occurred in the treatment of polymers, particularly Synthappret BAP. Biotechnological application in textile process is gaining more and more interest because of environmental-friendly and mild condition (Jegannathan and Nieisen, 2013; Maryan and Montazer, 2013; Ali et al., 2014). Jegannathan and Nieisen (2013) discussed the

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application of enzyme in the cleaner industrial production. It was shown that after biologically desized, scoured and bleached, the cotton fabrics performance in wettability, stiffness, tensile strength, loss in fabric weight, whiteness index and dye absorbance is very comparable with or superior than those treated chemically in the conventional methods. Maryan and Montazer (2013) applied amylase, cellulase, laccase, and their combinations on denim garment to conduct one step bio-desizing and bio-washing process to produce old-look appearance garment. Ali et al. (2014) reported integration of desizing, bleaching and dyeing processes without discharging each spent bath using enzymes in batchwise method. Integrated method showed water and thermal energy saving in comparison to the conventional method. Previous research on the use of protease for decreasing the shrinkage tendency of wool have been reported (Jus et al., 2007; Yuan et al., 2008; Queiroga et al., 2012). Jus et al. (2007) introduced the use of proteases modified with the soluble polymer polyethylene glycol (PEG) in the bio-finishing process of wool fibers to target enzyme action to the outer parts of wool fibers. Yuan et al. (2008) applied ionic liquid pretreatment and proteases treatment to improve shrink-resistance of wool. Queiroga et al. (2012) found several bacterial proteases with a great potential for degradation of wool, feathers and other keratinous material. However, protease treatment after chemical pretreatment is difficult to be controlled within scales and always causes excessive damage to fiber. Therefore, wool bio-finishing with protease was not yet implemented at an industrial scale. Transglutaminase (EC 2.3.2.13, referred to as TGase) is an enzyme capable of catalyzing acyl transfer reactions by introducing covalent cross-links among proteins as well as peptides and various primary amines (Griffin et al., 2002). TGase widely exists in hosts of different organisms including mammals, plants, fishes, and microorganisms. Commercial microbial transglutaminases is typically used to stabilize matrices in food systems (Norziah et al., 2009; Hsieh and Pan, 2012). Norziah et al. (2009) added transglutaminase in the fish gel to modified the gel properties and the results shown enzyme transglutaminase has significant effect on gel strength when used in appropriate amount. Hsieh and Pan (2012) applied transglutaminase to induce polymerization of individual milk proteins during incubation and found that addition of TGase (0.25–2.0 units/mL) caused the milk proteins to polymerize after a 3-h incubation period. Recently, some applications of TGase combined with chemical and protease pretreatment on the wool textile were reported (Cortez et al., 2004; Du et al., 2007; Cardamone, 2007). Cortez et al. (2004) applied transglutaminase in the modification of wool after chemical and protease treatment, the results shown that transglutaminase led to increase in tensile strength and imparted a reduction in fabrics shrinkage to some extent. Du et al. (2007) compared the TGase treatment with traditional resin treatment. Although the tensile strength of wool fabrics treated by TGase was lower than those treated by resin treatment, the fabrics had similar anti-felting properties, and the chemical oxygen demand of wastewater was only half of the latter. Cardamone (2007) applied TGase to knitted fabrics after peroxycarboximidic acid oxidation and protease treatments. The results shown no effect on shrinkage control was observed, however, approximately 3–4% strength was regained relative to the value of either blank or control fabrics. Fourier transform infrared spectra, optical and fluorescence microscopy, confocal microscopy revealed keratin substrates in the solid state can be self-cross-linked by TGase. Up to now, there is no report to apply the combination of air plasma, protease and TGase to produce the machine washable knitted wool fabrics with low strength damage.

In this study, knitted wool fabrics were treated with air plasma at atmospheric pressure (instead of conventional chemical pretreatment), protease, TGase and a combination of these processes

in an attempt to observe some characteristics of wool fiber and improve shrinkage resistance performance while decrease fiber damage. TGase was demonstrated to catalyze cross-linking reaction in wool protein by analyzing the thermal behavior of wool. All these work were expected to be a helpful guide for application of the plasma/enzymatic cleaner production technology in the textile finishing.

2. Experimental

2.1. Materials

Pure (100%) wool knitted fabrics supplied by Nantong Honglv Group were scoured. The enzymes used in this study were Savinase 16L (one kind of protease) and TGase acquired from Novozymes and Ajinomoto Co., Inc.

2.2. Chemical pretreatment

For hydrogen peroxide pretreatment, wool knitted fabrics were treated with 45 mL/L H₂O₂ (30%) at pH8.0 and 50 °C for 1 h with a liquor ratio of 20:1. For sodium hypochlorite pretreatment, wool knitted fabrics were treated with 1% NaClO pH 3.0–4.0 and 30 °C for 1 h with a liquor ratio of 20:1. For chlorine removal, samples were treated with Na₂SO₃ (3% o.w.f.) at 30 °C for 20 min with a liquor ratio of 20:1, and then at pH 8–9 and 45 °C for 8 min.

2.3. Low temperature plasma treatment

In this study, a dielectric barrier discharge (DBD) atmospheric plasma device was used. The samples were placed between the electrodes with (400VDC). Air was used as process gas under a constant power of 1000 W. Treatment time was 2 min.

2.4. Enzymatic treatment

For protease treatment, wool knitted fabrics were incubated with Savinase 16L (4% o.w.f.) at pH 8.5 and 50 °C for 40 min with a liquor ratio of 20:1.

For transglutaminase treatment, samples of wool knitted fabric were incubated with transglutaminase (5% o.w.f.) at pH 7 for 60 min at 50 °C with a liquor ratio of 20:1.

The samples treated with protease or transglutaminase were incubated in hot water at 80 °C for 10 min to deactivate the enzymes, then were rinsed and dried at 60 °C for the performance test.

2.5. Area shrinkage after washing

Samples were washed once according to program 7A of GB8629 for the relaxation shrinkage test, then dried at 60 °C and kept at room temperature (RT) for 4 h. Then samples were washed three times according to program 5A of GB8629 for the felting shrinkage test, then taken out and dried at 60 °C and kept at RT for 4 h. The measurement and the calculation of area shrinkage were made according to Eq. (1):

$$\text{Area shrinkage (\%)} = L_S + W_S - (L_S \times W_S)/100 \quad (1)$$

L_S is the percent length shrinkage and W_S is the percent width shrinkage.

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