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An ecofriendly phosphorylation of wool using Maillard reaction for improving cationic dye absorption

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A B S T R A C T

Phosphorylated wool with enhanced ability to absorb cationic dyes is helpful to dye wool fabrics using cationic dyes with good dyeing properties, which is more economic and ecofriendly compared to the traditional dyeing process of acid dyes with poor wet fastness. Phosphorylation can be performed by applying chemical reagents which tend to cause a problem of environmental pollution and the fibers can be damaged seriously under harsh reaction conditions, or using enzymes which are currently somewhat discouraged due to significant cost of the enzymes and their decreased stability at the reaction conditions. In this study, non-toxic glucose 6-phosphate was applied to phosphorylated modification of wool via Maillard reaction under a mild condition to enhance the dyeing properties of wool fabric for cationic dyes. The reaction between glucose 6-phosphate and wool keratin was demonstrated from the results of sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE), particle diameter, Fourier transform infrared spectra (FTIR) and Energy Dispersive X-ray test (EDS). It was found that phosphorylation modification scarcely changed the mechanical properties of the wool fabric. Maillard browning on the wool could be avoided by accurately controlling the reaction time. Dyeing properties of phosphorylated wool fabric with cationic dyes were markedly enhanced. The exhaustion of phosphorylated wool fabric for two cationic dyes: Cationic Brilliant Red 5 GN and Brilliant Yellow B 6 GL increased from 38.6% to 18.9%–84.5% and 67% respectively by comparing with that of the wool fabric without modification and better color strength (K/S) and very good wash fastness properties obtained. The results indicated that phosphorylated modification of wool with glucose 6-phosphate could be a potential, safe and cleaner approach to develop a more efficient and economic dyeing process for wool fibers with cationic dyes.

1. Introduction

The globalization of textile industry has accompanied by great changes in textile coloration and in textile functionalization. Global wool production is about 2 million tons per year. Wool comprises about 3% of the global textile market, but its value is higher owing to its out-standing properties, dyeing and other modifications of the material. Wool fibers are always dyed with acid dyes which usually are sodium salts of sulphonic acids and are therefore anionic in aqueous solution, in an acidic dyebath. The acidic pH of dyeing allows the dyes to interact with wool via ionic bonds because of the presence of amino groups in the fibers (Broadbent, 2001). However, acid dyes generally exhibit a poor wet fastness on wool fibers due to the reduction of the ionic interaction between the dyes and the fibers during daily textile washing. In order to obtain a high color strength (K/S) of wool fibers, much more acid dyes must be added and more dyes accordingly are discharged into the effluent during the dyeing process, which will lead to a serious waste of dyes and water pollution problem. Acrylic fiber, as a wool-like fabric, is widely used to blend with wool due to its excellent chemical and physical properties. Cationic dyes, which usually have brilliant colors and high tinctorial strength, are easily adsorbed onto acrylic fibers containing approximately 15% of vinyl co-monomers with carboxylate or sulphonate groups, via strong coulombic forces between anionic groups of the fiber and the cationic dye molecules. Acrylic fibers dyed with cationic dyes exhibit fairly good fastness to washing (Broadbent, 2001). Cationic dyes lack the capability to absorb for wool. The wool/acrylic blend fabrics are usually traditionally dyed separately with a two-bath,

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two-step process because of the different properties of each component fiber: acid dyes for wool and cationic dyes for acrylic fibers, which is time-consuming and energy-wasting. The modification of wool by introducing anionic groups could be a way to confer the ability to absorb cationic dyes on wool, which might be profitable to develop an economic and ecofriendly dyeing process with cationic dyes for wool with good dyeing properties and also potentially provide an approach to develop a one-bath one-step dyeing process for wool/acrylic blends with cationic dyes.

Many efforts have been made to endow wool or other materials with new functionalizations through anionic modification. Wool fabrics were rendered flame retardant upon treatment with sulfamic acid in the presence of urea at 140–160 °C (Lewin, 1997). A natural compound, caffeic acid, to provide an available carboxylic group, was grafted on the wool, which led to an increasing of exhaustion and fixation of cationic dye to wool (Gaffar et al., 2012). Acrylate and acrylamide compounds containing a sulfonate group were applied to grafting on reduced wool with tris(2-carboxyethyl) phosphine hydrochloride through thiol–ene click chemistry and the modified wool fabrics exhibited significantly improved anti-static and liquid moisture management properties (Yu et al., 2014). An adsorbent prepared from crosslinked β-cyclodextrin containing carboxylic groups exhibited high adsorption capacity for cationic dyes (Crini, 2008). Phosphorylation can introduce a big negatively charged (anionic) phosphate group in the side chain of proteins or polysaccharides to alter their structural conformations and modify their functions. Accordingly the phosphate groups with more negative charges than other anionic groups, such as sulfonate group and carboxylic group, in wool will be likely to make much more cationic dye molecules interact with modified wool fibers through coulombic forces. Phosphorylation can be performed using chemical or enzymatic modification process. It has been reported that the phosphorylation of a human hair keratin was performed using protein kinase to enhance fast adsorption of cationic moieties (Volkov and Cavaco-Paulo, 2016a,b). However, the broad utilization of enzymatic phosphorylation in industrial applications is currently somewhat discouraged due to significant cost of the enzyme and its decreased stability at the reaction conditions compared to purely chemical reagents (Volkov and Cavaco-Paulo, 2016a,b). The synthesis of phosphorylated products was performed by different systems of reactions: phosphoric acid (H_3PO_4), phosphorus pentoxide (P_2O_5), phosphorus trichloride (PCl_3) or dimethylphosphate. Water-soluble phosphorylated cellulose samples were synthesized by the reaction of microcrystalline cellulose with phosphorous acid (H_3PO_3) in molten urea at 150 °C (Suflet et al., 2006). Phosphorylation of chitosan was carried out by using the H_3PO_4/Et_3PO_4/P_2O_5/butanol reaction system to promote cell attachment and proliferation on chitosan membranes (Amaral et al., 2005). However, the application of these chemical reagents tends to cause a problem of environmental pollution and the fibers can be damaged seriously under harsh reaction conditions, which is actually not economically feasible for the fiber modification process.

New methods need to be brought forward to meet the demand of wool fiber modification for dyeing with an economic and green process. Maillard reaction is a chemical reaction between amino acids and reducing sugars that gives various foods yellowish or brownish coloration on an industrial scale. It is also useful for the protein modification to improve some food protein functionalities such as water solubility and heat stability (Kato et al., 1988, 1989). Some new applications of the Maillard reaction in textile industries have previously been investigated (Ohe et al., 2016). An increase in the pick-up of acid dyes was recorded after wool was pretreated with an aqueous glucose solution (Trezl et al., 1995). Textile fibers having amino groups, such as wool, silk, and nylon fibers, were colored by chemical reactions with reducing sugars, such as D-glucose and D-xylose, which indicated the application of the Maillard reaction could provide an option as an alternative to conventional dyeing methods (Ohe and Yoshimura, 2014; Ohe et al., 2016). Glucose 6-phosphate is a glucose sugar phosphorylated on carbon 6 with a hemiacetal bond of carbonyl group. It is a main metabolic product of sugars, which is non-toxic and does not cause environmental pollution. Hence, glucose 6-phosphate with both carbonyl and phosphoryl groups might be used as a safe protein modifier to introduce phosphoryl groups into proteins by the Maillard reaction as a mild and cleaner modification method.

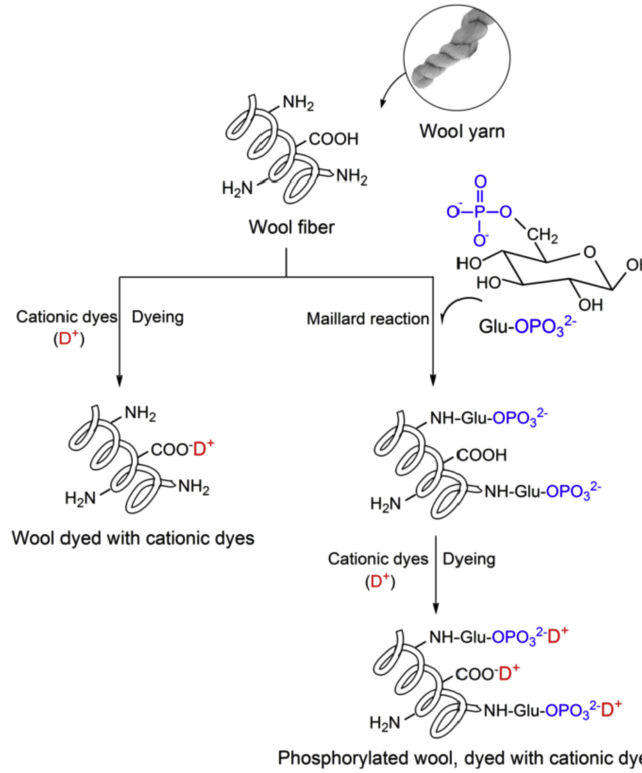

Fig. 1. The scheme of wool phosphorylation via Maillard reaction improving the dyeing properties with cationic dyes.

The objective of this report was to investigate an ecofriendly phosphorylated modification method of wool by using non-toxic glucose 6-phosphate under mild conditions, aiming at enhancing the dyeability of the modified wool with cationic dyes. This work was expected to provide a safe and cleaner production technology for developing an economic and ecofriendly dyeing process for wool and also potentially provide an approach to develop a one-bath one-step dyeing process for wool/acrylic blends with cationic dyes in the textile industry. The general outlook on the proposed idea for wool modification is illustrated in Fig. 1.

2. Materials and methods

2.1. Materials

The substrate used was a worsted wool fabric (33 tex × 33 tex, 325 g/m^2), a woven fabric made from worsted yarns and the worsted yarns were from wool by spinning. It was supplied by Wuxi Xiexin Group (China). All the wool fabrics were washed at 40 °C for 1 h with a solution containing 1 g/L non-ionic detergent Ninol-Coconut fatty acid monoethanolamide CMEA 6501 which is an alkanolamide of nonionic surfactant with the properties of decontamination, wetting, anti-hard water and biodegradability