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Click chemistry modification of natural keratin fibers for sustained shrink-resist performance

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ABSTRACT

This paper introduces a novel chemical treatment for achieving sustained shrink-resist performance on natural keratin fibers. The new treatment involves the controlled reduction of keratin in the cuticle region of the fiber, and the application of a water soluble diacrylate, namely glycerol 1,3-diglycerolate diacrylate (GDA), on the reduced keratin substrate. The acrylate groups of the GDA react with cysteine residues in the reduced keratin through thiol-ene click reactions at room temperature, leading to GDA grafting and the formation of GDA crosslinks in the keratin structure. The modified substrates were characterized by infrared spectroscopy and scanning electron microscopy, and assessed for its shrink-resistance and wet burst strength. This chemical modification has shown to alter the fiber surface morphology and hydrophilicity, resulting in substantially improved shrink-resistance with good fiber strength retention. Possible shrink-resistance mechanisms were also discussed.

1. Introduction

The biggest issue in the commercial application of natural keratin fibers is their extremely poor machine washability. Shrinking and felting are common phenomena observed during aqueous washing and processing. This is mainly attributed to the hydrophobic cuticle scales of the fiber and the associated differential friction effect. Wool, as the most widely used keratin fiber, encounters prominent shrinking/felting problems, therefore, shrink-resist treatments are one of the most important finishes in the wool industry.

At present, the most widely used commercial processes include chlorination and the combined chlorine/Hercosett process, which consists of a chlorination and a subsequent reduction step, followed by polymer deposition [1]. The anti-felting mechanisms involve: (1) an increased surface hydrophilicity and softening of cuticle scales through the oxidation of disulfide bonds to cysteic acid residues; and (2) further reduced fiber contacts and differential friction through covalent bonding of a super hydrophilic, cationic polyamide–epichlorohydrin polymer on fiber surfaces. These chlorine based processes are effective in producing shrink-resist and machine washable wool, but suffer from chlorine induced yellowing of wool, fiber strength loss and harmful effluents containing AOX [2,3].

Many chlorine-free processes have been studied in recent years including UV and plasma irradiation [4], enzyme treatment [5], oxidative treatment (e.g. **peroxymonosulfate**), sol–gel method [6], polymer coating, nanoparticle deposition, and a combination of these treatment processes. Although these treatments are able to provide a certain level of shrink-resistance to wool substrates, they all face some critical issues. For example, UV treatment causes significant fiber yellowing [7]. The use of plasma treatments often result in a harsh handle of the wool fabric and the treatment effect deteriorates over time [8]. In addition, the large capital cost of plasma equipment limits its wide industrial application. Enzyme treatment has been regarded as an environmentally friendly shrink-resist process, but the treatment effect is generally not satisfactory due to difficulties in controlling the interactions between enzymes and wool fibers [9,10]. To date, there is no viable commercial alternative to the chlorine based processes. In light of the above, there is a pressing need to develop a facile and reliable chlorine-free shrink-resist finish for natural keratin fibers. This is important for meeting the demand of our modern lifestyles and for a sustainable future for keratin fibers.

In this study, we employed a new and greener chemical treatment based on selective reduction of cystine disulphide bonds

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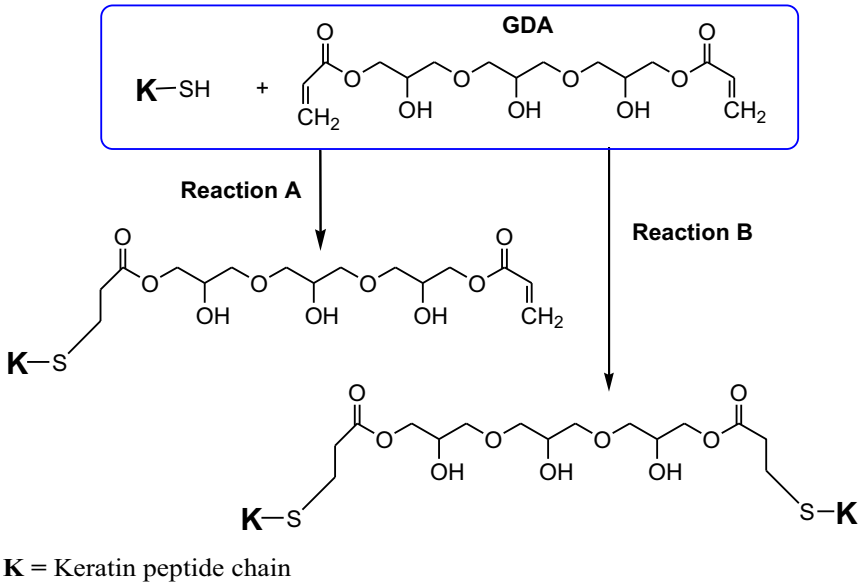

Scheme 1. Thiol-ene reactions between GDA and cysteine residues in a reduced keratin fiber.

and subsequent application of a water soluble diacrylate, namely glycerol 1,3-diglycerolate diacrylate (GDA), to alter the surface properties of keratin fibers, achieving a shrink resistant effect under very mild and facile conditions.

GDA is a highly reactive diacrylate monomer with multiple hydroxyl and ether groups. Introduction of GDA into the cuticle structure of keratin would be expected to change the fiber surface from hydrophobic to hydrophilic, and increase the aqueous swelling potential of the surface proteins, leading to a reduced felting shrinkage. In addition, GDA, with two acrylate groups and multiple polar functional groups, may be able to form crosslinks and extensive hydrogen bonding networks in keratin fibers, which would be expected to improve fiber strength retention and reduce fiber movement and friction for potentially further reduced felting shrinkage. The possible chemical reactions involved are shown in Scheme 1, where cysteine thiols present in keratin fibers react with the acrylate groups of GDA. Through this thiol-ene click reaction, the GDA is grafted onto the keratin structure. Crosslinks can be formed when both acrylate groups of the GDA react with keratin cysteine residues. With the introduction of GDA into the keratin structure, more hydrogen bonds may be readily formed either among the functional groups of the GDA (the hydroxyl ether and carbonyl groups) or between the functional groups of GDA and the carbonyl or amide groups of the peptide chains in a keratin fiber, as illustrated in Scheme 2a. These functional groups are also able to form hydrogen bonds with water (Scheme 2b).

To maximize the GDA grafting and/or crosslinking density and thus the treatment effect, a pre-treatment with tris(2-carboxyethyl)phosphine hydrochloride (TCEP) was employed for generating more cysteine thiols in the keratin fiber, as the cysteine residues inherently present in keratin fibers are very limited. TCEP is known as an effective reducing agent able to selectively reduce cystine disulfide bonds to cysteine residues, although peptide chain cleavage may also occur as a side reaction under certain conditions [11]. Therefore, care should be taken to prevent extensive fiber degradation with TCEP treatment. In our previous study, we have reported a controlled TCEP pre-treatment process for keratin fibers, and its applications for introducing sulfonate and quaternary amine moieties into the keratin structure [12,13]. This pre-treatment process was adopted in this investigation, prior to the application of GDA.

As cystine is mainly located in the cuticle of keratin fibers [14], the TCEP induced cystine reduction and the subsequent grafting and crosslinking reactions are expected to occur mainly in the cuticle region of the fiber. These changes would be expected to have a direct impact on the shrinking behavior of the substrate.

The TCEP–GDA treated substrates were characterized by scanning electron microscope (SEM) and infrared spectroscopy. Their shrink-resist performance and mechanical properties were also extensively evaluated in this study.

2. Experimental

2.1. Materials

The specifications of the two Merino wool plain weave fabrics used in this investigation are given in Table 1. Tris(2-carbonxyethyl)phosphine hydrochloride was obtained from Soltec Ventures (Beverly, USA). Glycerol 1,3-diglycerolate diacrylate (technical grade) was obtained from Sigma–Aldrich. Other chemicals were analytical grade reagents, and used without further purification.

2.2. Treatments

Wool fabric samples (20 cm × 20 cm each) were pre-treated with TCEP according to the method reported previously [12]. Briefly, pre-treatments were performed at room temperature for a specified period of time (2–24 h) in a water/ethanol (1:1) solution containing 20 mmol/L TCEP at pH 5.0. In the subsequent process, the TCEP pre-treated wool fabrics were immersed in a water/ethanol (1:1) solution containing GDA (1%, 5% and 10%) and a catalytic amount of TCEP. The pH of the treatment solution was adjusted to 7.5 and the liquor ratio was 50:1. The treatment was carried out at room temperature for 18 h under gentle agitation. After the treatment, the samples were thoroughly rinsed with deionized water and dried.

2.3. Characterization

2.3.1. Spectroscopic analysis

Infrared attenuated total reflectance (ATR) spectra were collected from the fabrics using a Perkin Elmer (Beaconsfield, UK)