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Study on novel eco-friendly anti-creasing agents for natural silk fabric

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Abstract

Three novel eco-friendly anti-creasing agents have been designed and synthesized. The natural silk fabrics treated with them exhibit higher wrinkle recovery degree, strength retention rate and whiteness than those finished with 1,2,3,4-butane tetracarboxylic acid (BTCA). The washing durability of the fabrics treated with the synthesized compounds and BTCA is similar. The chlorine atom, the carboxyl and the *s*-triazine ring in the synthesized structures and the surface roughness of the silk fabric are all contributive to the improvement of the crease resistance of silk.

Keywords: Cyanuric chloride; 1,3,5-Triazine; Silk; Anti-crease; 1,2,3,4-Butane tetracarboxylic acid

Silk is one of the most favored high quality textile materials because of its superior wear comfort and elegant appearance. Unfortunately, silk fabric wrinkles easily during home laundering or when wet, which causes considerable inconvenience in its use [1,2]. The poor wet resiliency of silk is caused by the structure of the fibroin which is low crystallinity and lack of intermolecular chemical crosslinkages. When suffering external force or water process, irreversible damage of hydrogen bonds and salt linkages between the protein polymers, and unretrievable deformation of the space in the amorphous region of the fibroin occur, and make silk fabric wrinkle [1,3]. Chemical crosslinking with anti-creasing agent is the most popular method for improving the wrinkle resistance of silk [4,5]. Urea formaldehyde resins, led by dimethylol dihydroxyethylene urea (DMDHEU), were adopted for early silk anti-crease finishing with prominent crease-resistance effect [6,7]. However, the finished fabric released formaldehyde in the process of depositing or wearing, which is greatly harmful to people's health [8,9]. Many nonformaldehyde alternatives of traditional *N*-methylol reagents were developed [10–13]. Among them 1,2,3,4-butane tetracarboxylic acid (BTCA) was considered as the most promising one. The silk fabric finished with BTCA obtained satisfactory resilience, whiteness and washability [2,14,15]. Nevertheless, silk anti-crease finishing with BTCA was troubled with the sizable strength loss and high cost. Citric acid is cheap, but the finished fabric is yellowing easily [1,16]. Other formaldehyde-free anti-creasing agents for silk such as epoxides [17–19], siloxanes [20,21], glyoxal [22–24],

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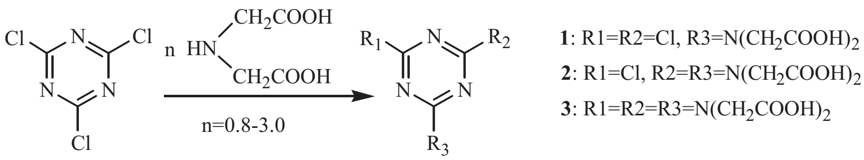

Scheme 1. Synthesis of compounds **1**, **2** and **3**.

glutaraldehyde [25,26] and natural or synthetic polymers [27–29] have been reported. They exhibited some crease-resistant effect, however, together with various problems. Therefore, research on more satisfactory eco-friendly anti-creasing agents for silk fabric is high desirable.

Herein we designed and synthesized a series of novel eco-friendly anti-creasing agents for silk fabric. They can be facilely prepared from easy available starting materials under mild conditions, and they will be formaldehyde-free in the process of depositing or wearing.

The novel anti-creasing agents **1**, **2** and **3** were prepared by nucleophilic substitution reaction between cyanuric chloride (CNC) and iminodiacetic acid (IDA) according to Scheme 1. Taking advantage of the temperature-controllable chemo-selectivity of three chlorine atoms in CNC, the first chlorine atoms in 0.8 equiv. CNC were substituted with one equivalent of IDA at 0–5 °C in water to give compound **1**. Compound **2** was obtained through the first and the second chlorine atoms in one equivalent CNC substituted by two equivalent of IDA in the mixture of water and chloroform at 0–5 °C and 45 °C successively. Compound **3** was synthesized according to the literature, in which it was used as a ligand [30]. Every compound was prepared in one pot reaction under very mild conditions. All reactions could be carried out in water, but the best solvent for the synthesis of **2** was the mixture of water and chloroform (volume ratio 1:1). Sodium hydroxide was employed to bind the produced chlorine hydride (HCl), but the carboxyl in IDA was also neutralized unavoidably. Thus, the acidification step after reaction is indispensable in order to recover the carboxyl in IDA from its sodium salt. The processing method for achieving **1**, **2** and **3** after reaction was very different. Crude **1** or **3** could be precipitated in a certain amount of water. Compound **1** could be purified by extraction with ether, and pure **3** could be gotten by wash with ethanol and water sequently. Compound **2** could not be precipitated in water, but it could be achieved by extraction with ethyl acetate from its aqueous solution. The structures of **1**, **2** and **3** were characterized by ^{1}H NMR, ^{13}C NMR, LC–MS and Elementary analysis. It is worth mentioning that **1**, **2** and **3** can be easily dissolved in the aqueous finishing bath.

Compounds **1**, **2** and **3** were employed to finish natural silk fabric for anti-crease purpose. Dry and wet slow resilience wrinkle recovery degree (WRD), tensile strength, whiteness and washing durability of the finished fabric were used to evaluate the finishing effectiveness (Table 1). From Table 1, it can be seen that the silk fabrics finished with **1**, **2** and **3** (No. 1–9) show higher dry and wet wrinkle recovery degree (WRD) than the unfinished silk fabric (No. 11). The dry WRD of the fabric finished with **1**, **2** and **3** is similar to that of the fabric treated with BTCA (No. 10), while the wet WRD of the fabric finished with **1**, **2** and **3** is obviously higher than that of the fabric treated with BTCA except for the wet WRD of the fabric finished with **1** at 100 °C. The reason for the smaller wet WRD of the fabric finished with **1** at 100 °C may be interpreted that only chlorine atoms in **1** react with the fabric and result in less crosslinkages at 100 °C, which can be supported by infrared spectroscopy hereinafter. The fabrics finished with **1**, **2** and **3** at 100 °C and 130 °C have exhibited good dry and wet resilience although raising curing temperature is generally beneficial to improving the wet WRD. The strength retention rates of the fabrics finished with **1**, **2** and **3** are larger than that of the fabric treated with BTCA. Most of them exceed 90% and the highest one reaches to 98.3%. Some of the fabrics finished with **1**, **2** and **3** have whiteness similar to the BTCA-treated fabric, others show better whiteness than the latter, even keep the same whiteness as the blank. Moreover, the fabrics treated with **1**, **2** and **3** show similar washing durability to those finished with BTCA after 10 cycles of home laundering. The excellent performance of **1**, **2** and **3** can be owed to the crosslinking from the chlorine atom and the carboxyl [2,14,15], and supporting function of the *s*-triazine ring in their structures.

The crosslinking reaction between the chlorine atoms or the carboxyl in the synthesized structure and the silk fabric can be verified by infrared spectroscopy (Fig. 1). When the fabric was finished with **1** at 100 °C, the peak around 3300 cm^{-1} in the IR spectrum (No. 1 in Fig. 1) almost overlapped with that of the untreated fabric (No. 11 in Fig. 1), and the peak around 1670 cm^{-1} only changed slightly. These results suggest that the carboxyl in **1** keep stable at 100 °C, since the crosslinking reaction between the carboxyl in BTCA and the silk is primarily indicated by the great decrease of the peaks around 3300 and 1670 cm^{-1} in IR spectrum (No. 10 in Fig. 1). However, the finished fabric showed higher dry and wet WRD than the unfinished silk fabric. It is reasonable to deduce that the fabric has been crosslinked by **1**. The most possible crosslinkage should be formed by the reaction of the chlorine atoms in **1** with the hydroxyl or amino in silk. This conjecture can be