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Structure and Properties of Modified Flax Yarn with Collagen

Abstract
The structure and property changes of collagen modified flax yarn were investigated in order to improve the usability of flax yarn. First flax yarn was treated with sodium hydroxide solution and next with chloroacetic acid to get carboxymethyl flax yarn. Then the carboxymethyl flax yarn was grafted with gelatin protein solution to obtain modified flax yarn. Reactive blue dye was used for the dyeing test of the modified flax yarn. Its structure was characterized and analysed by FT-IR, X-ray diffraction and SEM. Meanwhile breaking strength and elongation at break of the modified flax yarn and the exhaustion rate and fixation rate of reactive blue dye was tested, respectively. The results show that the carboxymethyl flax yarn and gelatin protein are combined with a chemical bond. The different mass concentration of the gelatin solution has some influence on the grafting rate of flax yarn grafted with collagen. After modification of the flax yarn, the breaking strength shows a little loss, the elongation at break increases to a certain degree, and the exhaustion and fixation rate of the reactive dye increase significantly.

Key words: *gelatin, flax yarn, grafting, breaking strength, dyeing properties.*

Introduction

In recent years, a series of research works on linen fibre modification have been conducted by researchers at home and abroad. They mainly included physical and biological technology, chemical modification, and so forth. Researches show that cellulose reactivity can be greatly improved after being activated by an ultrasonic wave, microwave, low temperature plasma technology, among others [1, 2]. At present, enzyme preparation is mainly used to improve the softness and dyeing performance of hemp fibre [3]. Ledakowicz et al. used enzymes to improve the dyeing performance of linen fibres [4]. The oxidoreductases modification of flax fibre was discussed by Ren et al [5]. The alkali and enzyme modification of flax fibre and its structure and properties were studied by Cao and others [6]. The chemical reactions of cellulose can be divided into two categories: the degradation reactions of the cellulose macromolecule chain and chemical reactions associated with the hydroxyl group. Cellulose modifications mainly rely on reactions associated with the cellulose hydroxyl group. The grafting results of several different forms of cellulose including filter paper, microcrystalline cellulose, Lyocell fibre and dialysis tubing were compared by Lindqvist and others [7] and it was found that the surface properties of different kinds of cellulose were different, and the graft polymerisation reaction was affected by it. The experimental results showed that the more polymers can be grafted onto natural rather than regenerated cellulose, then the cellulose surface with "active" grafting with PMA (polymethyl acrylate) can be placed even for a year. The ATRP (atom transfer radical polymerization) method has been successfully used for grafting on some common natural cellulose, such as jute fibres [8], ramie fibre [9], etc, and these studies are very helpful to expand the use of the cellulose resource in practical application. At the same time, some researchers have tried to graft more monomers onto cellulose, with the use of methyl acrylate, methyl methacrylate, methacrylamide, styrene, and dimethylaminoethyl methacrylate (DMAEMA) having been reported [10]. HBP (hyperbranched polymer) -NH_2 grafted oxidised linen fibre (HGLF:hyperbranched graft linen fibre) was prepared by the oxidation of linen fibre with sodium periodate and subsequently grafted with HBP-NH_2 by Zhao Bin and others [11]. The antimicrobial properties and anti-UV radiation of HGLF was also studied. The results indicated that HGLF showed a 90.74% in bacterial reduction of *S. aureus* and 93.12% in bacterial reduction of E. coli, respectively. The UPF value was increased from 3.44 to 13.19. HGLF, showing good antibacterial and anti-UV radiation performance.

Cellulose fibres are treated with sodium hydroxide lye to produce alkaline cellulose. The preparation of alkaline cellulose [12 - 14] and carboxymethyl cellulose applications in materials, food and medicine have been further researched both at home and abroad [15 - 17]. Collagen is widely used in composite fibre materials, with advantages of good comfort, good dyeing properties, strong wrinkle resistance, good affinity in contact with human skin, and others [18 - 20]. At present, not much has been reported about the research of flax fibre modified with protein [21 - 23], mostly about grafting modified flax fibre, treated by oxidation beforehand, with collagen or sericin protein. The combination of protein and flax fibre is not good, therefore the effect of linen fibre modification is not ideal.

The main purpose of this study was to improve the dyeing properties of fibre by guaranteeing flax yarn strength requirements by grafting collagen onto flax yarn, thus the wearability of flax fibre can be more satisfactory. In this paper, flax yarn was treated with sodium hydroxide lye, and on that basis alkaline cellulose fibre was carboxymethylated with chloroacetic acid to introduce carboxylic acid groups to improve the grafting rate of glutin, thus improving the effect of

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the modification of flax fibre grafted with collagen.

Experiment

The experimental material and reagents

Flax yarn with a linear density of 21.1 tex, twist of 6.7 T/cm, breaking force of 705 cN, and elongation of 1.36% after scouring and bleaching; gelatin (biochemical reagent) reactive blue KN-R dye; soap flakes, sodium hydroxide, chloroacetic acid, sodium sulfate and sodium carbonate. All reagents above were analytically pure.

Modification processing of flax yarn (spun yarn)

Quantitative flax yarn (spun yarn) was immersed in sodium hydroxide solution with amass concentration of 6% and bath ratio of 1:20 (mass ratio, similarly hereinafter), oscillated and kept out of the sun under 50 °C for 1 h, washed, fast dried and weighed under 50 °C, to obtain alkaline flax yarn. The alkaline flax yarn was soaked in chloroacetic acid solution with a mass concentration of 2% and bath ratio of 1:20 under 50 °C for 2 h, then washed adequately with deionised water and dried naturally to make carboxymethylated flax yarn. The carboxymethylated linen yarn was placed in gelatin protein solution at a bath ratio of 1:20 and mass concentration of 40 g/dm^3 under 50 °C for 2 h, baked in a drying oven under 80 °C, washed by soaking for 24 h and repeated for three times, then quickly dried and weighed at 50 °C to obtain flax yarn grafted with collagen.

Dyeing test

The dyeing process formula and process conditions are as follows [24].

- reactive blue KN-R/owf - 2
- sodium sulfate - 45 g·dm^{-3}
- sodium carbonate - 20 g·dm^{-3}
- dyeing temperature - 40 °C
- dyeing time - 30 min
- fixation temperature - 65 °C
- fixation time - 60 min
- bath ratio - 1:20

Soap boiling test

After finishing dyeing, the yarn was washed, soap boiled (soap flakes of 2 g/dm^3, sodium carbonate of 2 g/dm^3, 95 °C, 10 min, bath ratio 1:30) and dried.

Test methods

Determination of collagen graft rate

This was determinated by a type FA1004 electronic analytical balance (Shanghai Shangping Instruments Company in China). To attain the quantity of flax yarn and the mass of modified flax yarn, respectively, the grafting rate was calculated by type (1):

$$grafting\ rate\ (\%) = \frac{G_2 - G_1}{G_1} \times 100 \quad (1)$$

where G1 is the unmodified flax yarn quality and G2 the modified flax yarn quality in g.

Determination of breaking force and elongation at break

This was measured on an electronic yarn strength instrument type YG061 YG061 (Laizhou Electronic Instrument Company Limited in China). The work length was 250 mm, the initial tension 0.05 cN/dtex and the drawing speed was 250 mm/min.

Determination of exhaustion rate E and fixation rate F

This was determined by a uv-vis spectrophotometer 754PC (Shanghai Spectrum Instruments Company Limited in China). The absorbance of the standard dye solution and dyeing residue liquid was determined, respectively, in reactive blue dye of the maximum absorption wavelength, λ_{max}, of 590 nm, and the exhaustion rate E and fixation rate F were calculated by types (2), (3), (4) & (5):

$$E = 100\% - X \quad (2)$$

$$X = \frac{B}{A \times n} \times 100\% \quad (3)$$

where X is the amount of dyes in the dyeing residual liquid in %, A the absorbance of standard dye solution, B the absorbance of dyeing residue liquid, and n is the test concentration multiple between the standard dyeing liquid and dyeing residual liquid;

$$F = E - Y \quad (4)$$

$$Y = \frac{D}{C \times n} \times 100\% \quad (5)$$

where E is the dye absorption rate in %, Y the amount of no fixation dye in soap boiling washing in %, C the absorbance of standard soap liquid, D the absorbance of soap boiling residual liquid, and n is the test concentration multiple between the standard soap and soap boiling residual liquid.

Infrared spectroscopy

This was determined using the method of KBr tabletting by means of a Fourier transform infrared spectrometer (PerkinElmer in the United States). Analyte should be reduced to powder before the determination, with a scanning range of 4000 ~ 600 cm^{-1}.

X-ray diffraction analysis

Tests were carried out using a D8 X- ray diffractometer (BRUKER AXS in Germany). The samples must be made into powder before the test, with a diffraction angle of 10 to 30°.

Scanning Electron Microscopy (SEM) analysis

The microstructure was analysed by a S-4300 scanning electron microscope (Japan's Hitachi LTD). The sample needed to be sprayed with gold before testing.

Results and discussion

Infrared spectrum analysis

Figure 1 shows the infrared spectra of unmodified, chloroacetic acid treated and gelatin protein grafted flax yarn.

Figure 1 (see page 32) highlights that a strong absorption peak emerges at 1725.5 cm^{-1} after flax yarn is given basification and carboxymethylated treatment, which is a C=O stretching vibration absorption peak, and at the same time, a relatively strong broad peak emerges at 1044.9 cm^{-1}, which is a two-molecule associated body O-H nonplanar rocking vibration absorption peak, also characteristic peak of the carboxylic acid structure. After chloroacetic acid treated linen yarn is grafted with gelatin protein, a strong absorption peak emerges at 1528.4 cm^{-1}, which is a N-H bending vibration absorption peak, and the characteristic peak at 1725.5 cm^{-1} disappears. All of these shows that gelatin protein was grafted onto the flax yarn successfully [25].

XRD analysis

Figure 2 (see page 32) shows XRD curves of carboxymethylated flax yarn treated by chloroacetic acid and modified flax yarn grafted with glutin.

As shown in ***Figure 2***, the shapes of the curves of a and b are similar, with both of the diffraction angles of the maximum diffraction peaks being 22.8°. Compared with curve a, although the intensity of

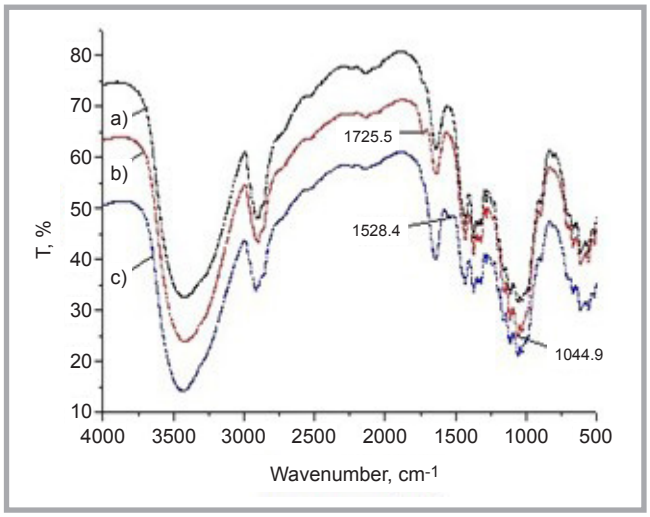


Figure 1. FT-IR of unmodified and modified flax yarn: a) unmodified flax yarn; b) chloroacetic acid treated flax yarn; c) collagen-flax yarn.

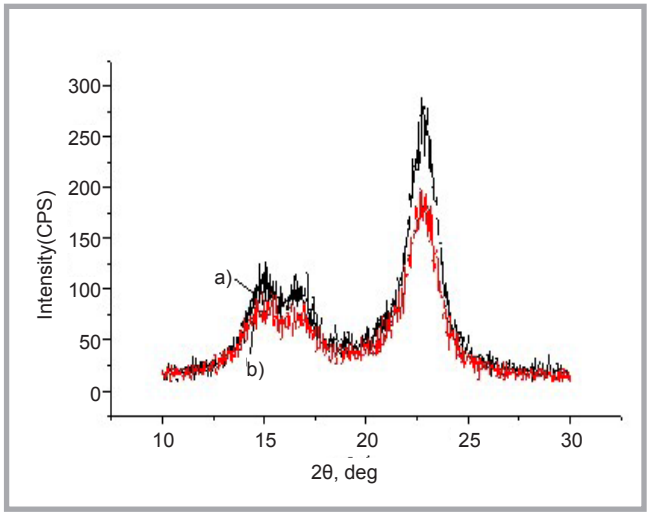


Figure 2. XRD curves of modified flax yarn: a) flax yarn treated with chloroactic acid, b) collagen-flax yarn.

diffraction peaks of curve b in the crystalline region decreases relatively, the crystallisation little changes. In the non-crystalline area, due to grafting with collagen, the XRD curve of the flax fibre fluctuates slowly. In general, the crystal structure features of flax fibre did not change.

Scanning electron micrograph analysis

Figure 3.a, 3.b, 3.c and ***3.d*** are SEM photos of unmodified, chloroacetic acid treated and gelatin protein grafted flax yarn, respectively.

Figure 3.a, 3.b, 3.c and ***3.d*** show that there are many defective spots on the surface of untreated flax fibre, with the surface being not very smooth; however there are fewer cracks. There appear a lot of deep stripping damage striations on the fibre surface of flax yarn treated with chloroacetic acid, and fibre smoothness is greatly reduced. But after grafting with gelatin protein, the yarn surface levels off, becoming smooth, and streaks almost disappear. It is suggested that gelatin protein reacts with flax fibre treated with chloroacetic acid and adsorbs on the fibre surface [26]. Gelatin molecules can not only form film after crosslinking in the large grooves of the carboxymethylated flax fibre surface, they can also enter the surface's tiny cracks and porous structure inside the fibre to react with the reactive group to deposit and form film after crosslinking in the carboxymethylated flax fibre surface. Because gelatin protein forms a membrane by crosslinking on the surface of linen yarn treated with chloroacetic acid, this makes the yarn surface level off and smooth, which can effectively improve the rough feeling of linen fabric in apparel fabrics and improve the quality of flax fibre materials.

Breaking force and elongation at break of flax yarn

According to test methods "***Determination of collagen graft rate***" and "***Determination of breaking strength and breaking elongation***", the collagen graft rate, yarn breaking force and elongation at break are determined, respectively, under different gelatin mass concentrations. The influence of the glutin grafting rate on flax yarn breaking force is shown in ***Table 1***, and the relationship curve is shown in ***Figures 4*** and ***5***.

You can see from ***Figure 4*** that changes in the collagen graft rate have much to do with its mass concentration. Overall the collagen graft rate increases following with an increase in the gelatin solution mass concentration, because the greater the gelatin concentration, the more polar functional groups of amino, hydroxyl, carboxyl etc. there are in the solution, and the rates of reaction with carboxylic acid groups in flax yarn treated with chloroacetic acid are greatly increased, consequently the collagen graft rate obviously improves. When the mass concentration of gelatin protein solution reaches a constant value, the increase in the grafting ratio gradually slows down, with an increase in gelatin protein concentration being of no big significance to the grafting yield increase. The reason may be that the number of the activated functional groups reacting with collagen is limited. That is to say, the activated

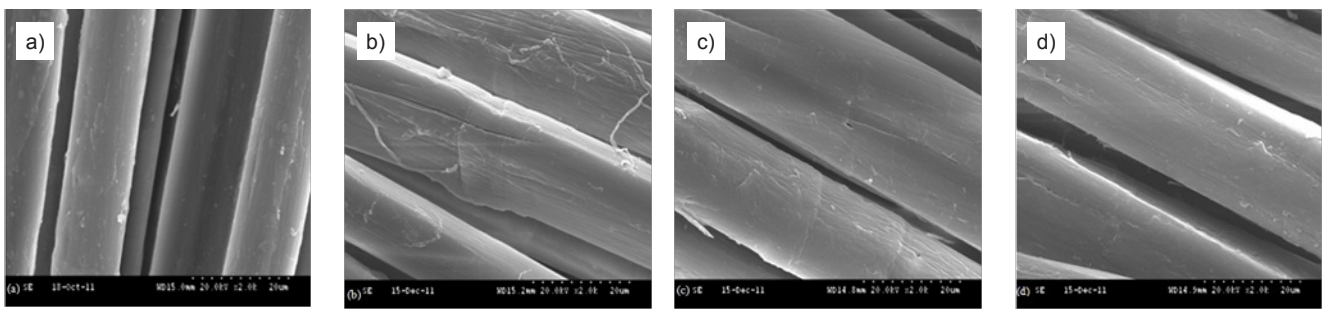
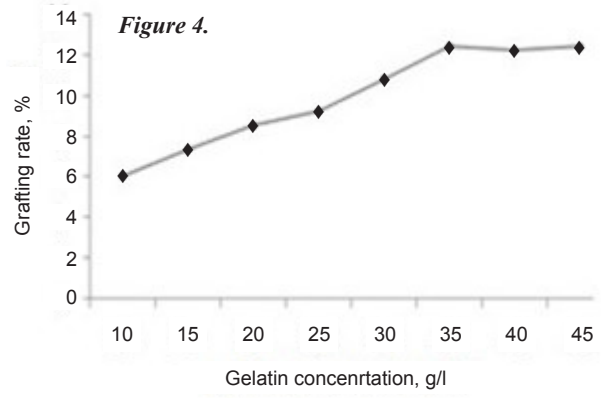
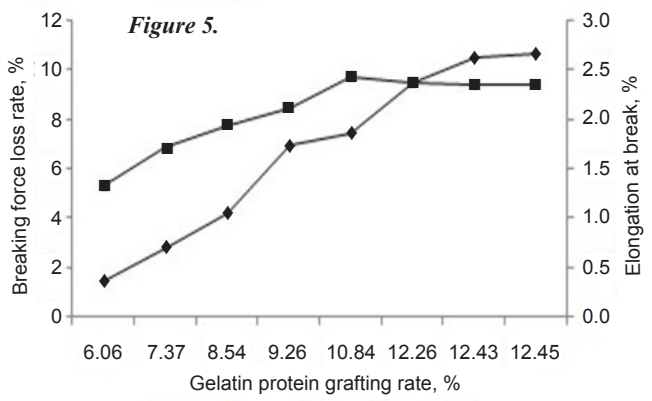


Figure 3. SEM photos of unmodified and modified flax yarn: a) unmodified flax yarn, b) chloroacetic acid treated flax yarn, c) & d) collagen-flax yarn.





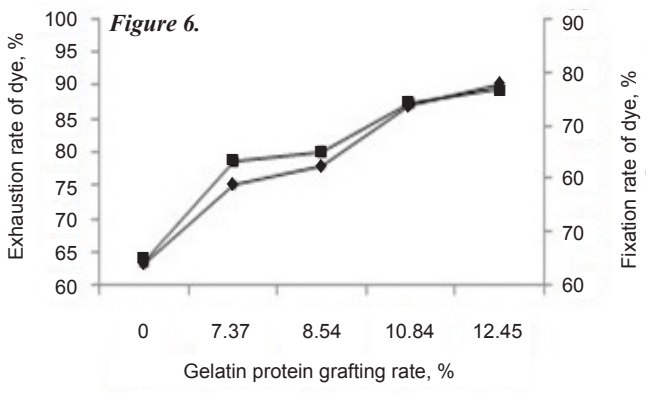


Figure 4. *Effect of gelatin concentration on grafting rate of collagen.*

Figure 5. *Effect of gelatin protein grafting rate on mechanical properties of flax yarn: (■)elongation at break and (♦)breaking force loss rate.*

Figure 6. *Effect of gelatin protein grafting rate on exhaustion and fixation rate of dye: (♦)exhaustion rate of dye and (■)fixation rate of dye.*

groups on flax yarn have mostly reacted with collagen. As shown in the ***Figure 4***, when the mass concentration of gelatin protein reaches 35 g/dm^3, the grafting rate tends to be stable.

Table 1 and ***Figure 5*** show that the breaking force loss rate of linen yarn increases to a certain degree following the increase in the collagen graft rate, but when the graft rate is up to 12%, the breaking force loss rate is less than 8%, in general, and the breaking strength loss rate is small, which does not affect the flax yarn's mechanical properties. When the elongation at break increases to a certain extent, especially when the grafting rate is at about 10% to 2.43%, this has certain benefits that improve the hardness of flax yarn.

Table 1. *The influence of glutin grafting rate on the flax yarn breaking strength.*

Glutin grafting rate, %	Strength of unmodified yarn, cN	Strength of modified yarn, cN
6.06	705	693
7.37		688
8.54		677
9.26		659
10.84		655
12.26		640
12.43		631
12.45		630

Dyeing performance of collagen grafted flax yarn

According to experimental methods "**Dyeing test**" and "**Soap boiling test**", glutin grafted flax yarn is treated by the dyeing and soap boiling processes. According to test method "***Determination of exhaustion rate E and fixation rate F***", the reactive blue dye exhaustion rate and fixation rate of flax yarns of different gelatin protein grafting rates are tested, respectively, the results of which are shown in ***Figure 6***.

As shown in ***Figure 6***, flax yarn dyeing performance can be improved effectively when grafted with gelatin protein, with an increase of the glutin grafting rate and dye exhaustion rate. Moreover the fixation rate of the yarn obviously increases, because the gelatin protein forms a membrane by crosslinking on the yarn surface after glutin grafting, introducing a number of amino active groups onto flax yarn surface. Compared to the hydroxyl groups in cellulose, the nucleophilicity of amino is better and more likely to combine with reactive dyes, forming a covalent bond. Therefore the reactive dye exhaustion and fixation rate of flax yarn after glutin grafting treatment are obviously improved.

Conclusions

1) Infrared spectrum analysis shows that glutin is successfully grafted onto flax yarn containing carboxymethyl, after which the flax yarn is given sodium hydroxide alkaline and chloroacetic acid carboxymethylated treatment.
2) XRD curve analysis shows that the original crystal structure characteristics of flax fibres grafted with collagen do not change. The SEM photo analysis shows that the surface of flax fibre grafted with collagen is very smooth, which helps to improve the quality of flax fibre materials in apparel fabrics.
3) The collagen graft rate is within 12%, which is an improvement, with the breaking force of flax yarn showing little loss and the elongation at break increasing to a certain degree.
4) After glutin treatment, the adhesion force of flax yarns with reactive dyes can be effectively improved, with the exhaustion rate and fixation rate of yarn with reactive blue dye obviously improved.

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