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Study on the Modification and Properties of Silk Sericin Protein/Nano-Titanium Dioxide Composite for Textile Applications

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Abstract

Silk sericin protein is a natural high-molecular-weight compound that contains eighteen types of amino acids. It is non-toxic, biodegradable, and biocompatible, with simple preparation methods and low cost. It finds widespread application in functional clothing, medical and pharmaceutical fields, tissue engineering, and more. Nano-titanium dioxide, on the other hand, possesses non-toxic, self-cleaning, antibacterial, and deodorizing properties. To develop multifunctional textiles with deodorization, UV protection, and good thermal and mechanical properties, this study utilized a compounding method to modify citric acid-pretreated cotton fabrics through a two-dipping and two-padding process using a blend finishing solution of silk sericin protein and nano-titanium dioxide. Observations of the microstructure before and after fabric finishing, along with evaluations of deodorization, UV protection, and thermal properties, revealed that controlling the proportion of the silk sericin protein/nano-titanium dioxide blend finishing solution can result in a smooth surface of the modified cotton fabric. This modification not only enhances the fabric's UV protection and tensile strength but also improves its thermal properties while imparting certain deodorization capabilities. Comprehensive analysis concludes that using silk sericin protein and nano-titanium dioxide for modifying cotton fabric to prepare multifunctional textiles with deodorization, UV protection, and good thermal and mechanical performance is feasibly viable.

Keywords

Silk sericin protein, nano-titanium dioxide, deodorizing performance, UV protection, tensile strength, thermal properties.

Silk sericin is a natural high-molecular-weight material derived from the hydrolysis of silk under specific conditions, typically having a molecular weight of around 300,000 kDa. Its intermolecular forces and molecular structure are complex. According to literature [1-2], silk sericin is composed of three subunits: glycoproteins (approximately 25 kDa), light chains (L chains, approximately 26 kDa), and heavy chains (approximately 390 kDa). The heavy (H) and light (L) chains are bonded together by disulfide bonds to form an H-L complex. This complex contains a high concentration of amino acids such as serine (Ser), alanine (Ala), and glycine (Gly), which form a peptide sequence of Gly-Ala-Gly-Ala-Gly-Ser that leads to the formation of β-sheet structures in the crystalline regions. The amorphous regions, on the other hand, contain a large amount of tryptophan (Try), tyrosine (Tyr), and phenylalanine (Phe), forming peptide sequences of Gly-Ala-Gly-Ala-Gly-Y (where Y stands for Tyr and other amino acids). The H and L chains are linked to the glycoprotein P25 through hydrophobic bonds.

The secondary structure of silk sericin protein primarily consists of α-helices, random coils, and β-sheets. The highly ordered β-sheet structures in the crystalline regions of silk sericin fibers, especially the more regularly arranged and energetically favorable antiparallel β-sheets, impart excellent mechanical properties to silk sericin. The presence of a large amount of α-helices and random coils, along with a small amount of β-turns in the amorphous regions, provides good elasticity to silk sericin [3]. With its excellent mechanical properties and rich content of eighteen amino acids, silk sericin shows good compatibility with nonionic, cationic and anionic substances, PVA, 40% alcohol, water, and amphoteric surfactants. It is widely applied in medical carriers with sustained release, skin care and cosmetics, and biosensors [4-6]. Utilizing silk sericin for cotton fabric finishing can fully exploit its skin health and affinity benefits while ensuring the comfort of the fabric.

Nanomaterials exhibit unique physicochemical properties due to their small size effect, surface and interface effect, quantum size effect, and macro quantum tunneling effect. These characteristic differences lead to changes in their intrinsic properties as the particle size varies [7].

Some researchers, both domestically and abroad, have done extensive work on silk sericin protein, suggesting that organic and inorganic materials can be fully utilized through blending to modify materials [8-9]. Nano-titanium dioxide (TiO2 NPs), available in anatase and rutile forms, features small particle size, low cost, non-toxicity, and colorlessness under natural conditions. Besides the characteristics common to nanomaterials, it also possesses non-toxic, self-cleaning, antibacterial, and deodorizing properties, making it widely applied in cosmetics, antibacterial and UV-protective textiles, wastewater treatment, air purification, and other fields [10-11]. Currently, the blending of nano-titanium dioxide with silk sericin mainly focuses on blended spinning and composite film materials. Pan Hui [12] mixed nano-titanium dioxide with silk sericin solution for dry spinning to prepare RSF fibers, showing that the incorporation of nano-titanium dioxide can effectively improve the mechanical properties of RSF fibers. Ahadi et al. [13] used electrospinning technology to spin RSF fiber mats from a blend solution of nano-titanium dioxide and silk sericin, also proving that the addition of nano-titanium dioxide improves the mechanical properties of RSF fiber mats. Lu Yanhua et al. [14] treated tussah silk with nano-titanium dioxide and chitosan sol-gel, indicating a trend towards an increase in oriented β-sheet transformation in the treated silk sericin, which improved the thermal stability of the composite material. Feng Xinxing et al. [15] prepared RSF/nano-titanium dioxide composite films using the sol-gel method, and their tests found that the introduction of nano-titanium dioxide could induce a conformational transition in silk sericin towards a β-sheet-rich silk II structure, thus enhancing the mechanical properties and thermal stability of the composite film. Xia Youyi et al. [16-17] tested composite films of nano-titanium dioxide and silk sericin, finding a lower dissolution rate compared to pure silk films. The use of the blend solution for finishing viscose and cotton fabrics showed that after composite film finishing, the surface of the fabric had uniformly dispersed nano-titanium dioxide with a smaller particle size, while also improving the fabric's dye uptake rate. This paper attempted to use the prepared silk sericin/nano-titanium dioxide blend for finishing cotton fabrics and to evaluate the functional performance of the fabrics before and after finishing, providing a reference for the functional modification and performance enhancement of wearable fabrics through the blend of organic and inorganic materials.

1. Materials and Equipment

Materials: Silkworm cocoon, purchased from a local market; citric acid, provided by Nantong Merck Co., Ltd.; sodium hydroxide (in the form of brucite), supplied by Shanghai Chemical Reagent Co., Ltd.; anhydrous ethanol, from Laiyang Development Zone Fine Chemical Factory; anhydrous calcium chloride, provided by Chengdu Jinshan Chemical Reagent Co., Ltd.; ammonia solution, supplied by Wuxi Jingke Chemical Co., Ltd.; anhydrous sodium carbonate and sodium hypophosphite, from Tianjin Kemio Chemical Reagent Co., Ltd.; nano-titanium dioxide, from Nanjing Haitai Nanomaterial Co., Ltd.; all the chemical reagents used above are of analytical grade.

Equipment: An M305A small sample calender, Qingdao Shanfang Instruments Co., Ltd.; an INSTRON 5582 universal material testing machine, from Instron Corporation; a JCM-7000 scanning electron microscope, JEOL Ltd.; a ZH-TH-80 constant temperature and humidity test chamber, Dongguan Zhengheng Instrument Equipment Co., Ltd.; 202-00A a vertical constant temperature drying oven, Qingdao Juchuang Genesis Environmental Protection Co., Ltd.; an M1416R high-speed table-top centrifuge, Shenzhen Ruide Life Science and Technology Co., Ltd.; a TGA/DSC 3+ simultaneous thermal analyzer, Mettler Toledo Technology (China) Co., Ltd.

2. Sample Preparation and Performance Testing

2.1. Sample Preparation

Preparation of silk sericin protein: In accordance with the literature [18], boiled silkworm cocoons without impurities were boiled in a 0.5% sodium carbonate solution at a ratio of 1:30 for 30 minutes. They were then washed with distilled water and dried. Anhydrous calcium chloride, anhydrous ethanol, and distilled water were mixed in a molar ratio of 1:2:8. The degummed silkworm cocoons were dissolved in the ternary mixture at 75°C for 2 hours. The solution was cooled and dialyzed in deionized water with a conductivity below 0.8 μS/cm. The filtrate was filtered through 5 layers of medical gauze, centrifuged at 7500 rpm for 8 minutes, and freeze-dried to obtain silk sericin protein particles, which were ground into powder for future use.

Preparation of silk sericin protein/nano-titanium dioxide composite solution: 10 g of silk sericin protein was weighed and completely dissolved in 90 mL of distilled water. The nano-titanium dioxide solution was added to the above mixture, and the components were stirred to prepare composite finishing solutions with titanium dioxide concentrations of 3, 5, 7, and 9 g/L.

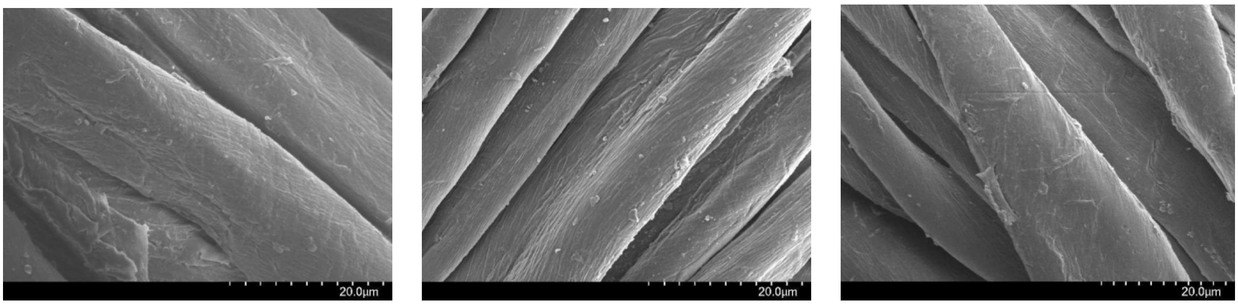
Fabric modification using composite solution:

(1) Citric acid pre-treatment: To enhance the cross-linking of the composite finishing agent with cotton fabric and increase the content of free carboxyl groups in the fabric, cotton fabric pre-treatment was carried out according to reference [19]. The specific process involved the preparation of a mixed solution containing 8% and 4% citric acid and sodium hypophosphite by mass concentration. Under a padding ratio of 85%, the cotton fabric samples underwent two dips and two pads of finishing in the mixture. They were pre-baked at 80°C for 5 minutes and heat-set at 150°C for 150 seconds. The fabric modified under these conditions was labeled as a-fabric.

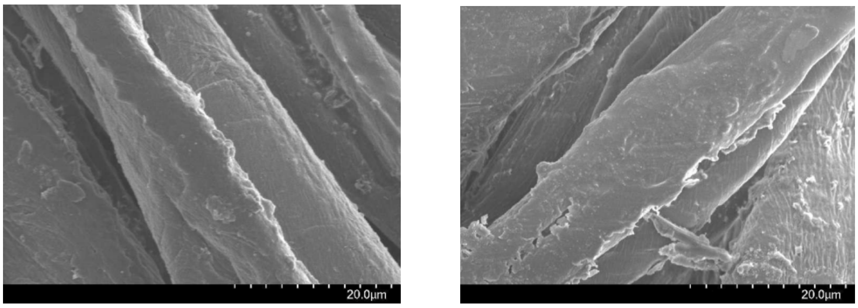
(2) Fabric modification using composite solution: Cotton fabric pre-treated with citric acid was immersed in the silk sericin/nano-titanium dioxide composite solution at 50°C for 1 hour. Following a padding ratio of 85%, the cotton fabric samples underwent two dips and two pads. They were then pre-baked at 80°C for 5 minutes and heat-set at 110°C for 3 minutes. The fabric modified with composite finishing solutions containing titanium dioxide concentrations of 3, 5, 7, and 9 /L was labeled as b-fabric, c-fabric, d-fabric, and e-fabric, respectively.

2.2. Performance Testing

Microscopic morphology observation: Scanning electron microscopy was used to observe the microscopic morphology of the treated fabric and determine the adhesion performance of the fabric with the composite finishing solution. Test parameters: voltage 20 kV, gold sputtering time 15 s.



a) a-fabric b) b-fabric c) c-fabric



d) d-fabric e) e-fabric

Fig. 1. Scanning electron microscope images of the finished cotton fabric

Deodorizing performance measurement: Following the methods of Hong Wenjin, Qiu Chunyan, and others [19-20], the deodorizing performance of the modified fabric was determined. The procedure was as follows: 2 grams of sodium hydroxide were added to a surface dish, diluted with 10 mL of ammonia by 1000 times, and transferred to a sealed glass container for 1 hour. The ammonia gas concentration at this time was noted as C (mg/m³). Cut fabric samples measuring 15×15 cm were placed in a sealed glass container and irradiated for 12, 24, and 36 hours under simulated sunlight (18 W power, color temperature 6500 K). The ammonia gas concentration C' (mg/m³) was recorded at different time intervals. The deodorizing rate of the treated fabric was calculated using Equation 1, where W is the deodorizing rate. The experiment measured 30 samples and calculated the average, with statistical analysis conducted on data within an absolute error of ±3.5%.

$$W = \frac{C' - C}{C} \times 100\% \qquad (1)$$

UV Protection Performance Testing: According to GB/T 18830-2009 'Textiles - Evaluation for solar ultraviolet radiation protective properties,' in the experiment an average of 30 sample groups was measured and statistical analysis conducted on data within an absolute error of ±3%.

Thermal Properties Testing: To determine the thermal properties, the cotton fabric, both before and after modification, was shredded into foam. Using a simultaneous thermal analyzer under a nitrogen atmosphere, the samples were heated from 20°C to 600°C at a heating rate of 20°C/min. TG (Thermogravimetric) and DSC (Differential Scanning Calorimetry) curves of the samples were measured.

Tensile Strength Testing: Pre-treated cotton fabric, both before and after modification, was dried in an oven at 105°C until constant weight. The samples were then conditioned for 24 hours in a standard environment with a relative humidity of 65% and temperature of 20°C. The tensile strength and elongation at break in the warp direction of the fabric samples were measured using a universal testing machine with a clamping length of 20 cm and tensile speed of 20 mm/min at a constant rate of extension. An average of 30 sample groups was measured and statistical analysis conducted on data within an absolute error of ±0.2%.

3. Results and Discussion

3.1. Microscopic Morphology Observation

Scanning electron microscope images of the finished cotton fabric are shown in Figure 1. From the images, it can be observed that the cotton fabric pre-treated with citric acid appears smoother, and the elliptical shape of cotton fibers is more distinct. After the modification with a silk sericin/nano-titanium dioxide blend finishing solution, the surface of the fibers in the cotton fabric gradually exhibits a dense coating. This indicates that the components of silk sericin and nano-titanium dioxide penetrate each other, forming a uniform structure, which is beneficial for enhancing the overall effect of the modification. Additionally, due to the hollow structure of the cotton fibers, the interior of the finished fabric fibers presents a loose structure, effectively combining functions such as radiation protection and thermal insulation. As the content of nano-titanium dioxide in the blend finishing solution increases, granular protrusions gradually appear on the fiber surface, with phenomena of clumping, adhesion, and uneven coverage becoming evident. This is because the increase in the content of nano-titanium dioxide affects the uniform structure of the blend solution. It is inferred that when the content of titanium dioxide in the finishing solution is too high, it will lead to an increase in weak links, reducing the mechanical properties of the fabric, which will be corroborated in the mechanical property analysis below.

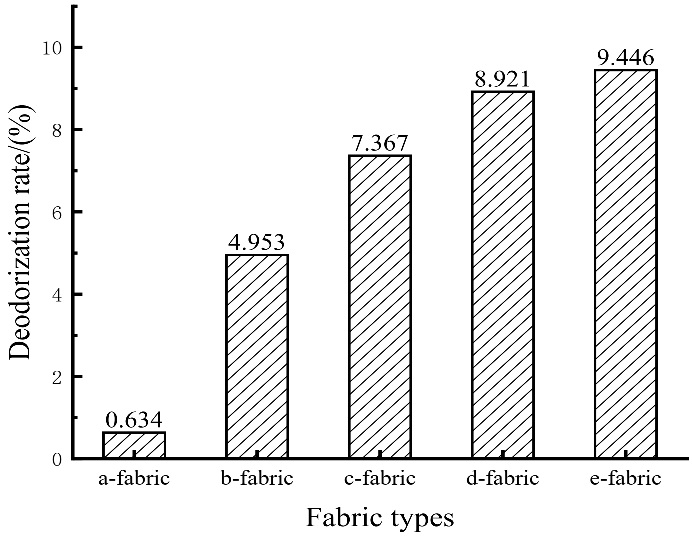


Fig. 2. Column chart of the deodorizing rate of the modified cotton fabric

3.2. Deodorizing Performance Analysis

Previous scholars have primarily focused their research on the deodorization capabilities of nano-titanium dioxide (TiO2) through direct photocatalysis or ultraviolet light catalysis on titanium dioxide or its composites with inorganic materials, with less emphasis on composites prepared with organic materials [21-23]. This experiment attempted to analyze the deodorization performance of nano-titanium dioxide when blended with organic materials, providing a reference for the development of deodorizing textile products. The deodorizing rate of the modified cotton fabric is presented in the column chart in Figure 2. Analysis of the column chart indicates that the modified cotton fabric exhibits a certain degree of deodorizing effect against ammonia gas. This is due to the catalytic action of nano-titanium dioxide in the composite finishing solution when exposed to UV radiation. The titanium dioxide catalyzes the oxidation of sericin protein and hydroxyl groups in cotton fibers, producing free radicals, including hydroxyl and superoxide radicals [24-25]. These radicals react with ammonia gas, leading to the multi-step oxidation and degradation of ammonia into non-toxic nitrogen gas [26]. The deodorizing rate of the modified cotton fabric increases with the higher content of nano-titanium dioxide in the composite finishing solution but with diminishing returns. Two primary reasons contribute to this trend: first, the initial stage of the catalytic oxidation reaction involves the generation of hydroxyl radicals at the surface of the nano-titanium dioxide particles. As the reaction progresses, the generation of hydroxyl radicals inside the sericin protein matrix requires more energy, and sericin protein itself offers some resistance to UV radiation. This internal encapsulation of nano-titanium dioxide makes its catalytic action less effective. Second, as ammonia gas is degraded to nitrogen gas within a sealed glass container, the concentration of ammonia gas decreases, resulting in reduced opportunities for hydroxyl radicals to capture ammonia molecules, leading to a decrease in the deodorizing rate. In conclusion, the sericin protein/nano-titanium dioxide composite-modified cotton fabric demonstrates a certain degree of deodorizing effect, and the ratio of sericin protein to nano-titanium dioxide in practical applications should be adjusted based on the usage environment.

3.3. UV Protection Performance Analysis

The UPF (Ultraviolet Protection Factor) values of the modified cotton fabric are presented in the column chart in Figure 3. Analysis of the column chart indicates that the UPF values of the modified cotton fabric increase with higher concentrations of nano-titanium dioxide in the composite finishing solution, but the rate of increase diminishes. This behavior is attributed to the pre-treatment of the cotton fabric with citric acid and subsequent modification with the composite finishing solution, which forms a network structure interwoven with citric acid and sericin protein. The nano-titanium dioxide is randomly distributed within this network structure. Due to the crystalline structure of nano-titanium dioxide (rutile), which has a melting point of 1870°C, it remains stable at the temperatures encountered in the analysis. When exposed to UV radiation, nano-titanium dioxide absorbs UV energy, scatters UV radiation, and offers enhanced UV protection. Additionally, the small particle size and higher quantity of nano-titanium dioxide particles in the composite provide more efficient UV interception and blockage. This is the main reason for the increase in UPF values of the modified cotton fabric with higher concentrations of nano-titanium dioxide in the composite finishing solution. As sericin protein itself has some UV protection properties, the test results represent a combination of these two factors. Since the UV protection efficiency of sericin protein is lower than that of nano-titanium dioxide, and the encapsulation of nano-titanium dioxide within sericin protein reduces its catalytic oxidation efficiency, the UPF values of the modified cotton fabric increase with higher nano-titanium dioxide content in the composite but with diminishing returns. Therefore, in the practical application of functional clothing, the

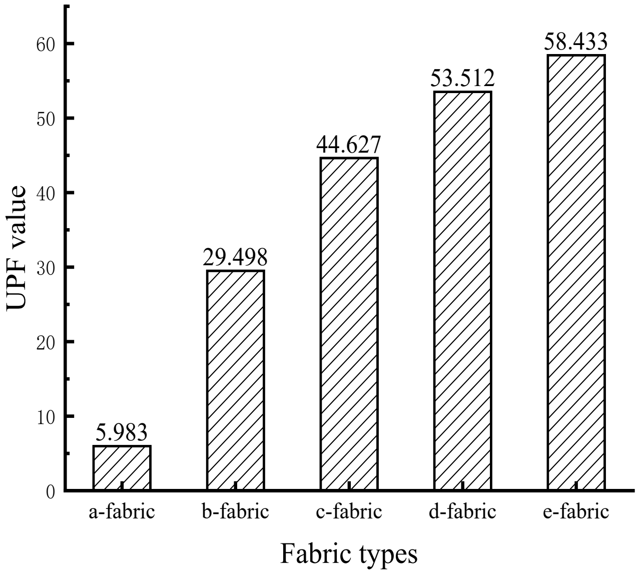


Fig. 3. Column chart of UPF values of the modified cotton fabric

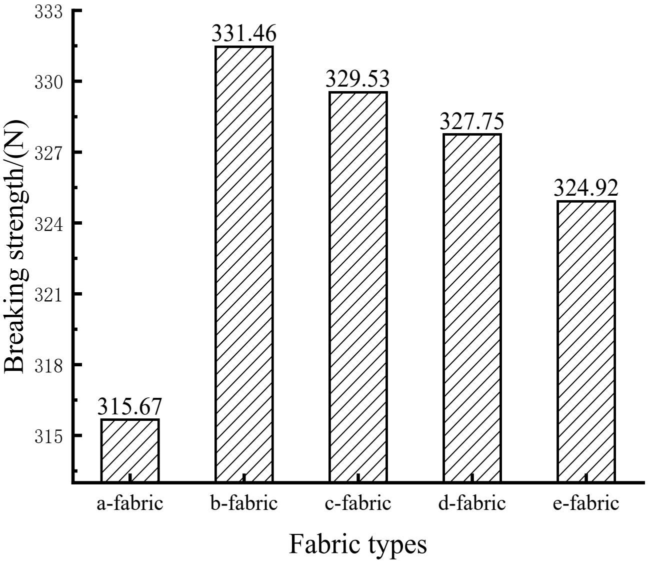


Fig. 4: Column chart of the tensile strength of the modified cotton fabric

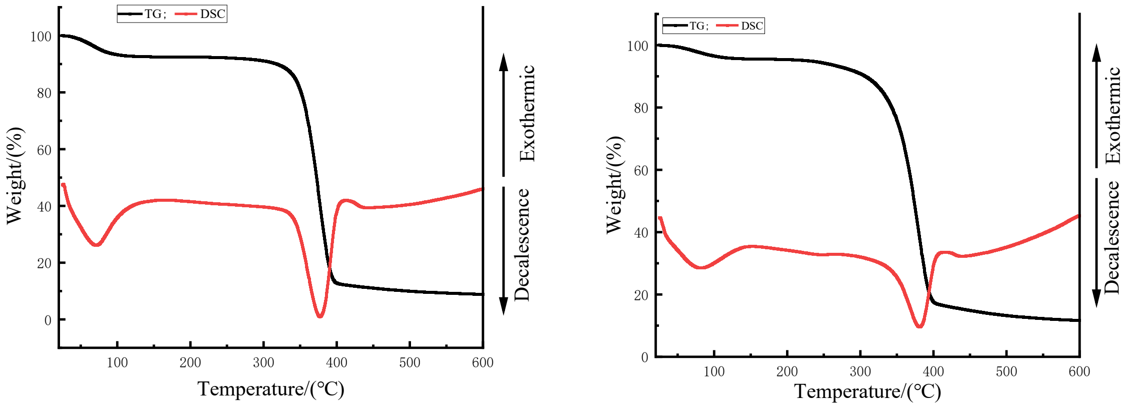
ratio of sericin protein to nano-titanium dioxide should be adjusted according to the usage environment.

3.4. Tensile Strength Analysis

The column chart in Figure 4 shows the tensile strength of the modified cotton fabric. Analysis of the column chart reveals that the tensile strength of the cotton fabric is significantly higher after modification with sericin protein and nano-titanium dioxide composite finishing solution. This increase in tensile strength is attributed to the formation of a composite material layer on the fabric's surface, which is formed by the interweaving of citric acid and sericin protein. This layer cross-links and adheres to the fabric, providing some plasticization effect, ultimately enhancing the fabric's tensile strength. However, as the concentration of nano-titanium dioxide in the composite finishing solution increases, the tensile strength of the modified cotton fabric decreases. This is due to the random distribution of nano-titanium dioxide within the network structure, which disrupts the cross-linking between the citric acid, sericin protein, and composite film. Higher nano-titanium dioxide concentrations result in more pronounced disruptions. Additionally, due to the strong oxidizing and reducing properties of TiO2, it can damage the molecular structure of the cotton fiber substrate, leading to a decrease in mechanical properties. In summary, the tensile strength of the cotton fabric shows a relatively small variation before and after modification, with no significant impact on the fabric's performance.

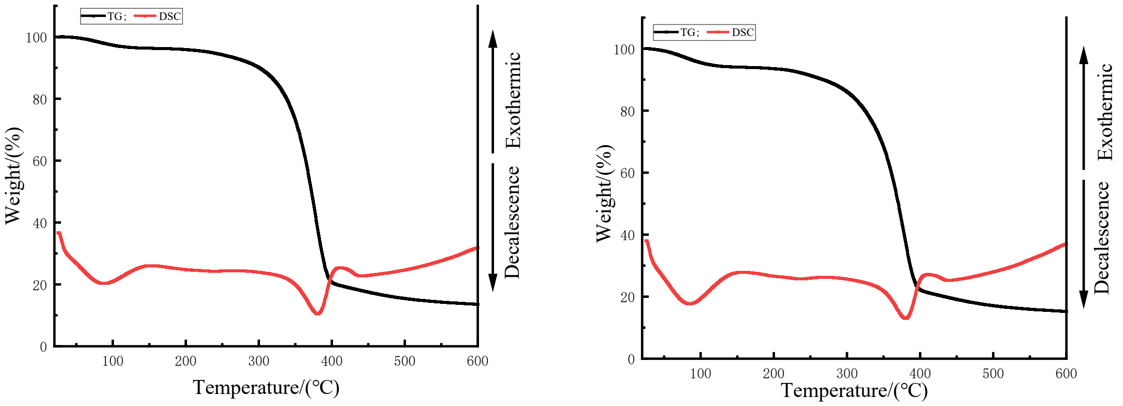
3.5. Thermal Properties Analysis

Thermal curves of the modified cotton fabric are shown in Figure 5. Observing the curves, it is evident that the trend of the curves in all five graphs is quite similar and can be divided into four descending stages. The first stage, from 20°C to 150°C, shows a slight decrease in sample mass, attributed to the volatilization of moisture and minor particles. The second stage, from 150°C to 350°C, exhibits relatively stable sample mass. The third stage, from 350°C to 400°C, indicates a rapid decrease in sample mass as the macromolecular chains in the modified cotton fabric start to break. The fourth stage, from 400°C to 600°C, represents the carbonization of the fabric components, maintaining a stable remaining mass. Analyzing the TG curves, the residual mass at 600°C is approximately 8.86%, 11.64%, 13.57%, 15.26%, and 18.14% for a-fabric, b-fabric, c-fabric, d-fabric, and e-fabric, respectively. As the concentration of nano-titanium dioxide in the composite finishing solution increases, the residual mass of the modified cotton fabric also increases. This is because the rutile-type nano-titanium dioxide particles have a high melting point of 1870°C, and the added nano-titanium dioxide remains in a stable structure at these temperatures, leading to higher residual mass. Observing the DSC curves in the temperature range of 350°C to 400°C, a decrease in the intensity of the endothermic peak indicates that nano-titanium dioxide did not absorb a significant amount of



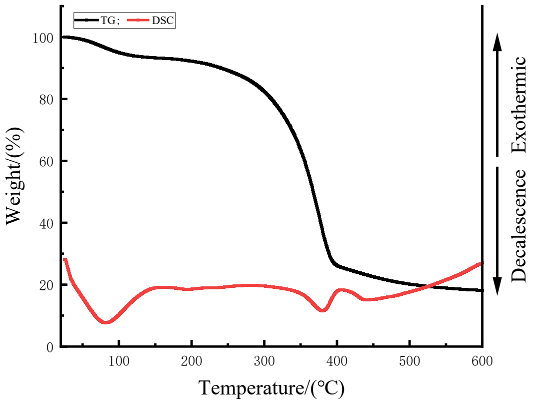
a) a-fabric

b) b-fabric



c) c-fabric

d) d-fabric



e) e-fabric

Fig. 5. Thermal curves of the modified cotton fabric

heat in this temperature range, further validating the increase in residual mass of the modified cotton fabric with higher nano-titanium dioxide concentrations. Therefore, to enhance the thermal properties of the modified cotton fabric, the content of nano-titanium dioxide in the composite finishing solution can be increased reasonably.

4. Conclusion

With the innovation of materials and the heightened awareness of protection, clothing has gradually moved away from the simple design mode of warmth and comfort towards a direction of safety and intelligence in functionality. Clothing design now places greater emphasis on the integration of modern science and technology with traditional garment crafting techniques, enhancing the protective capabilities for the wearer through functional design. Utilizing a silk sericin/nano-titanium dioxide blend finishing solution for the two-dip-two-nip modification process on citric acid pre-treated cotton fabrics, and testing the properties of the modified fabrics, has shown promising results. Tests indicate that controlling the composition of the blend finishing solution can result in a smooth surface of the modified cotton fabric, while improving the fabric's UV protection, tensile strength, and thermal properties, as well as imparting certain deodorization capabilities. The research concludes that the blending of silk sericin and nano-titanium dioxide can fully leverage the advantages of both organic and inorganic substances to modify the material, providing the garment with more practical functionalities and demonstrating strong feasibility.

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