Preparation and Warmth Retention of Down Fiber Grafted with Zirconium Oxychloride

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ABSTRACT
A new product, referred to herein as modified down, was produced by grafting down fiber with zirconium oxychloride. Grafting modification brings new functionalities to down fiber. For example, the warmth retention of modified down is greatly improved. The reaction mechanism and reason for the improved warmth retention of the modified down was investigated. Using response surface methodology (RSM), we found that the optimal preparation conditions for modified down were 15.1% zirconium oxychloride, 15.06% sodium tripolyphosphate, and 1.39 h duration. The warmth retention of the modified down was 80.95%, the CLO value increased by 35.38%, the thermal resistance increased by 35.43%, the filling power substantially increased by 31.35%. The zirconium oxychloride was successfully modified and grafted onto the down fiber, as was confirmed by scanning electron microscopy, energy-dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy, and thermogravimetric analysis. The ultimate residual quantities of the modified down fibers were 30.06%. The results show that the active groups of zirconium and down fibers firmly combined via chemical bonds, which made the warmth retention of modified down a lasting property.

Keywords: down fiber; warmth retention property; EDX; RSM; functionalization

INTRODUCTION
In recent years, natural protein materials have attracted substantial attention for their potential to be used in various applications [1–3]. Down fiber is an excellent natural protein material and is similar to other protein fibers such as wool, silk, and camel hair. The main component of down is called down protein and is composed of various amino acids. These amino acid molecules link polypeptide chains to form the primary structure of the down protein. There are also several transverse links condensed by most of these amino acids among the down protein macromolecules. The main links are salt bonds, amino bonds, ester bonds, disulfide bonds and hydrogen bonds [4]. These bonds will allow chemical modification of down fibers.

As a natural protein fiber, down is well known for its extensive applications. Surface modification has been demonstrated to be a useful approach to functionalizing fiber materials with properties superior to those of unfunctionalized fibers. Wool fibers have a long history of surface modification to achieve extra value or features. Therefore, surface modifications, such as chemical treatment, surface functionalization and plasma treatment [5,6], are feasible for down fiber to achieve new and improved properties. However, the literature contains few reports of the application of surface modification on down fiber to improve its warmth retention property. We have only been able to identify a limited number of papers specifically, albeit briefly and qualitatively, analyzing the structure and properties of down fibers and down assemblies [4,7,8]. In addition, few studies on the fractal methods of down fiber [9,10] and limited papers on the properties of poultry feathers [11,12] have been reported. In this paper, the integrative physical properties of down fibers and down fiber assemblies are studied and evaluated based on the fiber compression behavior [13] and the fiber softness [14].

Down fiber is a high-quality natural protein fiber applied in different products. Very fine and high-quality down fiber is valuable and expensive and is widely used. However, some low-quality down fiber is cheap and is currently wasted. Thus, improvement of the warmth retention of ordinary down fiber is necessary to reduce the cost of down, which would lead to a reduction in the quantity of natural biomaterial used, an improved rate of utilization of natural biomaterial, increased value, and a reduced dependence on down production, as well as reducing the water, land and other environmental pollution caused by animal rearing.

Modification of the warmth retention of down is imperative for improved utilization. Grafting modification of down fibers brings new functions and properties to down. Understanding the warmth retention of the down after surface modification would benefit the further development of the functionalization technology and protein fiber, which may be useful for exploiting new functional materials by connecting metal ions to proteins and imparting new characteristics to the final materials via grafting. This technology may be potentially useful in other fields, such as biomaterials [15], the textile industry, food and chemical engineering.

ZrO_2 is a derivative of Zirconium Oxychloride. It exhibits excellent optical marking, self-cleaning, thermal stability, fire retardancy and antibacterial activity on textile products due to intrinsic physico-chemical properties such as hardness, shock wear, strong acid and alkali resistance, low frictional resistance and high melting temperature. Gashti, et al [16,17] have investigated the thermal and self-cleaning properties of Ca/ZrO_2 nanocomposite coated wool fibers. They used a crosslinking agent for embedding nano-zirconia on wool fibers due to the fact that there is no attraction between inorganic particles and wool. They investigated different physical and chemical properties of citric acid/nano-zirconia composite coated wool fiber.

In this work, we reveal a new technology for the grafting reaction of zirconium oxychloride onto down fiber; the literature contains no previous reports of this technology or the resultant material. The main purpose is to improve the warmth retention properties of down fiber such that the natural fiber is not destroyed. A response surface methodology (RSM) experiment was carried out, and the optimal preparation conditions and the influence of the reaction conditions on the warmth retention properties of modified down were investigated to obtain the best formula and experimental model. The excellent warmth retention of the modified down was confirmed using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA).

MATERIALS AND METHODS

Materials

Down was supplied by BOSIDENG group. Sodium tripolyphosphate (STPP) was purchased from Tianjin Guangfu Fine Chemical Research Institute. Zirconium oxychloride was purchased from Tianjin Kemiou Chemical Reagent Co. Ltd.

Methods

Preparation of Modified Down

Down fibers weighing 6 g were dipped into distilled water (60°C, 500 ml) and mixed with an oscillator to ensure that they were well dispersed in the solution. Specific amounts of zirconium oxychloride and sodium tripolyphosphate (STPP) were then weighed out and separately dissolved in distilled water (100 ml). The two solutions were then transferred to the flask containing the dispersed down solution. The samples were refluxed and mechanically stirred at a specified temperature for a selected period of time. After the reaction was completed, the modified down were washed 6-9 times with copious amounts of distilled water to remove any traces of additives on the fiber surface. Afterward, the modified down samples were dried in an oven at 50°C for 3 h.

Optimization of the Preparation Parameters of Modified Down

An RSM experiment with a Box-Behnken design was performed to elucidate the optimal processing conditions [18]. The concentrations of zirconium oxychloride and STPP and the treatment time were selected as the factors affecting the warmth retention rate. The test factors and levels are shown in *Table I*, and the experimental plan and results are shown in *Table II*.

TABLE I. Coded variables and their coded levels used in the response surface methodology.

Experimental factor	Factor levels and coding		
	-1	0	1
zirconium oxychloride (A)/%	12.5	15	17.5
STPP (B)/%	12.5	15	17.5
time (C)/h	1.25	1.5	1.75

TABLE II. Experimental design and results obtained using response surface methodology.

Run	Factor 1 A (%)	Factor 2 B (%)	Factor 3 C (h)	Response warmth retention rate （%）
1	1	1	0	79.47
2	0	-1	1	78.39
3	1	0	1	78.53
4	-1	-1	0	79.04
5	0	1	1	78.04
6	0	-1	-1	79.96
7	-1	1	0	79.17
8	-1	0	1	78.41
9	0	1	-1	80.04
10	1	0	-1	79.24
11	1	-1	0	79.54
12	-1	0	-1	79.47
13	0	0	0	79.96
14	0	0	0	80.31
15	0	0	0	80.42

SEM-EDX

In this study, the surface morphology of down was investigated by SEM (Quanta200, FEI). Samples were mounted with carbon tape onto aluminum stubs and then sputter coated with gold to make them conductive prior to SEM observation. Samples were observed at an accelerating voltage of 10 kV.

FTIR Spectroscopy

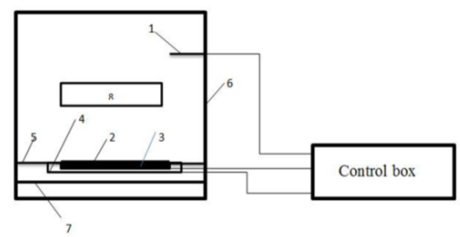
The FTIR spectra of the down fibers were collected using a TENSOR37 FTIR spectrometer (Bruker). The down fiber was combined with KBr and compacted into a disk using a grease-coated die. The attenuated total reflectance (ATR) spectrum of the samples between 500 and 4000 cm^{-1} was collected using 32 scans for each spectrum; the resolution of the ATR spectra was 4 cm^{-1}.

Warmth Retention Property

Warmth retention is usually measured using the thermal conductivity coefficient (U) [19,20], CLO value (CLO), thermal resistance, and warmth retention rate (Q). In these experiments, the warmth retention rate was predominantly used; its formula is given as follows:

$$Q=(Q_1-Q_2)\ /\ Q_1\times 100\% \qquad (1)$$

Where Q_1 is the heat dissipation capacity of no down (W/°C), and Q_2 is the heat dissipation capacity of down fiber (W/°C). The warmth retention of the modified and unmodified down was measured according to textile warmth retention property test methods. Different down samples were tested in an YG606 flat-plate warmth retention tester (Nantong Sansi Electromechanical Science & Technology Co. Ltd), as shown in *Figure 1*. Down samples were first placed into a 30 cm × 30 cm × 30 cm nonwoven bag, which was subsequently placed into the instrument. The sample mass was 10 g, and the test conditions were a temperature of 20°C and a relative humidity of 65%. The warmth retention rate was determined by measuring the heat flowing at a known temperature gradient through the down sample; the results were read directly from the instrument.



1-temperature sensor, 2-experiment panel, 3-heating panel, 4-shielding panel, 5-insulated panel, 6-experimental box, 7-baseplate, 8-operation window

FIGURE 1. Schematic of the flat-plate warmth retention tester.

Bulkiness

In general, a higher the filling power of the down results in better warmth retention. Therefore, the filling power can indicate the warmth retention to a certain extent. The filling power of the unmodified and modified down was measured according to the feather testing method (GB/T10288－2003), and the filling power of the down was evaluated using a filling power instrument.

Turbidity Test

The turbidity or transparency of the down is an important health technology index in the process of feather testing. The turbidity of down reflects the processing quality, indicating the presence of residual impurities, dirt and other free materials found in down.

The turbidity of the modified and the unmodified down was measured according to the washed feather test method (FZ/T 80001-2002). The turbidity of down was evaluated using a special turbidity meter (TBM-101, Feather Down Testing Laboratory, Zhejiang entry-exit inspection and quarantine bureau).

TGA

The TGA of the down was carried out using a thermogravimetric analyzer (STA409PC, NETZSCH). The analytical conditions were a sample mass of 5 mg, an initial temperature of 20°C, a final temperature of 800°C, a heating rate of 10°C/min, and the purging gas was nitrogen.

X-ray Diffraction (XRD)

The use of XRD counts offers a simple and fast method to calculate the crystallinity index of fibers. A BRUKER X-ray diffractometer (D8 DISCOVER), employing Cu Kα radiation was used. The diffraction intensity was in the range of 5-40° of 2θ (bragg angle).

Limiting Oxygen Index (LOI) Measurement

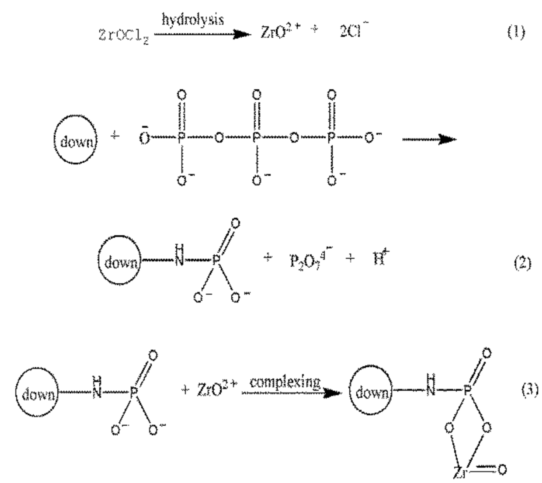
The LOI value is the minimum amount of oxygen in an oxygen-nitrogen mixture required to support complete combustion of a vertically held sample that burns downward from the top. The Limiting Oxygen Index (LOI) values of down was carried out using a JF-3 Limit Oxygen Index tester.

RESULTS AND DISCUSSION

Reaction Mechanism

Down fiber with side-groups such as amino, carboxyl and hydroxyl groups can be easily modified. In particular, the nitrogen atom of the amino group, with a pair of unsaturated electrons, is more nucleophilic than the atoms of other groups. The STPP exhibits strong activity, leading to easy substitution. The mechanism of the reaction is expressed as shown in *Scheme 1*.

SCHEME 1.Reaction mechanism of down fiber with zirconium oxychloride.



Optimization of the Preparation Parameters of Modified Down

The analysis of variance (ANOVA) from the obtained data is given in *Table III*.

According to the ANOVA results, the fitted model is

$$Y=+80.23+0.086*A-0.026*B-0.67*C-0.05*A*B+0.088*A*C-0.11*B*C-0.56*A^2-0.36*B^2-0.76*C^2$$

In this equation, Y, A, B and C are the warmth retention rate (%), the zirconium oxychloride concentration (%), the STPP concentration (%) and time (h), respectively. The plus sign indicates positive effects, whereas the minus sign indicates negative effects.

The model F-value of 6.14 in the ANOVA results (*Table III*) implies that the model is statistically significant. There is only a 2.99% chance that an F-value this large could occur due to noise. The lack-of-fit F-value of 3.02 implies that the lack of fit is not significant relative to the pure error.

TABLE III. ANOVA for the response surface quadratic model.

Source	Sum of squares	DF	Mean square	F value	P value	Significance
Model	7.04	9	0.78	6.14	0.0299	significant
A	0.060	1	0.060	0.47	0.5249	
B	5.513E-003	1	5.513E-003	0.043	0.8435	
C	3.56	1	3.56	27.96	0.0032	significant
AB	1.000E-002	1	1.000E-002	0.078	0.7907	
AC	0.031	1	0.031	0.24	0.6448	
BC	0.046	1	0.046	0.36	0.5734	
A^2	1.16	1	1.16	9.08	0.0296	significant
B^2	0.49	1	0.49	3.86	0.1067	
C^2	2.12	1	2.12	16.62	0.0096	significant
Residual	0.64	5	0.13			
Lack of Fit	0.52	3	0.17	3.02	0.2588	not significant
Pure Error	0.12	2	0.058			
Cor Total	7.68	14				
	C.V.% =0.45	R-Squared=0.9170	Adj R-Squared=0.7676	Adeq Precision=7.404		

There is a 25.88% chance that a lack of fit F-value this large could occur due to noise. A non-significant lack of fit is desired because it indicates the model well fits the experimental data. The "Adeq Precision" parameter is a measure of the signal-to-noise ratio; a ratio greater than 4 is desirable. The determined ratio of 7.404 indicates an adequately strong signal for this model to be used to navigate the design space. In summary, the warmth retention rate of the model is credible and the fitting degree is high, which supports the use of the model.

The significant effects of various factors on the response value can also be observed in the ANOVA results in *Table III*. The 27.9 F-value of C implies that C significantly affects the response value (warmth retention rate), the order of significance of a single factor can be ranked according to the F-value as follows: time (C) > zirconium oxychloride (A) > STPP (B), it also were determined from *Figure 2*. In this case, C, A2, C2 are significant model terms.

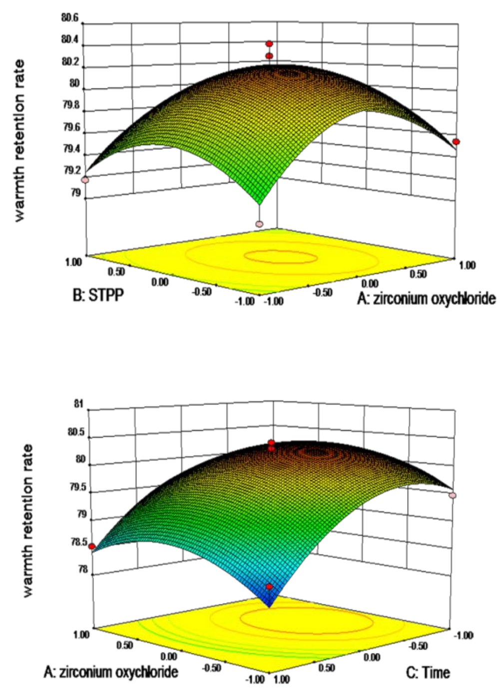


FIGURE 2.Response surface of A, B, and C and their mutual interactions on the warmth retention rate.

The three independent variables were optimized using a numerical optimization function. The optimal parameters of the modified down that resulted in the highest warmth retention rate were as follows: zirconium oxychloride (A): 15.1%, STPP (B): 15.06%, time (C): 1.39 h, with a predicted warmth retention rate of 80.38%. As verified by experiments, the actual result was 80.95% and the fitting degree was 99.3%. These results suggest that this model can be used to guide the preparation process of modified down and to predict the warmth retention rate.

SEM-EDX Analysis

SEM was used to evaluate the effects of the zirconium oxychloride on the down fiber. *Figure 3* shows the morphological structures of the down and the modified down, each magnified by 1000×, 4000× and 5000×.

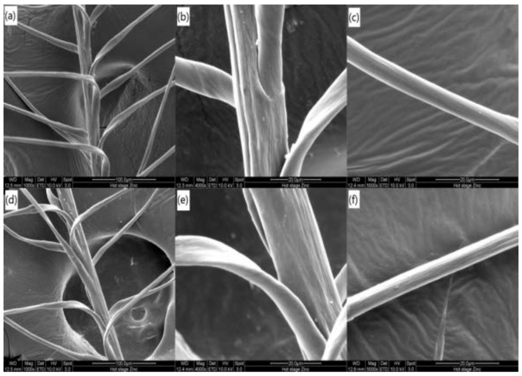


FIGURE 3. SEM micrographs of the surface morphology of unmodified down (a: 1000×, b: 4000×, c: 5000×) and modified down (d: 1000×, e: 4000×, f: 5000×).

Analysis of the mechanism behind the excellent warmth retention property of the modified down is important. The SEM images in *Figure 3* show that the down exhibits a tree-like morphology. The structure comprises tiny velvet nuclei and several velvet branchlets [21]. The velvet nuclei are analogous to a tree root located in the center. *Figure 3* shows that the velvet branchlets have numerous branches aligned almost parallel. The velvet branchlets constitute the main body of the velvet flowers growing from velvet nuclei. The velvet branchlets stretch in different directions around the velvet nuclei, forming spherical velvet flowers. The velvet branchlets maintain a certain distance between the respective stretches in different directions to occupy a larger space [22]. Each sub-branch, in turn, carries a large number of fibrils, which protrude from the main branch at approximately 30° to 90° from the tip to the root. Because the fibers maintain a certain distance from each other, the tree structure provides sufficient space to store static air internally to improve the warmth retention of the down.

The unique branch-like and fractal structure evident in *Figure 3* plays a critical role in its superb warmth retention. Several smaller velvet branchlets form a web. The web retains a substantial amount of air, which is firmly fixed in the web [22]. The unique bifurcated morphological structure and excellent warmth retention of goose down are inextricably linked, and the structure provides an enclosed space that can store more static air. This special relationship between fibers and air is responsible for the excellent warmth retention of down fiber. Such a structure can first entrap more air and then retain more air after compression. In comparison to the surface structure of the unmodified down fiber, that of the modified down fiber remains intact, and the modified down fiber maintains its natural shape.

The presence of zirconium and other elements on the surfaces of the modified down was investigated by EDX analysis; the results are reported in *Table IV*. The EDX spectrum of the modified down is shown in *Figure 4*. The analysis of the modified down fiber indicates an aggregation of zirconium and scattering on the surface of the down fibers. According to *Figure 4*, the down contains 4.62 mass% Zr. Thus, the EDX analysis results indicate that the zirconium oxychloride was grafted onto the modified down. The active groups of the zirconium oxychloride and down fibers firmly bonded, which imparted the modified down with durable warmth retention characteristics.

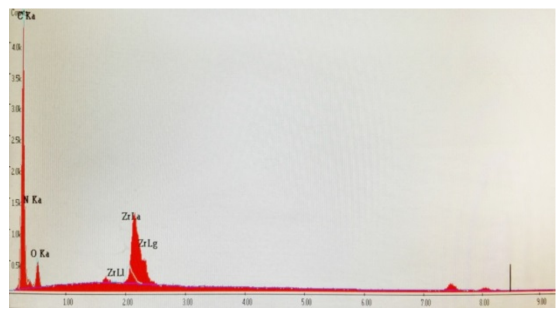


FIGURE 4.EDX spectrum of the modified down.

TABLE IV. Elemental analysis results for the modified down.

Element	C	N	O	Zr	Cl
Unmodified down (Wt %)	61.51	16.42	22.07	0	0
Modified down (Wt %)	68.46	11.76	15.16	4.62	0

FTIR Analysis of Modified Down

Figure 5 shows the FTIR spectra of the modified and the unmodified down. A comparison of the two spectra reveals two definite differences.

First, in the spectrum of the modified down, the characteristic absorption peaks appeared at 883 cm^{-1} and 1171 cm^{-1}, corresponding to the Zr—O—Zr of zirconium oxychloride and to the P＝O stretching vibration of STPP, respectively; these peaks are absent in the spectrum of the unmodified down. The results indicate that the zirconium oxychloride was grafted onto the modified down. Second, in the spectrum of the modified down, additional characteristic absorption peaks appeared at 2243 cm^{-1} and 1731 cm^{-1}, which correspond to the stretching vibrations of the C＝O and N–H groups of the modified down, respectively; these peaks are also absent in the spectrum of the unmodified down. These results demonstrate that the NH_2 groups of the down participate in the grafting modification and that the zirconium oxychloride is grafted onto the modified down. The active groups of the zirconium oxychloride and down fibers combined firmly via chemical bonding, which imparted the modified down with a durable warmth retention property.

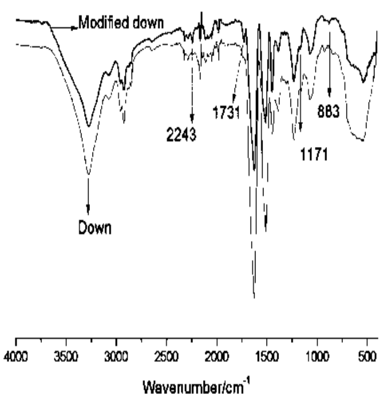


FIGURE 5. FTIR spectra of the modified and the unmodified down.

The two spectra exhibit similar absorption bands at approximately 3281 (N–H and O–H), 2923 (–CH_2), 1633 (amide I), 1516 (amide II), and 1236 cm^{-1} (amide III) [23]. Therefore, the modification does not destroy the surface structure of the down fiber, and its natural shape remains intact.

Warmth Retention Property Analysis

The warmth retention rates of unmodified down and modified down were measured according to the textile warmth retention property test methods. Before the measurement was conducted, the sample was washed, shocked and dried. *Table V* shows the effects of grafting modifications on the warmth retention of down. Although the improvement of the warmth retention is not obvious in *Table V, Figure 6* conclusively shows that the improvement is significant.

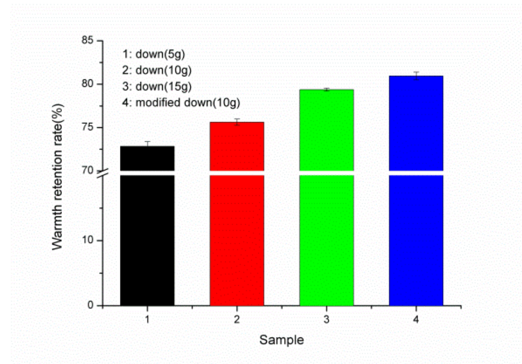


FIGURE 6.The change in the warmth retention rate across different samples.

TABLE V. Comparison of the warmth retention properties of unmodified down and modified down.

Sample	U	CLO	Rja (-K.m^2/w)	Q (%)
unmodified down	4.211	1.532	0.2374	75.81
modified down	3.109	2.074	0.3215	80.95

The results in *Table V* show that the warmth retention of down fibers after modification is significantly improved. From the unmodified down, the CLO value increased by 35.38%, the thermal resistance increased by 35.43%, and the overall warmth retention rate increased by 6.78%. The modified down exhibited excellent warmth retention characteristics, withstanding at least 12 washing cycles at 50°C. These results demonstrate that the active groups of zirconium oxychloride and down fibers were firmly combined, which imparted the modified down with a durable warmth retention property.

The down's excellent warmth retention is attributable to its unique tree structure. The large quantity of tree structures could occupy abundant space and entrap more air. The modified down exhibits improved warmth retention characteristics compared to the unmodified down for two reasons. First, the modifications increase the interaction force between the fibers and enhance the network structure, enlarging the enclosed space. The larger space can accommodate more static air. The modification increases the internal specific surface area and greatly increases the flow resistance of air [24]. To accommodate the air within, static air fixes inside the fiber aggregates, resulting in improved warmth retention. This effect results in a smaller coefficient of heat conductivity for the modified down compared to that of the unmodified down.

Second, the modified down grafted with zirconium exhibits far-infrared absorption properties. According to Kirchhoff's law, the far-infrared absorption wavelengths of the down match the skin absorption wavelength of the human body. These wavelengths coincide with the resonance absorption perfectly, thus, human skin is a good absorber of far-infrared rays. Clothing made from far-infrared-absorbing down can effectively absorb the far-infrared rays (3-15 μm) emitted from the human body. If the modified down efficiently emits far-infrared radiation of the same wavelength at the same time, the majority of the far-infrared rays emitted from the down can be absorbed by the skin and turned into heat because of the infrared absorption properties of human skin. From testing, the far-infrared emissivity of the modified down in the range from 5 to 25 μm (full-wavelength) is 0.89, and the far-infrared emissivity of raw down is only 0.84. Consequently, the temperature on the surface of the skin will increase. Thus, the heat preservation effect of the modified down is better than that of the unmodified down.

Bulkiness

Table VI illustrates that the filling power of the modified down after graft modification with the zirconium oxychloride increased relative to that of the unmodified down by 31.35 percent. This increase indicates that the modification did not damage the structure of the down fibers. The high degree of bulkiness of down produces excellent warmth retention. Substantial space exists between individual fibers in down, which is the main source of its bulkiness. The modifications increase the interaction force between fibers and enhance the network structure, enlarging the enclosed space. Static air can be easily stored in the down fiber, which substantially impedes the airflow circulation. This in turn leads to a limited amount of static air that leaves from the down, enhancing its overall bulkiness. Because the filling power of the down is related to its warmth retention within a certain range, greater filling power results in better warmth retention.

TABLE VI. Comparison of the filling power of unmodified down and modified down.

Sample	No.	Filling power	
		Imperial units（in^3）	Height（cm）
unmodified down	1	472.5	16.42
	2	472.5	16.42
	3	475	16.51
	average value	473.3	16.45
modified down	1	615	21.38
	2	630	21.9
	3	620	21.55
	average value	621.7	21.61

Turbidity Analysis

Table VII illustrates that the turbidity of the modified down is not reduced compared to that of the unmodified down. The down quality of the modified down satisfied the standard of the quality inspection and was greater than the quality of the unmodified down. At the same time, zirconium oxychloride is not a simple coating or residue on the surface of the down fiber. Instead, the active groups of the zirconium oxychloride and down fibers combined through a stable bond, giving the modified down a durable warmth retention property.

TABLE VII. Comparison of the turbidity of down.

Sample	No.	Turbidity	
		Turbidity（mm）	Absorbency (A)
unmodified down	1	542	0.198
	2	550	0.195
	3	570	0.188
	average value	554	0.194
modified down	1	675	0.16
	2	682	0.158
	3	687	0.157
	average value	681.3	0.158

Thermogravimetric Analysis

TG curves of the modified down and the unmodified down are shown in *Figure 7*.

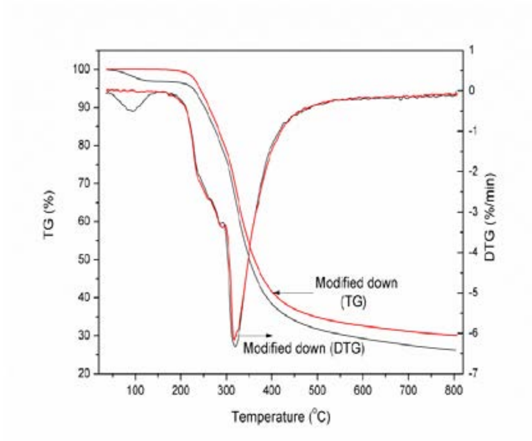


FIGURE 7.TGA/DTG curves of the modified and unmodified down.

Figure 7 shows two substantial weight-loss steps in the TGA curve. The first process is ascribed to the evaporation of water. The second important process is associated with the thermal decomposition of down. This pyrolytic region includes several chemical reactions in which the protein compounds are decomposed into lower-molecular-weight products and volatile compounds such as CO_2, H_2O and SO_2.

From *Figure 7*, the rate of weight loss for the unmodified down reached a maximum of 6.32%/min at 319.4°C. The modified down reached a maximum rate of weight loss of 6.16%/min at 317.16°C. The ultimate residual quantities of the unmodified and modified down fibers were 26.16% and 30.06%, respectively. The modified down experienced a slower thermal weight loss rate and a greater residual quantity compared to the unmodified down as a result of the chemical bonding between the zirconium and the down fibers.

XRD Analysis

X-ray diffractograms of the modified and unmodified down are shown in *Figure 8*. As can be seen, all the samples showed the characteristic peak of protein, the measured crystallinity index of the modified and unmodified down is illustrated in *Table VIII*, the crystallinity of unmodified down is 13.5%; the crystallinity of modified down is 33.53 percent. The improved crystallinity of the modified down suggests that treatment with zirconium oxychloride removes non-crystalline components from the downs to some extent.

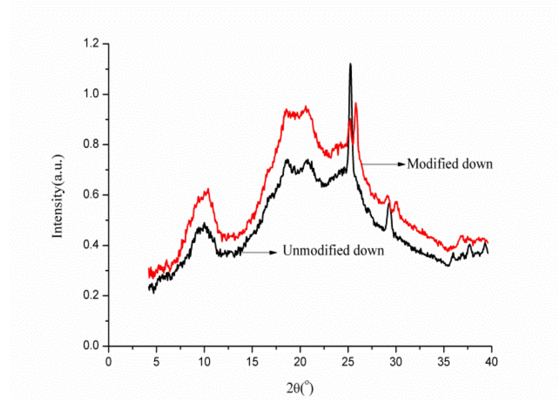


FIGURE 8. X-ray diffractogram of modified and unmodified down.

TABLE VIII. The crystallinity of modified and unmodified down.

sample	Crystallinity (%)
Unmodified Down	13.50
Modified Down	33.53

Thermal Stability Properties

TABLE IX. The LOI (%) of the modified and unmodified down.

sample	LOI (%)
Unmodified Down	24
Modified Down	30

The LOI values are presented in the *Table IX*. The LOI value of modified down is 30; the LOI value of down is 24. The higher the LOI value, the better performance of thermal stability, thus confirming that the modified down had higher thermal stability than raw down. The presence of zirconium oxychloride appears to have resulted in thermal stability improvement, possibly due to the chemical bonds between zirconium and down fibers.

CONCLUSION

In this paper, a chemical modification was successfully carried out between down fiber and zirconium oxychloride, resulting in a new product denoted as modified down. The modified down had better warmth retention than the unmodified down. The underlying mechanism for the improved warmth retention and the reaction mechanism of the modified down were investigated.

The optimal parameters for preparing the modified down that correspond to the greatest warmth retention were selected on the basis of an RSM experiment. The highest warmth retention of the modified down was obtained at a zirconium oxychloride concentration of 15.1%, an STPP concentration of 15.06%, a reaction time of 1.39 h, and a reaction temperature of 70°C. The warmth retention rate of the down modified under these conditions was 80.95%, the CLO value increased by 35.38%, the thermal resistance increased by 35.43%, and filling power increased by 31.35%. The successful modification of the down was confirmed by SEM, EDX, FTIR, and TGA. The ultimate residual quantities of the modified down fibers were 30.06%. The active groups of the zirconium oxychloride and down fibers combined via a chemical bond, which gave the modified down durable warmth retention characteristics. This technology may be useful in other fields such as biomaterials, the textile industry, the food industry and chemical engineering.

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