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Controllable Synthesis of Carboxymethyl Cellulose and Its Application in Tobacco Sheets

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Abstract: Carboxymethyl cellulose (CMC) with different degree of substitution (DS) was prepared by controlling feed ratio and times of alkalization and etherification. CMC with different molecular weight was prepared by degradation of hydrochloric acid solution. Orthogonal experiments were designed to study the effects of addition amount, molecular weight and DS of CMC on the tensile strength of tobacco sheets. The effects of CMC on the thermal properties and aerosol release of tobacco sheets were also studied. The results showed that the addition amount and the molecular weight of CMC had obvious effect on the tensile strength of tobacco sheets. The DS of CMC had no significant effect on the tensile strength of tobacco sheets. The addition of CMC improved the thermal stability of tobacco sheets to a certain extent, and had certain influence on the content of nicotine in aerosol.

Key words: tobacco sheets; carboxymethyl cellulose; tensile strength; thermal performance

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0 Introduction

Carboxymethyl cellulose (CMC) is one of the most widely used water-soluble cellulose derivatives and used as adhesive in thickening, bonding, film forming, water holding, emulsification and so on. CMC has good biocompatibility, which makes it widely used in food and pharmaceutical industry^[1].

CMC is synthesized from alkali cellulose and chlo-

roacetic acid^[2]. According to medium, it can be divided into water medium method and solvent method. The water medium method uses water as the reaction medium. This method has a lower production cost but more side effects, so it is usually used to produce medium and low-grade CMC in industry. The solvent method uses ethanol, isopropanol or other organic solvents as the reaction medium. Its preparation process is relatively simple. The process has few side reactions, high purity, but high cost. It is used in the industrial production of medium

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and high-grade CMC^[3].

The heating not burning cigarette is a new type of tobacco product. Compared with electronic cigarettes, it not only retains the taste of traditional cigarettes, but also effectively reduces the release of nicotine and other harmful ingredients^[4,5], so its market is huge in future^[6,7]. Tobacco sheets are made of tobacco powder, glycerin, water and adhesives. Adhesive is one of the essential components for the production of tobacco sheets. It not only plays a role in bonding each component material, but also improves the mechanical properties of tobacco sheets to a certain extent, greatly affecting the flexibility of tobacco sheets. In recent years, CMC has been one of the adhesives commonly used in the preparation of tobacco sheets. Liu *et al*^[8] prepared an adhesive with chitin as the main raw material, which improved the water resistance and tensile strength of tobacco sheets. Wei *et al*^[9] applied cellulose etherification modification to tobacco sheets, which significantly improved the tensile strength of tobacco sheets. When the content of carboxyl group ≥ 0.65 mmol/g, compared with the samples added with wood pulp fiber, the tensile strength of tobacco sheets added with etherified fiber increased by 35.8% -106.6%. The research work on tobacco sheets mainly focuses on the production process and formula. In this article, the influence of CMC on the tensile strength of tobacco sheets and the influence of CMC on the thermal properties of tobacco sheets and the content of nicotine in aerosols were studied. It will play a guiding role in the research of tobacco sheets.

1 Experimental

1.1 Reagents and Instruments

Reagents: Anhydrous ethanol, sodium chloroacetate (Thain Chemical Technology Shanghai Limited Company); sodium hydroxide (Shanghai Wokai Biotechnology Limited Company); Glycerol, isopropanol (Shanghai Linen Technology Development Limited Company); Nitric acid (Xinyang Chemical Reagent Factory); Hydrochloric acid (Wuhan Huasong Fine Chemical Limited Company); Tobacco powder, bleached Beimu chemical pulp (Hubei Xinye Tobacco Sheets Development Limited Company). All reagents are of analytical purity.

Instruments: S65 laboratory three roll grinder (Chengdu Xindu Yongtong Machinery Factory); Multifunctional grinding and dispersing machine (Shanghai Weite Motor Limited Company); Roller press (Jiangsu

Furi Precision Machinery Limited Company); SH10A moisture rapid tester (Shanghai Precision Instrument Limited Company); Ubbelohde viscometer; Nicolet6700 fourier transform infrared spectrometer (NIGOLI Instruments, USA); STA449F3 comprehensive thermal analyzer (Netzsch Scientific Instrument Trading Shanghai Limited Company); WDW-5D electronic universal testing machine (Hebei Hangxin Instrument Manufacturing Limited Company); Agilent 6890N/5975 gas chromatography-mass spectrometer (Agilent Technologies, USA).

1.2 Controllable Preparation of CMC

A certain amount of cellulose was put into a round bottom flask, and an appropriate amount of isopropanol was added in. Then 50% (wt) sodium hydroxide aqueous solution was added while stirring, alkalized at 40 °C for 1 h. Sodium chloroacetate was added, etherified at 55 °C for 2 h, then acetic acid was added to neutralize excess sodium hydroxide immediately. The samples were washed with 80% ethanol water solution^[10,11], then filtered, dried and grinded. CMC with different degree of substitution (DS) was prepared by changing the feed ratio, etherification times and alkalization times. CMC with different molecular weight was degraded by different concentrations of hydrochloric acid^[12].

1.3 Preparation of Tobacco Sheets

The cigarette powder, CMC, external fiber, water and glycerin were accurately weighed. The outer fiber, water and glycerin were weighed in proportion and stirred into a uniform slurry with multifunctional grinding and dispersing machine. Then CMC and cigarette powder were mixed evenly before being added to the above slurry. After preliminary mixing, the powder and slurry were rolled by three-roll grinder. Then the mixtures were made into about 0.16 mm tobacco sheets and dried at 60 °C.

1.4 Testing and Characterization

Test for DS: The CMC sample was dissolved in 95% ethanol, and stirred until the slurry was uniform. 5 mL nitric acid was added during stirring. The solution was boiled for 5 min, then filtered, and washed with 80% ethanol until no nitrate was detected with diphenylamine reagent. After being dried to constant weight, a certain amount of acidic CMC was added to water for dispersion. A certain amount of 0.3 mol/L NaOH aqueous solution was added. After boiling for about 15 min, the excess NaOH was titrated with 0.3 mol/L HCl stan-

dard solution immediately and the titration end point was indicated with phenolphthalein^[13]. The calculation formula of DS is as follows:

$$A = \frac{BC - DE}{F} \quad (1)$$

$$DS = \frac{162A}{1000 - 58A} \quad (2)$$

where A (mol) is amount of substance of acid consumed per milligram of sample, B (mL) volume of NaOH solution added, C (mol/L) molar concentration of NaOH, D (mL) volume of HCl consumed by titrating excessive NaOH, E (mol/L) molar concentration of HCl, and F (g) mass of acid CMC consumed. 162 is molar mass of dehydrated glucose unit, and 58 is the relative molecular weight of dehydrated glucose unit increased after the introduction of a carboxymethyl group.

Test for molecular weight: CMC solution of certain concentration with 0.1 mol/L NaCl aqueous solution as solvent was prepared, and the retention time with Ubbelohde viscometer in a 25 °C thermostatic water bath was measured. Then the solution was diluted in equal proportion for four times, and the retention time was determined. Finally, the retention time of 0.1 mol/L NaCl solution was determined^[14]. The extrapolation method was used to obtain the fitting equation. Mark Houwink equation was used to calculate viscosity:

$$[\eta] = KM^\alpha \quad (3)$$

where $[\eta]$ is intrinsic viscosity, M is viscosity average molecular weight, $K=1.23 \times 10^{-5}$ L/g, and $\alpha=0.91$.

Design of orthogonal test: Orthogonal experiment was used to explore the influence of CMC molecular structure (molecular weight, DS) and addition amount on the tensile strength of tobacco sheets, and a mathematical model was established to analyze and optimize the preparation process of tobacco sheets. An orthogonal experiment with three factors and four levels was designed with CMC addition amount (measured by CMC content in dry state percentage), molecular weight and DS as experimental factors. The factor levels are shown in Table 1.

Test for release of aerosol components: The capillary chromatographic column was HP-INNOWax (length: 30 m, inner diameter: 0.25 mm, thickness: 0.25 mm). Injection volume was set to 1 μ L. The inlet temperature was set to 300 °C, the split ratio was set to 1:1, and the flow rate was set to 1.0 mL/min. The column temperature program was as follows: the column temperature program was 40 °C during initial 3 min, then in-

Table 1 Level of orthogonal experimental factors

Group	CMC addition amount/%	Molecular weight/kDa	DS
1	1.5	180	0.9
2	2.5	310	1.1
3	3.5	360	1.3
4	4.5	440	1.5

creased to 300 °C at 5 °C/min and stayed for 10 min^[15].

Test for thermal properties: 20 mg sample was accurately weighed and heated from 20 °C to 500 °C at a heating rate of 10 °C/min under nitrogen protection.

2 Results and Discussion

2.1 Controllable Preparation of CMC with Different Molecular Structure Parameters

2.1.1 Preparation of CMC with different degrees of substitution

In this experiment, CMC with different DS was prepared by controlling the feed ratio of raw materials, alkalization times and etherification times^[16, 17]. The reaction conditions were in Table 2.

Table 2 DS of CMC prepared under different experimental conditions

Number	Feeding ratio	Alkalization times	Etherification times	DS
1	1:2	1	1	0.9
2	1:2	3	1	1.1
3	1:2	1	2	1.3
4	1:2	2	1	1.5
5	1:3	1	2	1.8

According to Table 2, it can be analyzed that alkalization times and etherification times have a great impact on the DS of CMC. Multiple alkalization and etherification significantly improve the etherification efficiency of chloroacetic acid. In the case of the same molar ratio of raw material, according to the chemical reaction kinetics, adding sodium hydroxide for more times can improve the alkalization efficiency of cellulose, so that cellulose is alkalized and expanded better. The molecular chains of cellulose are dispersed, making the etherifying agents more accessible. The nucleophilic substitution efficiency of sodium chloroacetate is improved. However,

the concentration of alkali liquor in the system is low when the alkalization times are too many, which make the alkalization of cellulose insufficient and affect the subsequent etherification process. The principle of multiple etherification is similar to multiple alkalization. Adding sodium chloroacetate in multiple batches can also improve the conversion efficiency of sodium chloroacetate. However, the reaction time of adding etherified reagent later is short when the etherification times are too many, which cannot reach the reaction equilibrium stage, thus affecting the overall etherification efficiency.

2.1.2 Preparation of CMC with different molecular weight

The degradation of CMC by hydrochloric acid is a reaction that is violent first and then mild. That is, the molecular weight of CMC will drop sharply at the moment when hydrochloric acid is added to CMC solution, and then slowly. Therefore, it is difficult to control the molecular weight of CMC by reaction time. Here, the molecular weight of CMC was mainly controlled by the concentration (% , mass fraction(wt)) of hydrochloric acid. Since CMC is a non-Newtonian fluid, in order to ensure the good fluidity of the solution, the concentration of CMC was 5 g/L, and the concentration of hydrochloric acid was 0.1%, 0.3%, 0.5%, 1%, 3% and 5% respectively. The reaction took place at 40 °C for 30 min. The specific experimental results are shown in Fig. 1.

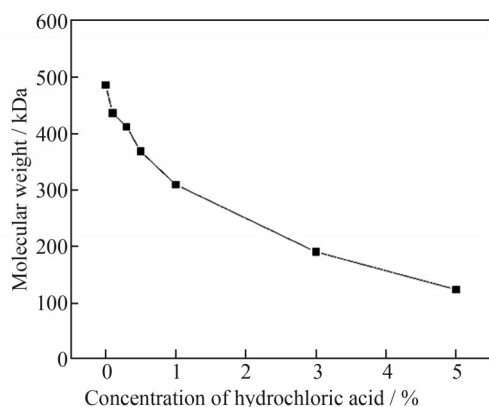


Fig. 1 CMC molecular weight after degradation with different hydrochloric acid concentrations

It can be seen from Fig. 1 that the final molecular weight of CMC decreases with the increase of hydrochloric acid concentration. This is because β -1,4-glycosidic bond of CMC molecular chain is easy to be broken under acidic conditions to generate CMC with low molecular weight.

2.2 Characterization of CMC

2.2.1 Nuclear magnetic resonance hydrogen spectrogram

Figure 2 shows the ^1H -NMR hydrogen spectrum of CMC. The characteristic peak of the proton on the glucose unit is in the range of 3.0 to 4.0 mg/kg. The characteristic peak of $-\text{CH}_2\text{COOH}$ on C_6 is near 4.15 mg/kg. The characteristic peak of $-\text{CH}_2\text{COOH}$ at α and β on C_2 is near 4.25 and 4.35 mg/kg, respectively. The characteristic peak of $-\text{CH}_2\text{COOH}$ on C_2 is near 4.38 mg/kg. It is CMC substituted monomer on the glucose reduction terminal C_1 characteristic peak of β -H where the chemical shift is about 4.1 and 4.2 mg/kg. It is CMC substituted monomer on the glucose reduction terminal C_1 characteristic peak of α -H where the chemical shift is about 5.2 and 5.3 mg/kg^[18].

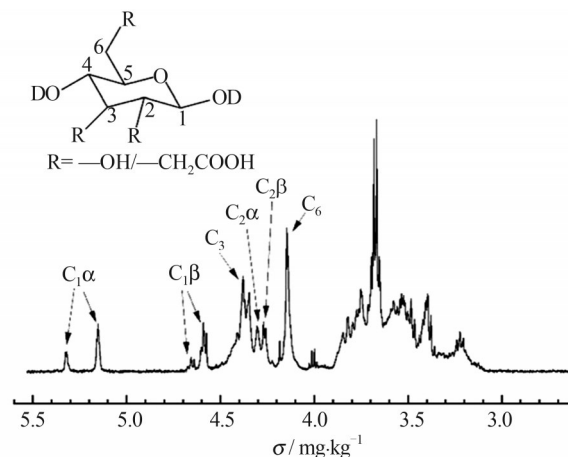


Fig. 2 ^1H -NMR hydrogen spectrum of CMC

2.2.2 Fourier transform infrared spectrogram

Figure 3 is Fourier transform infrared spectra of CMC and cellulose. There are obvious absorption peaks at 1 329 cm^{-1} and 1 620 cm^{-1} after etherification, corre-

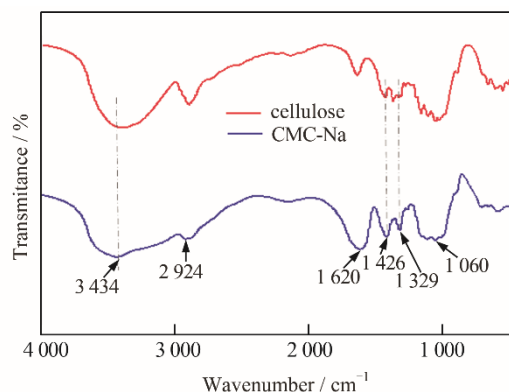


Fig. 3 Fourier transform infrared spectroscopy of CMC

sponding to the tensile vibration absorption peak of C—O and C=O on CMC—COO— respectively, resulting from the introduction of —COO—. There is a stretching vibration absorption peak of —CH₂ in carboxymethyl at 1 426 cm⁻¹. The peak at 3 434 cm⁻¹ is the telescopic vibration absorption peak of —OH. Comparing the infrared spectra of cellulose before and after etherification, we found that new absorption peaks appeared at 1 426 cm⁻¹, 1 620 cm⁻¹ and 1 329 cm⁻¹ after etherification, which was the result of the introduction of carboxymethyl. In addition, the peak value of cellulose at 3 434 cm⁻¹ decreased after etherification, which is the result of the substitution of —OH. These indicated that cellulose was successfully carboxymethylated.

2.3 Results of Orthogonal Test

According to the factor level in Table 2, SPSS (Statistical Package for the Social Sciences) was used to design the orthogonal experiment, and the results are shown in Table 3.

2.3.1 Analysis of range

Based on the results of orthogonal experiments in Table 3, the range analysis of the tensile strength of tobacco sheets under different factor levels was carried out, and the results are shown in Table 4.

Table 3 Results of orthogonal experiment

Number	A	B	C	Tensile strength /N·m ⁻¹
1	1	3	4	406
2	1	1	1	339
3	1	4	2	361
4	1	2	3	386
5	2	2	4	557
6	2	1	2	459
7	2	4	1	459
8	2	3	3	498
9	3	2	1	577
10	3	1	3	470
11	3	4	4	468
12	3	3	2	515
13	4	1	4	470
14	4	2	2	608
15	4	4	3	454
16	4	3	1	546

A: CMC addition amount; B: molecular weight; C: DS

Table 4 Results of range analysis

Item	Tensile strength /N·m ⁻¹		
	A	B	C
k_1	373	435	480
k_2	494	532	486
k_3	508	491	452
k_4	520	436	475
Variance	135	97	34

k_i ($i=1, 2, 3, 4$) is the average value of the i -th level tensile strength of a factor

The variance reflects the influence of each factor on tensile strength. The larger the variance, the greater the influence of this factor on tensile strength. According to Table 4, it can be concluded that the main order of influence of each factor on the tensile strength of tobacco sheets is: addition amount > molecular weight > DS.

2.3.2 Analysis of variance

Analysis of variance reflects the influence of various factors and levels on the tensile strength of tobacco sheets to a certain extent, but it cannot avoid the influence of error on the experimental results. The error option can be excluded by analysis of variance on the experimental results. SPSS (Statistical Product and Service Solutions) was used for analysis of variance (95% confidence interval), and the results are shown in Table 5.

As can be seen from the significance in Table 5, the main order of influence of each factor on the tensile strength of tobacco sheets is as follows: addition amount > molecular weight > DS, which is consistent with the previous analysis of variance results. The significances of factor A and factor B were less than 0.05, indicating that the addition amount and molecular weight of CMC had a significant impact on the tensile strength of tobacco sheets. The significance of factor C is greater than 0.05, indicating that the DS of CMC has no significant effect on the tensile strength of tobacco sheets.

2.3.3 Analysis of mechanism

In Table 4, k_i can reflect the influence law of each level of each factor on the tensile strength of tobacco sheets. With the level number as the abscissa and k_i value as the ordinate, the three factors of addition amount, molecular weight and DS were analyzed and plotted separately (Fig. 4).

It can be analyzed from Fig. 4(a) that the tensile strength of tobacco sheets is gradually increasing with

Table 5 Results of inter subject effect analysis

Item	Quadratic sum	Free degree	Mean square	F value	Significance
Revised model	84 500.563	9	9 388.951	21.123	0.001
Intercept	3 584 395.563	1	3 584 395.563	8 064.260	0.000
<i>A</i>	55 048.687	3	18 349.562	41.283	0.000
<i>B</i>	26 808.688	3	8 936.229	20.105	0.002
<i>C</i>	2 643.187	3	881.062	1.982	0.218
Error	2 666.875	6	444.479	—	—
Sum	3 671 563.000	16	—	—	—
Sum after correction	87 167.438	15	—	—	—

the increasing addition amount of CMC. When the addition amount of CMC reaches about 2.5%, the increase rate slows down. CMC can be well dispersed and dissolved when the content is low, and tobacco sheets can form a uniform continuous phase after drying. At this time, with the increase of CMC addition amount, the introduction of carboxyl and hydroxyl groups in the system gradually increases, which is easier to form hydrogen bonds, so that the tensile strength of tobacco sheets gradually increases. However, when adding amount increases to a certain degree, the CMC of the performance is reduced, which results in the area of the molecular chain of the winding. Tobacco sheets after drying is difficult to form a completely uniform continuous phase. At the same time, when the addition amount is increased, the number of CMC molecular units increase, and the CMC content in each area of tobacco sheets also increase, so that the hydrogen bonds in the system will increase. Under the combined influence of the above reasons, the tensile strength of tobacco sheets increases at this time and the increase rate slows down.

It can be analyzed from Fig. 4(b) that the tensile strength of tobacco sheet increases gradually with the increase of CMC molecular weight, and reaches the maxi-

um value when the molecular weight is about 310 kDa, and then decreases gradually. CMC has good solubility in the water system when the molecular weight is low. It can be well dispersed and dissolved in the wet system. After drying, it forms a more uniform continuous phase, and the tensile strength of tobacco sheets gradually increases. However, with the increasing molecular weight of CMC, its solubility gradually decreases, and CMC molecular chains form serious entanglement. Meanwhile, due to pseudoplasticity and other factors, CMC molecular chains cannot be well dispersed in the wet system, resulting in the failure to form a continuous phase after drying. At the same time, the number of CMC molecular units gradually decrease with the increase of molecular weight. As a result, CMC content in some areas is low, resulting in slightly worse mechanical properties in this area, and the overall tensile strength of tobacco sheets is reduced.

It can be analyzed from Fig. 4(c) that there is no obvious effect on the tensile strength of tobacco sheets with the increase of CMC DS. With a certain molecular weight, the electrostatic repulsive force between the carboxyl anions formed by the carboxyl group ionization in the wet system gradually increases with the increase of

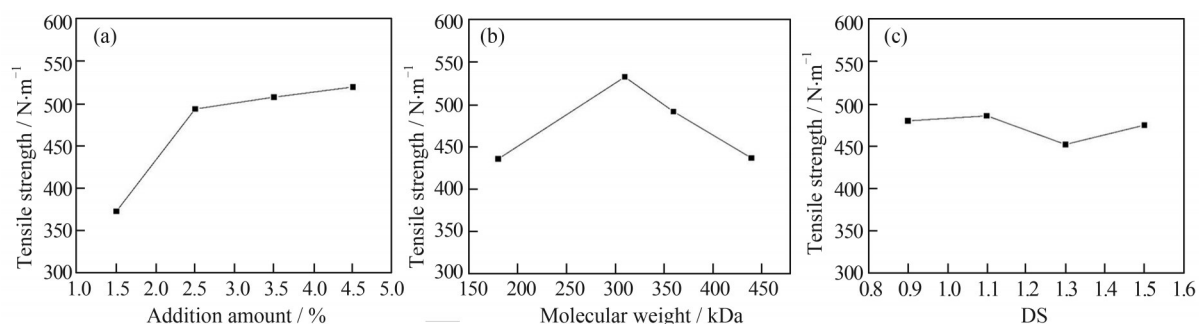


Fig. 4 Effect of addition amount (a), molecular weight (b), DS (c) on tensile strength of tobacco sheets

the DS of CMC, so that the CMC molecular chain can be better dispersed. In addition, the chain length of CMC molecular chain also decreases slightly, which makes CMC have better solubility, and it is easier to form uniform continuous phase after drying, but it also reduces the complexity of molecular chain entanglement in each region. At the same time, because the strength of hydrogen bond formed by carboxyl group is stronger than that formed by hydroxyl group, the introduction of carboxyl group in the system increases the van der Waals force between molecules. Meanwhile, the distribution of substituents between CMC molecular chains also affects the winding mode and complexity of the molecular chains and the tensile strength of tobacco sheets to a certain extent. Based on the above factors, the DS has no obvious influence on the overall tensile strength of tobacco sheets.

2.3.4 Establishment of regression model

It can be seen from Fig. 4 that the influence of the addition amount, molecular weight and DS on the tensile strength shows a nonlinear relationship. According to the results in Table 3, multiple linear regression was conducted on the data using SPSS. The curve of the experimental results was estimated firstly, and found that the multivariate quadratic equation has a good fitting effect. Since the DS has no significant effect on the tensile strength of tobacco sheets, the curve model was established as follows: $T = \alpha_1 A^2 + \alpha_2 A + \alpha_3 B^2 + \alpha_4 B + \alpha_5$. SPSS was used for multivariate quadratic equation regression, and the parameter results obtained are shown in Table 6.

Table 6 Estimated values of multivariate quadratic nonlinear regression parameters

Parameter	Estimate	Standard error	95% confidence interval	
			Lower limit	Upper limit
α_1	-27.062	7.161	-42.823	-11.302
α_2	207.750	43.440	112.139	303.361
α_3	-0.506	0.091	-0.708	-0.305
α_4	31.215	5.640	18.802	43.628
α_5	-307.435	100.063	-527.673	-87.198

According to Table 6, the relationship between the tensile strength of tobacco sheets and the added amount and molecular weight is as follows:

$$T = -27.062A^2 + 207.750A - 0.506B^2 + 31.215B - 307.435$$

The correlation coefficient of the simulation equa-

tion is 0.946 7, and its absolute value is close to 1, indicating that the equation has a great fitting effect. It can predict the tensile strength of tobacco sheets after adding different CMC has good reference value.

2.4 Effect of CMC on Thermal Properties and Aerosol Composition of Tobacco Sheets

CMC with DS of 0.9 and molecular weight of 310 kDa was selected to prepare tobacco sheets with different contents. For ease of description, tobacco sheets with different amounts of CMC are denoted as B_0 , $B_{1.5}$, $B_{2.5}$, $B_{3.5}$, $B_{4.5}$ and $B_{5.5}$ (the subscripts represent the percentage of CMC in dry tobacco sheets).

2.4.1 Aerosol composition analysis

The results of nicotine release in the aerosol of tobacco sheets with different CMC dosage are shown in Fig. 5.

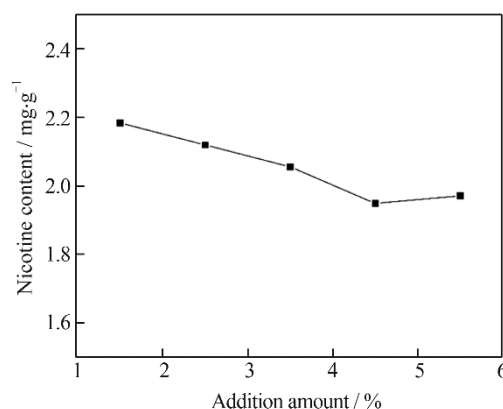


Fig. 5 Change curve of nicotine release in aerosol with CMC addition amount

It can be seen from Fig. 5 that the nicotine content in the aerosol gradually decreases with the increase of CMC addition amount. The possible reason is that CMC makes the tobacco sheets more thermal stable, resulting in a reduction of nicotine content in the aerosol released at the same temperature. CMC has certain influence on nicotine content in aerosol

2.4.2 Thermogravimetric analysis

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) curves are shown in Fig. 6 for each component (including cigarette powder, glycerol, external fiber, CMC, tobacco sheet B_0 and $B_{1.5}$).

From Fig. 6, it can be analyzed as follows: Among all single components, glycerol is the first substance to evaporate completely in the component. Starting from about 180 °C, glycerol starts to evaporate rapidly and volatilizes completely at about 250 °C. CMC begins ther-

mal cracking at about 255 °C and almost completely cracks at about 330 °C. The main process is the break of molecular chains between glucose units to form small molecules with low polymerization degree. At the same time, the carbonization and dehydration between molecules begin to precipitate gas, so that the mass is constantly reduced. The last fiber to be thermally cleaved is the external fiber, which starts to be thermally cleaved at about 290 °C and almost completely cleaved at about 390 °C. The main process is similar to that of CMC. For tobacco powder, its composition is relatively complex. From about 150 °C, the weight loss rate of tobacco powder begins to accelerate slightly, and at this time some small molecular monosaccharides begin to crack and

volatile substances volatilize. At about 330 °C, it is the thermal cracking of hemicellulose and cellulose in cigarette powder.

By comparing the TGA and DTG of tobacco sheets and that of each component, it can be concluded that the thermal cracking of tobacco sheets is mainly divided into three stages: The first stage is the escape of free water and bound water inside tobacco sheet at about 100 °C; The second stage is the degradation of small molecular monosaccharides and the escape of volatile substances in tobacco sheets at about 230 °C; The third stage is the pyrolysis of macromolecular polysaccharides (such as hemicellulose, cellulose and carboxymethyl cellulose) at about 330 °C^[19, 20].

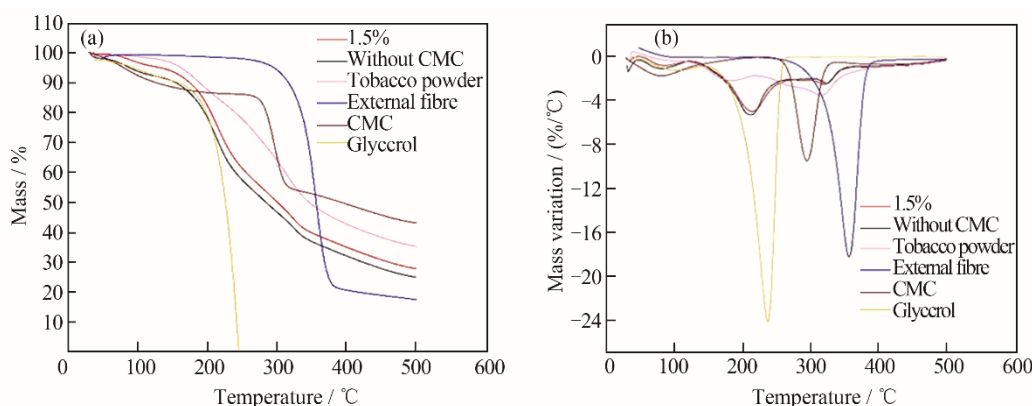


Fig. 6 TGA (a) and DTG (b) of each component in tobacco sheets

The TGA and DTG curves of tobacco sheets with different CMC dosage were analyzed by thermogravimetric analysis, as shown in Fig. 7. It can be analyzed from Fig. 7 that the addition amount of CMC to tobacco sheets only affect the thermal weight loss of tobacco sheets to a certain extent, but do not affect the overall trend. At about 100 °C, the peak value of binding water

is slightly different in each tobacco sheet, which is mainly caused by the slight difference of moisture content in tobacco sheets after drying. For monosaccharide cleavage and small molecule escape rate at about 230 °C. The results are as follows: $B_{5.5} < B_{3.5} < B_{4.5} < B_{2.5} < B_{1.5} < B_0$, which tends to decrease with the increase of the amount of CMC, indicating that the addition amount

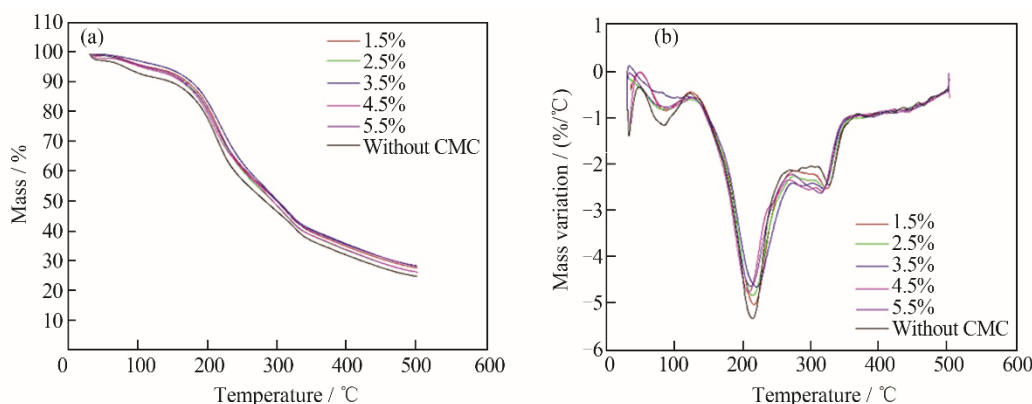


Fig. 7 TGA (a) and DTG (b) of tobacco sheets under different CMC contents

of CMC could slow down the escape rate of small molecules to a certain extent. This is because the addition amount of CMC leads to the formation of a large number of hydrogen bonds in the system, resulting in the slow rate of small molecule escape. At about 330 °C, the rate of thermal decomposition of polysaccharides in $B_{1.5}$, $B_{2.5}$, $B_{3.5}$, $B_{4.5}$ and $B_{5.5}$ is slightly higher than that in B_0 , which is mainly due to the slightly increase of polysaccharides in tobacco sheets by adding CMC. In addition, it can be seen from Fig. 7(a) that when the temperature is the same, the thermal weight loss of tobacco sheets after adding CMC is smaller than B_0 , which indicates that the addition amount of CMC improves the overall thermal stability of tobacco sheets.

2.4.3 Differential scanning calorimetry

Differential scanning calorimetry (DSC) analysis was performed on tobacco sheets with each component and each addition amount of CMC. The results are shown in Fig. 8.

As can be seen from Fig. 8(a), external fiber, glycerol and CMC all have obvious peak values, corresponding to the pyrolysis or escape temperature of each component, which is basically consistent with the previous results of thermogravimetry analysis. CMC is similar to external fiber, and there is an obvious exothermic peak,

which is caused by cracking. There is an obvious endothermic peak in glycerol, which is due to the endothermic escape of glycerol. The composition of cigarette powder is relatively complex. Before about 250 °C, the heat flux rate is negative and maintains the endothermic state, at which point it is mainly the escape of small molecules. After about 250 °C, the heat flux rate is positive and presents the exothermic state, at which point it is mainly the cleavage of macromolecules.

It can be seen from Fig. 8(b) that there is an obvious endothermic peak at around 90 °C, which is caused by the escape of water molecules. An obvious endothermic peak appears at about 230 °C, which is caused by the escape of glycerol and other small molecules. The exothermic peak appears at around 330 °C, which is caused by the cleavage of macromolecular polysaccharide. It is basically consistent with the previous results of thermogravimetric analysis. On the whole, with the increase of CMC addition amount, the overall curve in DSC constantly moves downward, and the peak values of endothermic and exothermic peaks also decrease, which indicates that with the increase of CMC content in tobacco sheets, the internal structure of tobacco sheets is more stable, and more heat needs to be absorbed to destroy this stability.

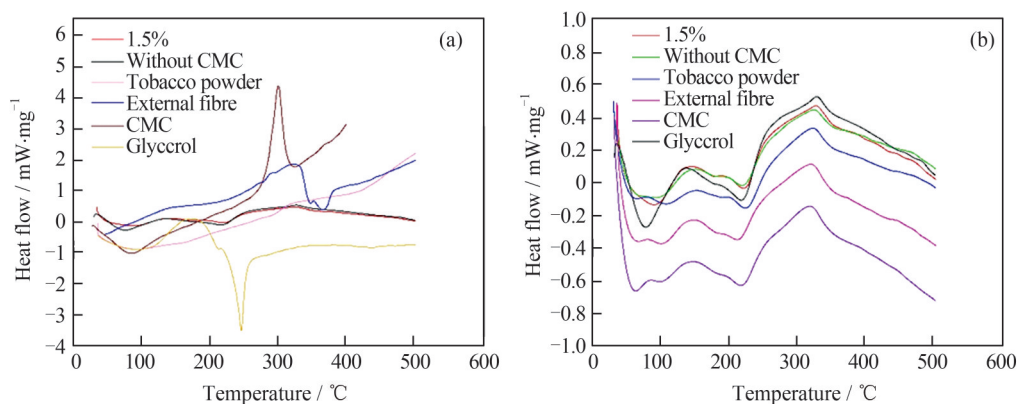


Fig. 8 DSC of tobacco sheets with each component (a) and each addition amount of CMC (b)

3 Conclusion

The CMC with DS was prepared by controlling the feeding ratio, alkalization times and etherification times, and the CMC with different molecular weight was prepared by controlling the concentration of hydrochloric acid. The effects of CMC on the properties of tobacco sheets were studied, and the conclusions were as follows:

1) Alkalization times and etherification times have a great impact on the DS of CMC, multiple alkalization and etherification significantly improve the etherification efficiency of chloroacetic acid. Twice alkalization and twice etherification make the highest etherification efficiency.

2) The addition amount and molecular weight of CMC have a significant impact on the tensile strength of

tobacco sheets, while the DS has no significant impact. Through regression simulation, the relationship between the tensile strength of tobacco sheets and the addition amount A and molecular weight B is obtained as $T = -27.062A^2 + 207.750A - 0.506B^2 + 31.215B - 307.435$.

3) The pyrolysis of tobacco sheets can be divided into three stages: free water and bound water escape from tobacco sheets at about 100 °C; The degradation of small monosaccharides and the escape of volatile substances in tobacco sheets at 230 °C; Pyrolysis of polysaccharides at 330 °C. The thermal stability of tobacco sheets increases with the increase of CMC content. CMC has certain influence on the content of nicotine in aerosol.

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