Preparation and Properties of Soybean Protein/Compound Carboxylic Acid Modified Cotton Fabric

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Abstract: For exploiting the ecological multifunctional cotton fabric, the citric acid, maleic acid and soybean protein were used to treat the cotton fabric so that the chemical bonding between soybean protein and cotton fabric was formed through the bridging function of multcarboxylic acids. Effects of treating conditions on the weight gain of cotton fabric were analyzed and the optimized process parameters were also obtained. The characterization of infrared spectra showed that the esterification crosslinking occurred between multcarboxylic acids and macromolecules of cotton fiber according to ring-anhydride mechanism, while the soybean protein was combined on cotton fabric with the amido bond by the bridging function of multcarboxylic acids. The breaking strength of soybean protein modified cotton fabric slightly decreased, whereas the anti-ultraviolet property of modified cotton fabric after cactus extract treatment improved remarkably.

1. Introduction
Soybean protein is a rich plant protein in nature, which contains all kinds of amino acids and vitamins necessary for human body. It has the advantages of renewable, biocompatible, biodegradable, water-holding, solubility, oil absorption and emulsification. It has great application prospect in food processing, medical care, biomaterials, textile printing and dyeing and so on[1-3]. In recent years, a new type of soybean protein fiber was prepared by wet spinning by polycondensation reaction[4]; or use of crosslinkers to graft soybean protein onto fibers or fabricsto improve the related wearability of textiles [5]. However, there are few reports of grafting modified cotton fabric with soybean protein as finishing agent.

In this paper, citric acid and maleic acid were used as crosslinkers, and soybean protein finishing solution was used to modify cotton fabric. The flavonoids, steroids and terpenoids in cactus have some absorption and isolation effects on sunlight UVA and UVB, which can effectively prevent ultraviolet rays of sunlight, and the flavonoids of cactus have prominent effects on inhibiting tumor, anti-aging, anti-allergic and so on, and the bacteriostatic effect is remarkable[6]. Using soybean protein modified cotton fabric as drug carrier, it can give full play to its pharmacological effect and achieve antibacterial and anti-inflammatory, anti-ultraviolet and so on.

In this experiment, the effects of soybean protein concentration, compound carboxylic acid concentration and material ratio on cotton fabric weight gain rate were analyzed, the test parameters were optimized, the internal structure of soybean protein modified cotton fabric was characterized, and
the taking properties of modified cotton fabric and the slow release effect of cactus extract were tested, with a view to developing green health care cotton fabric products.

2. Experimental

2.1 Materials and Reagents
Pretreated khaki cotton fabric (21.5 tex ×21.5 tex, 262/10 cm ×262/10 cm); Soy protein isolate SP, Protein content ≥90%; Cactus extract (the main active ingredient is flavonoids); Citric acid (CA), Maleic acid (TPMA), Sodium hypophosphite (SHP), Sodium hydroxide, Sodium sulfite, Hydrochloric acid and so on are AR grade.

2.2 Test instruments
DHG-9240 electrothermal drying box; M982 electric rolling stock; DF-101S constant temperature magnetic stirrer; JMU-513 heat forming machine; American Brucker VERTEX-80 Fourier Infrared Spectrometer; BL310 automatic electronic balance; British Kratos XSAM-800 photoelectron spectrometer; YG (B)026D-250 Electronic Fabric Strength Instrument; UNICTMUV-2100 UV spectrophotometer; YG (B)912-E textile anti-UV performance tester.

2.3 Cotton Fabric Modified by Soybean Protein Composite Carboxylic Acid
The soybean protein was dissolved in the compound carboxylic acid solution to form a certain concentration of finishing liquid → the cotton fabric was impregnated in the finishing solution (bath ratio 1:100)→ the continuous stirring reaction was carried out for a certain time → the rolling residual rate 100% was rolled on the electric rolling mill (Two dipping and two rolling)→ pre-drying on the heat forming machine(90℃×5 min )→ high temperature baking (170℃×2min)→Washing fully with deionized water → ironing → tiling drying → testing various performance indexes of cotton fabric.

2.4 Test methods
2.4.1 Test of Weight Gain of Cotton Fabric. If the weight of soybean protein before and after cross-linking of cotton fabric is as follows:M1 and M2, than the calculation formula of weight gain rate (WRG) is:

\[ WGR = \frac{M_2 - M_1}{M_1} \times 100\% \]  

2.4.2 FT-IR test. At a temperature of 20℃ and a relative humidity of 65%, the sample powder was mixed with potassium bromide and ground.

2.4.3 tensile strength test. Under the condition of temperature 20℃ and relative humidity 65%, according to GB/T3923-1997 textile fabric tensile properties test conditions test method.

2.4.4 UV Transmission Test. Under the condition of temperature 20℃ and relative humidity 65%, the sample cloth is cut into a square which can cover the size of ultraviolet transmission hole. The transmittance and UPF value of fabric to different wavelength ultraviolet light are obtained. If the UV transmittance is lower, the UV resistance of the fabric is better, and the higher the UPF value is, the stronger the UV resistance of the fabric is[7].

2.4.5 soybean protein modified cotton fabric sustained release cactus extract. The raw cotton fabric treated with cactus flavone extract solution and soybean protein modified cotton fabric were respectively placed in a triangle bottle. physiological NaCl solution was added and oscillated for 4,6,8,10 days at constant temperature 37℃. The absorbance of cactus flavonoids released into NaCl solution was determined at the maximum absorption wavelength 505 nm.
3. Results and discussion

3.1 Effect of reaction conditions of SP in composite carboxylic acid on weight gain of cotton fabric

Fig. 1 is effect of molar ratio of polycarboxylic acid, CA and SP mass fraction concentration on weight gain of cotton fabric. The increase of maleic acid addition in citric acid finishing solution can increase the weight gain rate of fabric. When the mass ratio of TPMA to CA mixture exceeds 1:1, the weight gain of cotton fabric tends to be flat. This is because under the catalysis of sodium hypophosphate and high temperature energy, the secondary hydroxyl groups in citric acid molecules can be esterified by the carboxyl groups of maleic acid molecules to form a sterically solid network of quaternary carboxylic acids. CA and TPMA can form the pentahydrate rings needed for cellulose grafting and crosslinking by polycondensation, especially when mixed at 1:1 molar mixing, which leads to the better finishing effect of CA and TPMA.

With the increase of mass concentration of polycarboxylic acid, the weight gain rate of cotton fabric increased first and then decreased. When the mass concentration of citric acid is 3%, the weight gain rate of fabric reaches the maximum value of 20.26%. This is because when the concentration of carboxylic acid is low, there are enough free hydroxyl groups on the cotton fabric matrix to participate in the vinegar reaction of polycarboxylic acid, and more carboxyl groups are crosslinked on cotton fabric to increase the binding soybean protein molecules.

It can be seen from the Figure .1 that the weight gain rate of cotton fabric increases with the increase of soybean protein mass concentration, while the weight gain of cotton fabric is slow after soybean protein mass concentration is higher than 1%. This indicates that the mass concentration of soybean protein increases, the probability of contact between amino groups in soybean protein molecules and carboxyl groups on esterified cotton fabric and the probability of amide reaction increase, so the amount of soybean protein binding on cotton fabric increases.

3.2 Infrared spectrum of cotton fabric before and after soybean protein treatment
Fig. 6 is the infrared spectrum of cotton fabric before and after soy protein grafting. The strong absorption peak of ester Group C = O was located at 1726.21 cm\(^{-1}\) according to the infrared curve of cotton fabric grafted with soybean protein. It was found that the esterification and cross-linking reaction took place between cotton cellulose and complex polycarboxylic acid after treated with complex carboxylic acid and soybean protein, the characteristic absorption peak of amide at 1552.63 cm\(^{-1}\) is caused by the stretching vibration of c-n bond formed by the reaction of the cross-linked carboxyl group on the cotton fabric with the Amino group in the soybean protein. At the same time, the infrared curve of cotton fabric grafted with soy protein disappeared in -OH plane at 1239.09 cm\(^{-1}\), while the strong absorption peak of amide bond appeared at 813.92 cm\(^{-1}\), it is inferred that there are covalent bond and ionic bond between soybean protein and cotton fabric. Thus, the infrared analysis shows that under the esterification-bridging action of complex carboxylic acid, soy protein molecules cross-link with cotton fabric through amide bond.

![Fig.2 FT-IR spectra of cotton fabric before and after soybean protein modification](image)

(A-original cotton fabric; B-soybean protein modified cotton fabric)

3.3 Mechanical and UV Resistance of Cotton Fabrics Before and After Modification

From the data of Table 1, it can be seen that the breaking strength of the two modified cotton fabrics is reduced, which may be that soybean protein and cactus treatment will weaken the hydrogen bond binding force between cotton fibers, and the erosion of composite carboxylic acid solution weakens the internal structure of cotton fibers. The breaking strength of the fabric decreased. The UV transmittance and UPF value of the modified cotton fabric decreased significantly, especially the UPF and UV resistance of soybean protein modified cotton fabric treated by cactus extract were greatly enhanced.

| Test indicators | Break strength/ N | UV A transmittance/% | UV B transmittance/% | UPF |
|-----------------|-----------------|---------------------|---------------------|-----|
| Cotton fabrics  | 338.2           | 10.35               | 7.01                | 12.82 |
| Soybean Protein Modified Cotton Fabric | 277.5 | 4.79 | 1.48 | 52.56 |
| Soybean protein modified cotton fabric treated with cactus | 265.8 | 2.14 | 1.10 | 77.24 |

3.4 Analysis of sustained-release cactus extract from modified cotton fabric

It can be seen from Table 2 that the absorbance value of cactus flavonoids extracted from soybean protein modified cotton fabric is 3.5 times that of original cotton fabric by slow release and ethanol extraction at different indicates that the modified cotton fabric can not only physically adsorb cactus
extract, but also form chemical bond and ion bond through the binding force of soybean protein 
polycation amino group and acid group in cactus flavonoids extract. Therefore, using soybean protein 
modified cotton fabric as drug carrier, the effect of sustained-release cactus flavonoids extract is 
remarkable, and it has great potential in developing antibacterial and anti-inflammatory health care 
textiles.

**Tab. 2** Controlled release of cactus flavonoid extract adsorbed on soybean protein modified cotton fabric

| Time/ d | Absorbance          |
|--------|---------------------|
|        | Cotton fabrics | Soybean Protein Modified Cotton Fabric |
| 4      | 0.055       | 0.112          |
| 6      | 0.096       | 0.128          |
| 8      | 0.085       | 0.176          |
| 10     | 0.072       | 0.124          |
| Residual cactus extract* | 0.143 | 1.041 |

*: Absorbance analysis of the remaining cactus flavonoids extract from the fabric after extraction from ethanol.

4. Conclusion

Using citric acid and maleic acid as compound crosslinking agent, the optimum conditions for 
crosslinking reaction between soybean protein and cotton fabric were as follows: polycarboxylic acid 
ratio 1: 1, polycarboxylic acid 3%, soybean protein 1%. The weight gain rate of cotton fabric is 
20.26% and the strength retention rate is 82.1%. UPF value of modified cotton fabric treated with 
cactus extract was 5 times higher than that of original cotton fabric, UVA and UVB transmittance are 
2.14% and 1.10%, respectively. Infrared spectroscopy showed that the composite carboxylic acid was 
crosslinked with cotton fabric by esterification, By forming C-N amide bond, Soybean protein is 
firmly bound to the surface of cotton fabric. The drug release test showed that, Soybean protein 
modified cotton fabric released more cactus flavonoids extract in physiological NaCl solution than 
original cotton fabric.

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